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SULFUR EXTRUSION REACTIONS OF THIIRANES :

KINETICS AND MECHANISTIC INVESTIGATIONS

BY

WARREN CHEW

A THESIS SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
MCGILL UNIVERSITY
MONTREAL, QUEBEC
CANADA

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Canada

Sulfur Extrusion Reactions of Thiiranes : Kinetics and Mechanism

To Mom and Dad,

Anna and Eva

Sulfur Extrusion Reactions of Thiiranes : Kinetics and Mechanistic Investigations

by Warren Chew

Abstract

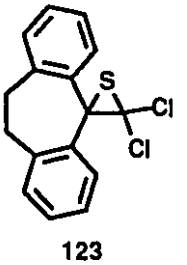
A kinetic study on the thermal decomposition of 2,2-dichloro-3-[9-fluorenyl] episulfide (**28**) was investigated in detail. Solid evidence as to the nature of the desulfurization process is given. A two-term rate equation is derived to account for the overall rate changes. Both a unimolecular and bimolecular ionic mechanism involving the concatenation of sulfur atoms was proposed to account for the observed kinetic behaviour. An extended study in 15 different solvents at different temperatures showed the desulfurization is ionic in nature. Activation parameters were calculated and rationalized with respect to differences in solvation of the ground and transition states. A linear isokinetic relationship was found indicating a similar mechanism of decomposition in these solvents. Rates of reaction were also found to be linearly correlated with dielectric constant as well as the π^* scale of Kamlet and Taft. A solvent isotope effect was found to exist and the rate of desulfurization is decreased in the presence of acetic acid. A radical mechanism is discounted from a rate study in the presence of radical inhibitors.

Several new disubstituted 9-fluorenones were prepared for the first time using Meyers methodology. These and other mono and disubstituted fluorenones were employed in an effort to synthesize a variety of novel stable thiiranes. Only three thiiranes were prepared in this manner. The X-ray crystal structures of 2,2-dichloro-3,3-diphenyl episulfide (**110**) and 2,2-dichloro-3-dibenzosuberonyl episulfide (**123**) were also obtained for the first time.

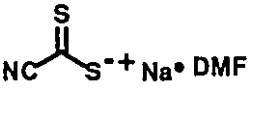
Thiirane **28** as well as sodium cyanodithioformate (**139**) were investigated as possible precursors to diatomic sulfur but no evidence of this interesting intermediate was detected. The chlorination of tetramethylthiuram disulfide, however, in the presence of 1,3-dienes, afforded products consistent with the trapping of diatomic sulfur.

28

110



123



139

REACTIONS D'EXTRUSION DU SOUFRE DES THIIRANES : ETUDES CINETIQUE ET MECANISTIQUE

par Warren Chew

RESUME

Une étude cinétique sur la décomposition thermique des 2,2-dichloro-3-[9-fluorényl] épisulfures (**28**) a été éffectuée en détail. Des preuves tangibles sur la nature du mécanisme de désulfurisation sont données. L'étude cinétique a débouché sur une équation de vitesse à deux termes. Deux mécanismes ioniques, unimoléculaire et bimoléculaire, tenant compte de la concentration en atome de soufre ont été proposés pour expliquer le comportement cinétique observé. Une étude approfondie utilisant 15 différents solvents à differentes températures a montré que cette réaction de désulfurisation est ionique. Les paramètres d'activation ont été calculés et rationalisés en tenant compte des différences de solvatation entre les états de base et de transition. Une relation linéaire d'isocinétique a été trouvée montrant un mécanisme de décomposition similaire dans tous les solvents. Les vitesses de réaction sont également apparues, corrélées linéairement avec les constantes diélectriques tout comme l'échelle π^* de Kamlet et Taft. Un effet isotopique du solvent a été mis en évidence et la vitesse de désulfurisation décroit en présence d'acide acétique. Le mécanisme radicalaire est rejeté par une étude de vitesse en présence d'inhibiteurs radicalaires.

De nouvelles 9-fluorènones disubstituées ont été synthétisées pour la première fois en employant la méthodologie de Meyers. Les fluorènones di et monosubstituées ont été utilisées pour tenter la synthèse de nouveaux et stables thiiranes, seulement trois ont été obtenues par cette méthode. Les structures aux rayons-X du 2,2-dichloro-3,3-diphényl épisulfure (**110**) et du 2,2-dichloro-3-dibenzosuberonyl épisulfure (**123**) sont également été obtenues pour la première fois.

La thiirane (**28**) et le cyanodithioformate de sodium (**138**) ont été utilisées comme possibles précurseurs de soufre diatomique mais aucune evidence de cet interessant intermediare a été detecté. Cependant, la chlorination de tétraméthylthiurame disulfure en présence de dienes-1,3 conduit aux produits d'addition du soufre diatomique.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Professor David N. Harpp who supported and guided me throughout this project. His patience, dedication and encouragement is greatly appreciated.

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Of course I cannot forget the cast of colleagues and friends who continuously supported me throughout my stay at McGill and who have provided invaluable assistance. These are Dr. Patricia Folkins, Dr. Charles Williams, Dr. Youla Tsantrizos, Gerard Derbesy, Dr. Jung Hee Kim, Dr. Vrej Jubian, Karen Mrejen, Denise Maher, Dr. Chao Jun Li, Dr. Daguan Gu, Imad Abu-Youssef, Sylvie Tardif, and the entire research group in Dr. Chin's laboratory who made life in the lab much more entertaining. I would also like to thank Gerard Derbesy for translating the abstract into French and Bryan Takasaki for providing the computer programs for kinetic analysis.

Finally, I would especially like to thank Nancy Kwan who not only proofread the manuscript but whose friendship and tremendous support means a great deal. Thank you for being there.

TABLE OF CONTENTS

INDEX OF FIGURES

INDEX OF TABLES

INDEX OF ABBREVIATIONS

[ ]	concentration
σ	standard deviation
Å	angstrom
abs.	absorbance
Bp.	boiling point
^{o}C	degrees Celsius
ca.	circa
cf.	confer
cm	centimeter
d	deuterium
D_c	dielectric constant
DME	dimethoxyethane
DMF	dimethylformamide
DMSO	dimethylsulfoxide
ε	extinction coefficient
EI	electron impact
eq.	equivalent
Eq.	equation
EtOAc	ethyl acetate
EtOH	ethanol
eu	entropy units
eV	electron volt
g	gram
HPLC	high performance liquid chromatography
hr	hour
IR	infrared
kcal	kilocalories
L	litre
lit.	literature
m	meta
mg	milligram
MHz	megahertz
min	minute

ml	milliliter
mM	millimolar
mm	millimeter
mmol	millimole
mol	mole
Mp.	melting point
MS	mass spectrometry
N	normality
nm	nanometer
NMR	nuclear magnetic resonance
o	ortho
p	para
ppm	parts per million
r	measure of best fit
R_f	relative mobility
s	second
S_N1	substitution nucleophilic unimolecular
S_N2	substitution nucleophilic bimolecular
t	tertiary
THF	tetrahydrofuran
TLC	thin layer chromatography
UV	ultraviolet

CHAPTER 1

INTRODUCTION

1.1 THIIRANES

It is almost inevitable that a comparison be made of thiiranes **1** with their oxygen counterpart oxiranes, in view of their similarities in structure and proximity of their heteroatoms to each other in the periodic table. In contrast to the chemistry of oxiranes which has been studied enormously, thiiranes or episulfides have received much less attention. The limited literature on thiirane chemistry may be attributed to their lack of easy availability, their limited stability and their characteristic unpleasant smell of the lower molecular weight members. Thiiranes are more prone to spontaneous polymerization than oxiranes and are less convenient to store. Desulfurization is a common pathway in the reaction of thiiranes but deoxygenation of oxiranes is seldom observed. The ring-opening reactions of thiiranes have received less consideration in contrast to the ring-opening reactions of oxiranes.

It is only in the last decade when researchers discovered the importance of thiirane and its chemistry. Several reviews on the synthesis, physical properties, and reactivity of thiiranes have appeared recently.[1] A number of novel methods of synthesis has been developed and the behaviour of thiiranes in many reactions has been examined. Several new technical applications of thiiranes have also been demonstrated in recent years. A variety of biologically active substances has been synthesized containing the thiirane functionality and in some cases have been found to be more potent than its oxirane analogue. Thiiranes have also been employed in synthetic carbohydrate chemistry.[2]

---

1 a) A. V. Fokin and A. F. Kolomiets, *Russ. Chem. Rev.*, **44**, 138 (1975); b) A. V. Fokin and A. F. Kolomiets, *Russ. Chem. Rev.*, **45**, 25 (1976); c) E. Vedejs and G. A. Krafft, *Tetrahedron*, **38**, 2857 (1982); d) A. V. Fokin, M. A. Allakhverdiev, and A. F. Kolomiets, *Russ. Chem. Rev.*, **59**, 405 (1990).

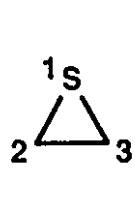
2 D. Miljkovic, M. Popsavin, N. Vukojevic, and N. A. Hughes, *J. Carbohydr. Res.*, **9**, 215 (1990).

1.2 Nomenclature

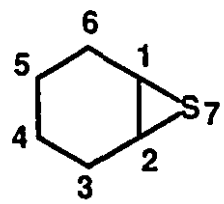
Three-membered rings containing one sulfur atom are named thiiranes **1** with the ring numbering starting at the sulfur atom. Several systems of nomenclature have been widely used :

a) Substitution method whereby the position of the sulfur atom which replaces the carbon atom in the parent molecule is indicated by number and the "thia" prefix;
b) Name of alkene + episulfide;
c) Name of alkene + sulfide;
d) Epithioalkane with position of functional group given by numbers;
e) Episulfide + "name of alkene".

Thus compound **2** may be called 7-thiabicyclo[4.1.0] heptane, cyclohexene episulfide, cyclohexene sulfide, 1,2-epithiocyclohexane, or episulfide of cyclohexene according to the nomenclature systems a) through e) respectively. For larger molecules, the episulfide or epithio designation is commonly used. In most cases, however, thiirane is the more general term used to define compounds containing this functional group.



1



2

1.3 Physical Properties

The physical properties of the parent thiirane has been reviewed by Dittmer[3] and Sander.[4] Typical C-C bond lengths in thiiranes fall between 1.37 Å to about 1.60 Å and C-S bonds range from 1.73 Å to 1.92 Å. The C-C bond length in thiirane suggests a partial double bond character as a typical sp^3-sp^3 C-C bond is about 1.55 Å and a C=C bond 1.34 Å. The CSC angle is about 48°C for the parent thiirane but this varies a little depending on the substituents present in the molecule. Table 1 lists bond lengths and angles for the parent thiirane and their oxides as well as data for its analogues, aziridine, oxirane, and phosphorane. The sharp difference between the strain energy of

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3 D.C. Dittmer, "*Comprehensive Heterocyclic Chemistry*", A. R. Katritzky and C. W. Rees, Eds., Pergamon Press: London, 1984, Vol. 7, Chapter 5.06.

4 M. Sander, *Chem. Rev.*, 66, 297 (1966).

cyclopropane and its heteroatom analogues is indicative of the higher degree of stabilization of the heterocyclic compounds by π–electrons of the heteroatom. The contribution of the π-electrons enhances the unsaturated character of the thiirane ring which is responsible for its greater stability compared with the oxirane ring. The increase in stability of thiirane is also reflected in a lower strain enthalpy and entropy compared with oxirane (59.2 eu. and 38.4 kcal/mol for oxirane and 21.5 eu. and 17.6 kcal/mole for thiirane).[5]

Table 1. Bond lengths and bond angles for 3-membered ring heterocycles.

	X					
	O[a]	NH[b]	P[c]	S[a]	SO[d]	SO_2[e]
C-C	1.472	1.480	1.502	1.492	1.504	1.590
C-X	1.436	1.488	1.807	1.819	1.822	1.731
C-X-C	61°24'	-	47°24'	48°24'	48°46'	54°40'
C-C-X	59°18'	-	66°18'	65°48'	65°37'	62°40'

[a] G. Cunningham, Jr., A. W. Boyd, R. J. Myers, W. D. Gwinn, and W. I. LeVan, *J. Chem. Phys.*, **19**, 676 (1951); [b] T. E. Turner, V. C. Fiora, W. M. Kendrick, and B. L. Hicks, *J. Chem. Phys.*, **21**, 564 (1953); [c] M. T. Bowers, R. A. Beaudet, H. Goldwhite, and R. Tang, *J. Am. Chem. Soc.*, **91**, 17 (1969); [d] S. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 663 (1969); [e] Y. Nakano, S. Saito and Y. Morino, *Bull. Chem. Soc. Jpn.*, **43**, 368 (1970).

The principle ions observed in mass spectra of thiiranes are due to loss of a hydrogen atom or alkyl group. Loss of neutral SH is often observed as well as loss of sulfur. A rearrangement to a thioaldehyde or thioketone followed by loss of hydrogen or alkyl group is also a preferred route in electron impact mass spectroscopy. Absorptions in the UV spectra of thiiranes are usually found between 205 nm to 260 nm. The IR spectrum of thiirane has been extensively analyzed[6] but aside from the parent compound, little IR and Raman work has been done on this class of compound. The reported C-S stretching vibration frequencies for thiirane are 651 cm^{-1} and 611 cm^{-1}.[7]

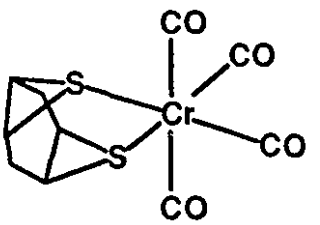
---

5 R. Ketcham and V. P. Shah, *J. Chem. Eng. Data*, **11**, 106 (1966).

6 Gas phase : H. W. Thompson and W. T. Cave, *J. Chem. Soc., Faraday Trans.*, **47**, 951 (1940); Liquid phase : G. B. Guthrie, D. W. Scott, and G. Waddington, *J. Am. Chem. Soc.*, **74**, 2795 (1952).

7 W. D. Allen, J. E. Bertie, M. V. Falk, B. A. Hess, Jr., G. B. Mast, D. A. Othen, L. J.Schaad, and H. F. Schaefer III, *J. Chem. Phys.*, **84**, 4211 (1986).

A number of X-ray crystallographic structures of thiiranes have been documented. The first X-ray structure of a thiirane ring system was reported in 1972 by Bates.[8] They found that the shortness of the C-C bond joining the episulfide ring supported the view that carbons in an episulfide ring are between sp^2 and sp^3 hybridized. The first metal carbonyl derivative containing two coordinated episulfide rings was recently reported.[9] The *cis*-1,4 cyclohexadiene bisepisulfide complex of chromium tetracarbonyl (**3**) showed that the C-S bond lengths of 1.915 Å appears to be the longest observed to date in episulfide ring systems. The C-S-C bond angles of 47.3° are within the expected range for the episulfide ring.



3

Another metal substituted thiirane, triphenylsilyl thiirane, was shown to have a propeller-type molecular structure and that the C-C and C-S bonds are significantly shortened.[10] The X-ray crystal structures of two highly hindered thiiranes, 2,2-di-t-butyl-3,3-diphenyl thiirane[11] and adamantylideneadamantane thiirane,[12] showed long C-S bond distances. Longer C-C bonds from the thiirane ring to the t-butyl and phenyl groups were also observed. Crystallographic data of thiiranes containing exocyclic double bonds have also been reported.[13] Thiirane **4a**, containing one exocyclic double bond, showed the inherent ring strain as well as the unsymmetrical ring structure whereas thiirane **4b** proved to be nearly symmetrical with a characteristic shortening of the C-C bond of the thiirane ring.

---

8 R. B. Bates, R. A. Grady, and T. C. Sneath, *J. Org. Chem.*, **37**, 2145 (1972).

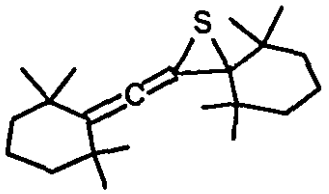
9 E. W. Abel, N. A. Cooley, K. Kite, K. G. Orrell, V. Šik, M. B. Hursthouse, and H. M. Dawes, *Polyhedron*, **8**, 887 (1989).

10 G. Barbieri, G. D. Andreetti, G. Bocelli, and P. Sgarabotto, *J. Organomet. Chem.*, **172**, 285 (1979).

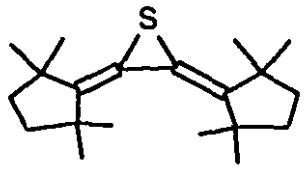
11 A. Mugnoli and M. Simonetta, *Acta. Cryst.*, **B32**, 1762 (1976).

12 G. A. Tolstikov, B. M. Lerman, L. I. Umanskaya, Y. T. Struchkov, A. A. Espenbetov, and A. L. Yanovsky, *Tetrahedron Lett.*, **21**, 4189 (1980).

13 a) W. Ando, Y. Hanyu, Y. Kumamoto, and T. Takata, *Tetrahedron*, **42**, 1989 (1986); b) N. Tokitoh, H. Hayakawa, M. Goto, and W. Ando, *Chem. Lett.*, 961 (1988).

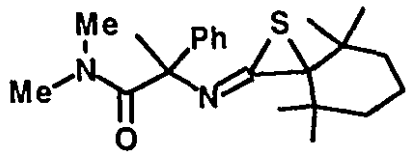


4a



4b

The crystal data of a related molecule, thiiranimine **5** also show the unsymmetrical nature of the thiirane ring due to an exocyclic C=N double bond.[14] Another thiiranimine was also reported[15] as well as the similar α-thiolactone which contains a exocyclic C=O.[16]



5

Several other crystal structures of thiiranes were examined including steroidal thiiranes,[17] spiro thiiranes,[18] a Dewar-type thiophene derivative,[19] and a polyether antibiotic, acanthifolicin, which contains the rare thiirane functionality in a natural product.[20] The reported bond lengths and bond angles are all within the expected range in episulfide rings. Only a few X-ray structures of episulfoxides[21] are reported and to our knowledge only one X-ray structure of an episulfone has been cited.[22]

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14 E. Schaumann, H. Nimmesgern, and G. Adiwidjaja, *Angew. Chem. Int. Ed. Engl.*, **21**, 694 (1982).

15 G. L'abbé, J.-P. Dekerk, J.-P. Declercq, G. Germain, and M. V. Meerssche, *Angew. Chem. Int. Ed. Engl.*, **17**, 195 (1978).

16 E. Schaumann and U. Behrens, *Angew. Chem. Int. Ed. Engl.*, **16**, 722 (1977).

17 a) K. U. Oda and H. Koyama, *J. Chem. Soc., Perkin Trans. II*, 1866 (1973); b) K. U. Oda and H. Koyama, *J. Chem. Soc., Perkin Trans. II*, 933 (1975).

18 a) W. W. Ng and S. C. Nyburg, *J. Chem. Soc., Chem. Comm.*, 555 (1978); b) K. Fukuyama, S. Fujii, and Y. Katsube, *Acta Cryst.*, **C39**, 248 (1983).

19 N. Kikutani and Y. Iitaka, *Acta. Cryst.*, **B31**, 1478 (1975).

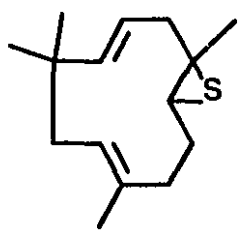
20 F. J. Schmitz, R. S. Prasad, Y. Gopichand, M. B. Hossain, and D. V. Helm, *J. Am. Chem. Soc.*, **103**, 2467 (1981).

21 a) H. Koyama and H. Nakai, *J. Chem. Soc., Perkin Trans. II*, 741 (1977); b) B. F. Bonini, E. Foresti, R. Leardini, G. Maccagnani, and G. Mazzanti, *Tetrahedron Lett.*, **25**, 445 (1984); c) W. Ando, Y. Hanyu, and T. Takata, *Tetrahedron Lett.*, **25**, 1483 (1984); d) W. Ando, Y. Hanyu, and T. Takata, *J. Org. Chem.*, **51**, 2122 (1986).

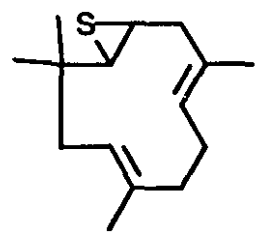
22 R. Desiderato and R. L. Sass, *Acta. Cryst.*, **23**, 430 (1967).

1.4 Naturally Occurring Thiiranes

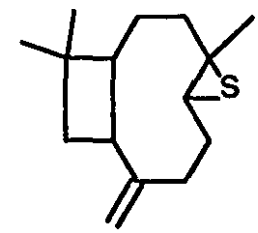
Only a small handful of naturally occurring substances containing the unique 3-membered heterocyclic are known. In 1980, Peppard and coworkers[23] discovered by gas chromatographic analysis that about 10-350 ppm of the components of hop oils were 3 sesquiterpenes, 2 humulenes **6a** and **6b** and an epithiocaryophyllene **6c**.



6a



6b



6c

An epithiospecifier protein was found to be present in both turnip tissue and crambe seed.[24] The parent thiirane molecule, ethylene sulfide, and 2-methyl thiirane were 2 compounds of over 90 other organic compounds identified in the aroma of canned beef and of cooking mutton.[25] Cabbage and rutabagas were found to contain 2-cyano methyl thiirane and thiirane carboxylic acid was found in white asparagus. Some thiiranes are found during degradation of the sulfur containing amino acids, cysteine, cystine, and methionine. Acanthifolicin, a polyether carboxylic acid from the extracts of a marine sponge was shown to contain an episulfide ring.[20]

1.5 Biological Activity

Many thiiranes are know to be very useful as potent drugs. Epitiostanol (**7**) and its derivatives are antitumor drugs which are effective against breast cancer but studies also show these compounds were toxic in rats.[26] Other epithiosteriodal derivatives such as the carbenolides are useful as respiratory stimulants and blood pressure increasing agents.[27] Two thiiranyl steroids which have been synthesized were demonstrated to be

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23 T. L. Peppard, F. R. Sharpe, and J. A. Elvidge, *J. Chem. Soc., Perkin Trans. I*, 311 (1980).

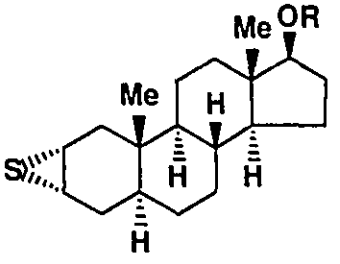
24 a) H. L. Tookey, *Can. J. Biochem.*, **51**, 1654 (1973); b) R. A. Cole, *Phytochem.*, **17**, 1563 (1978).

25 L. N. Nixon, E. Wong, C. B. Johnson, and E. J. Birch, *J. Agric. Food Chem.*, **27**, 355 (1979).

26 a) T. Hori, T. Miyake, K. Takeda, and J. Kato, *Prog. Canc. Res. Ther.*, **10**, 159 (1978); b) Y. Muraoka, I. Yahara, F. Itoh, H. Watanabe, and H. Nara, *Chem. Abs.*, **90**, 146152f (1979); c) K. Takeda, *Chem. Abs.*, **92**, 34512h (1980).

27 D. Sato, *Chem. Abs.*, **70**, 4442p (1969).

useful inhibitors of human placental aromatase[28] and lanosterol 14α demethylase ($P450_{14dm}$) which is a cytochrome enzyme responsible for the first stage in the biosynthesis of cholesterol from lanosterol.[29] Thioglycidates **8**, which have been shown to control hypertension, are useful as hypoglycemic agents.[30] They act by irreversible inhibition of mitochondrial carnitine palmitoyl transferase-A enzyme which is responsible for converting long-chain fatty acids into their ester derivatives. This inhibitory action effectively prevents further oxidation of these acids as they cannot enter the mitochondrion where oxidation takes place. Thus, the blood glucose levels are lowered.[31]



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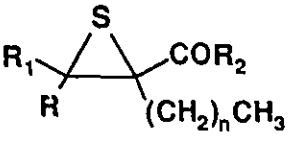

R = R_1 = H or Alkyl
R_2 = OH, alkoxy, amino
n = 10-15

8

Cyclohexene sulfide is known to inhibit both L-glutathione transferase and aryl hydrocarbon hydroxylase enzymes which are responsible for inducing skin tumors.[32] Substituted propylene sulfides were reported to be active against tuberculosis.[33] Thiirane is found to be more potent than oxirane as an antibacterial agent. Adducts of amines with thiiranes act as immunosuppressants. Furanoid epithio sugar **9** has also been reported as a potential immunostimulant.[34] The sulfur analogue of epoxyeicosatrienoic acid (**10**) has been synthesized as an arachidonate epoxygenase inhibitor albeit it is less potent than the nitrogen or oxygen analogues.[35] It was prepared by the treatment of the

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28 W. E. Childers, P. S. Furth, M. J. Shih, and C. H. Robinson, *J. Org. Chem.*, **53**, 5947 (1988).

29 S. F. Tuck, C. H. Robinson, and J. V. Silverton, *J. Org. Chem.*, **56**, 1260 (1991).

30 a) W. Ho, R. J. Mohrbacher, and G. Tutwiler, US Patent 4196300, *Chem. Abs.*, **93**, 71528j (1980); b) R. J. Mohrbacher, W. Ho, and G. Tutwiler, US Patent 4370343, *Chem. Abs.*, **98**, 149595d (1983).

31 W. Ho, G. F. Tutwiler, S. C. Cottrell, D. J. Morgans, O. Tarhan, and R. J. Mohrbacher, *J. Med. Chem.*, **29**, 2184 (1986).

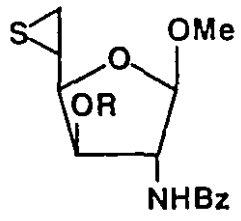
32 A. H. L. Chuang, H. Mukhtar, and E. Bresnick, *J. Natl. Cancer Inst.*, **60**, 321 (1978).

33 E. P. Adams, K. N. Ayad, F. P. Doyle, D. O. Holland, W. H. Hunter, J. H. C. Nayler, and A. Queen, *J. Chem. Soc.*, 2665 (1960).

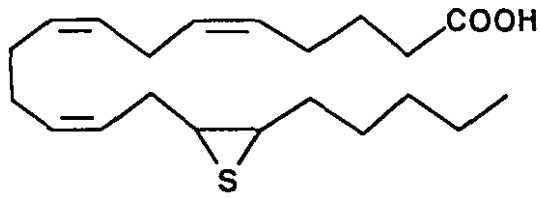
34 K. Adlgasser, H. Hünig, and R. Zenk, *Liebigs Ann. Chem.*, 283 (1987).

35 a) J. R. Falck, S. Manna, J. Viala, A. K. Siddhanta, C. A. Moustakis, and J. Capdevila, *Tetrahedron Lett.*, **26**, 2287 (1985); b) J. R. Falck, P. Yadagiri, and J. Capdevila, *Methods Enzymol.*, **187**, 357 (1990).

epoxyeicosatrienoic acids with KSCN. Alpha-adrenergic blocking agents were prepared using ethylene sulfide as the precursor.[36]



9



10

1.6 Thiiranes Used in Insecticides/Herbicides

Some thiiranes are effective as insecticides. A study has shown that thiiranes proved to be the most active against insects.[37] Thiophosphates of 2-mercapto methyl thiirane are strong insecticides[38] and several thiirane 1-oxides were reported to be sufficient to kill weeds, insects and snails.[39] Chloropropene sulfide has been claimed to be an effective nematocide.[40]

1.7 Technical Applications

A number of useful applications of thiiranes have been reported. 2-methyl thiirane has been used as a fuel gas odorant, 1,2-dimethyl and 1,2-diphenyl thiirane in liquid crystals,[41] thiirane in the enhancement of respiration of tobacco leaves and 2-(methoxy methyl) thiirane as tobacco additives which reduces the nicotine and phenol levels in smoke. Fluorinated thiiranes are useful as refrigerants or fire extinguisher agents.[42] Thiiranes have also appeared in components of paint and varnish coatings, insulating materials, semi-conductors and antioxidants.

Polymeric materials containing the epithio functionality possess excellent mechanical properties. Epoxy resin compound **11** was found to be resistant to heat[43] and

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36 R. Granados, M. Alvarez, N. Valls, and M. Salas, *J. Heter. Chem.*, **20**, 1271 (1983).

37 a) D. E. Frear and E. J. Seiferle, *J. Econ. Entomol.*, **40**, 736 (1947); b) J. B. Siddall and C. A. Henrick, US Patent 3723462, *Chem. Abs.*, **78**, 159402q (1973).

38 a) W. Lorenz, German Patent 1086712 (1960); b) G. Schrader and W. Lorenz, German Patent 1082915 (1960), *Chem. Abs.*, 55, 25983 (1961).

39 G. E. Hartzell, US Patent 3413306 (1969), *Chem. Abs.*, **70**, 57418s (1969).

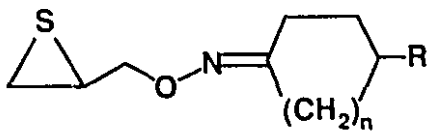
40 C. Harukawa, M. Sakai, and K. Konishi, Japanese Patent 9997 (1962), *Chem. Abs.*, **60**, 3440 (1964).

41 G. Gottarelli, P. Mariani, G. P. Spada, B. Samori, A. Forni, G. Solladie, and M. Hibert, *Tetrahedron*, **39**, 1337 (1983).

42 F. C. McGrew, US Patent 3136744 (1964), *Chem. Abs.*, **61**, 4312 (1964).

43 V. A. Dzhafarov, S. I. Sadykh-Zade, S. K. Kyazimov, A. V. Ragimov, and S. D. Abbasova, *Chem. Abs.*, **91**, 40423a (1979).

aryloxypropene sulfides have been proposed as light and heat stabilizers for poly(vinyl) chloride and co-polymers of vinyl chloride.



11

The oxirane analogues of the sulfides were found to be less effective.[44] Other resin compounds were useful as photoresistors. The poly(ethylene glycol) ether of 2-hydroxymethyl thiirane showed improvement of antistatic properties of fiber and films. Poly(ethylene) sulfides have high tensile strength.[45]

1.8 Thermal and Photochemical Reactions

1.8.1 Introduction

The lower ring strain of thiiranes compared to other 3-membered rings (oxirane, aziridine and cyclopropane) suggests thiiranes would be less reactive than oxirane (*cf.* Section 1.3). However, it is the lower bond energy of C-S (66 kcal/mol) compared with the C-O bond (91 kcal/mol) that overrules the lower strain energy and which accounts for much of the reactivity of this class of compounds. The thermal or photochemical reactions involve either the cleavage of the carbon-sulfur bond, which often lead to rearrangement products, isomeric or polymeric materials, or extrusion of sulfur which results in the formation of alkenes. Thiiranes that are highly aryl-substituted or whose molecule is substituted with electron attracting groups are more likely to promote the abstraction of sulfur. The gas phase thermal and photochemical reactions of thiirane and its nitrogen and oxygen relatives have been reviewed by Braslavsky.[46]

1.8.2 Sulfur Extrusion

There are many non-thermal reactions that involve the extrusion of sulfur from thiiranes but little work has been done on the thermally induced desulfurization reaction. A recent review on thermal decomposition of sulfur compounds including thiiranes is given by Williams and Harpp.[47] Articles on the elimination of sulfur from thiiranes have

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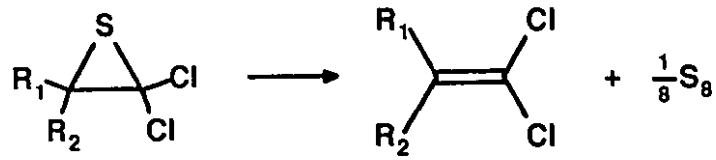
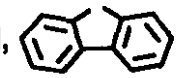
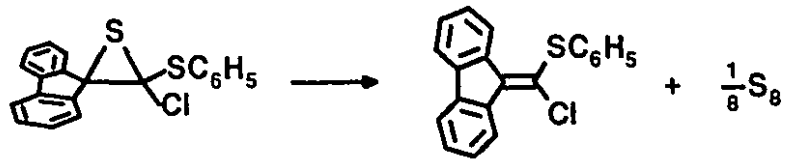
44 M. Kosmin, US Patent 2824845, *Chem. Abs.*, **52**, 9667 (1958).
45 P. Sigwalt, *Chim. Ind., Genie Chim.*, **104**, 47 (1971).
46 S. Braslavsky and J. Heicklen, *Chem. Rev.*, 473 (1977).
47 C. R. Williams and D. N. Harpp, *Sulfur Repts.*, **10**, 103 (1990).

also appeared in the last few years.[48] It appears that the first case involving spontaneous loss of sulfur from thiiranes substituted by aryl or halogen was reported by Staudinger and Siegwart[49] (Scheme 1) and Schönberg (Scheme 2).[50] The thermolysis reaction of *cis* or *trans*-2,3 divinyl thiirane (**12a**) loses sulfur at 90°C affording a mixture of *cis* and *trans* 1,3,5-hexatrienes plus rearrangement dihydrothiepins.[51]



$R_1 = R_2$ = phenyl, 

Scheme 1



Scheme 2

However, Bergman[52] showed that *trans*-2,3-diethynyl thiirane (**12b**) when heated at 100°C in toluene gave predominantly *trans* alkene but at 395°C in the gas phase, the stereoselectivity is lowered.

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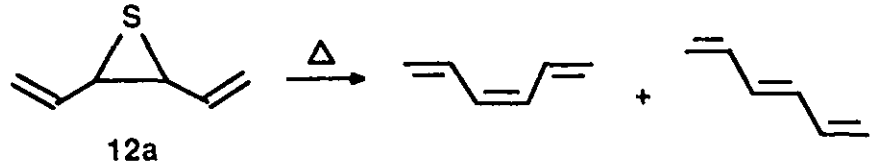
48 a) Y. Suhara, *Yukagaku*, 32, 466 (1983); b) F. S. Guziec, Jr. and L. J. Sanfilippo, *Tetrahedron*, **20**, 6241 (1988).

49 H. Staudinger and J. Siegwart, *Helv. Chim. Acta.*, 3, 840 (1920).

50 A. Schönberg and L. V. Vargha, *Liebigs Ann. Chem.*, **483**, 176 (1930).

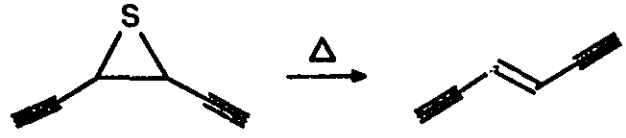
51 a) M. P. Schneider and M. Schnaithmann, *J. Am. Chem. Soc.*, **101**, 254 (1979); b) J. C. Pommelet and J. Chuche, *J. Chem. Res.* (S), 56 (1979).

52 K. P. C. Vollhardt and R. G. Bergman, *J. Am. Chem. Soc.*, **95**, 7538 (1973).



12a

cis or trans



12b

A chelotropic extrusion of a sulfur atom could explain the retention of stereochemistry but it was considered unlikely and the authors concluded that the reaction was more complicated.[53] In 1985, Lutz and Biellmann[54] studied the mechanism of sulfur extrusion of 2,2-dichloro-3-[9-fluorenyl] thiirane (*cf.* Scheme 1). Their conclusion was that sulfur loss was not a chelotropic extrusion but that a more complex process was involved. Bouda and co-workers[55] described the decomposition of furanic and aromatic thiiranes at moderate temperatures (90°C) but at low temperatures (0°C) desulfurization does not take place. When thiirane **13** was heated gently, elemental sulfur was obtained and the thiirane converted to the ethylene derivative **14**.[56] In the reaction of thiobenzophenone with diazomethane or diazoethane, thiirane **15** was produced but sulfur was lost at room temperature with a half-life of 16 hr to give the olefin **16**.[57]

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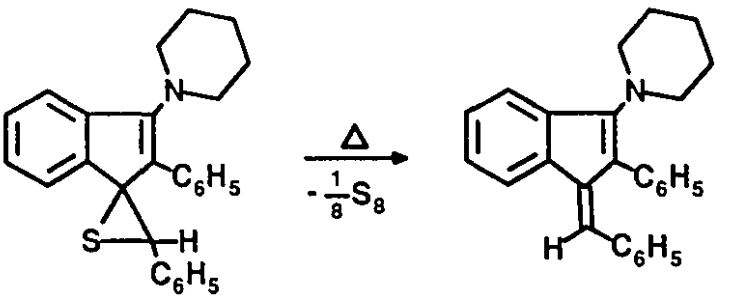
53 The mechanism of desulfurization of a related molecule, an allene episulfide, was studied by Ando and rationalized *via* a thioxyallyl radical intermediate although no clear conclusions were justified; W. Ando, A. Itami, T. Furuhata and N. Tokitoh, *Tetrahedron Lett.*, **28**, 1787 (1987).

54 E. Lutz and J. F. Biellmann, *Tetrahedron Lett.*, **26**, 2789 (1985).

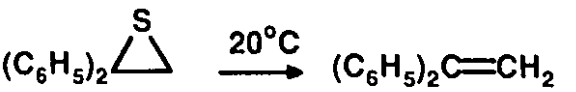
55 H. Bouda, M. E. Borredon, M. Delmas and A. Gaset, *Synth. Comm.*, **19**, 491 (1989).

56 N. A. Korchevin, V. A. Usov, and M. G. Voronkov, *Chem. Hetero. Cmpds.*, 623 (1974).

57 a) I. Kalwinsch, L. Xingya, J. Gottstein, and R. Huisgen, *J. Am. Chem. Soc.*, **103**, 7032 (1981); b) R. Huisgen and L. Xingya, *Heterocycles*, **20**, 2363 (1983).

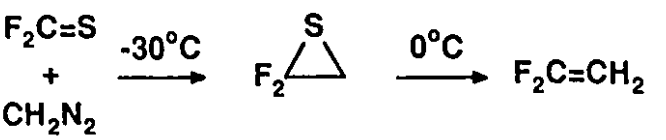


13 14

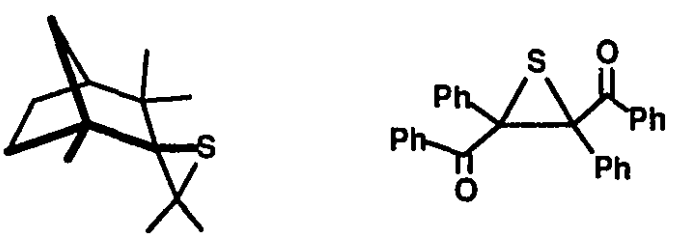


15 16

In the reaction of thiocarbonyl fluoride with diazomethane, 2,2-difluorothiirane was formed but spontaneously lost sulfur at 0°C (Scheme 3).[58] Aliphatically substituted thiiranes such as fenchane-spirothiirane (**17**) extrude sulfur when heated.[59] Three recent articles have appeared which showed that episulfide compounds lose sulfur spontaneously to give the olefin,[60a] biaryl compounds,[60b] and a diazepine.[60c]



Scheme 3



17 18

Several examples are reported in the literature where photochemical reactions involve sulfur loss. The photolysis of dibenzoylstilbene thiirane (**18**) afforded

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58 W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, 30, 1375 (1965).

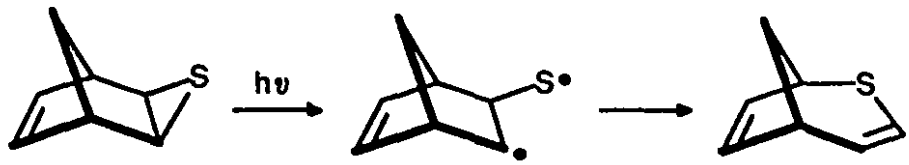
59 J. M. Beiner, D. Lecadet, D. Paquer, and A. Thuillier, *Bull. Soc. Chim. Fr.*, 1983 (1973).

60 a) K. C. Nicolaou, C.-K. Hwang, M. E. Duggan, and P. J. Carroll, *J. Am. Chem. Soc.*, **109**, 3801 (1987); b) M. A. Francisco, A. Kurs, A. R. Katritzky , and D. Rasala, *J. Org. Chem.* ,53, 4821 (1988); c) J. Svetlik, F. Turecek, and I. Goljer, *J. Org. Chem.* ,55, 4740 (1990).

dibenzoylstilbene. The loss of sulfur was explained by assuming a cleavage of the C-S bond of the three-membered ring forming a biradical intermediate which is then followed by loss of atomic sulfur.[61] A similar conclusion was proposed when Becker[62] investigated the photochemistry of tetraphenylthiirane. Another photochemical study was conducted by Trozzolo on tetraphenyloxirane but the authors favoured an ionic mechanism rather than homolytic cleavage.[63]

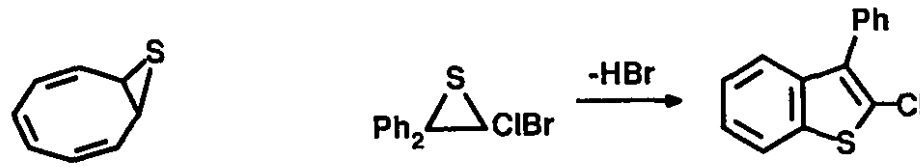
1.8.3 C-S AND C-C BOND CLEAVAGE

The other pathways in thermal reactions of thiiranes involve C-S or C-C bond fission. Many unusual rearrangement or isomeric products are isolated, especially in substituted thiiranes. The C-S bond is either cleaved homolytically or heterolytically leading to various products. When *exo*-2,3-epithionorborn-5-ene (**19**) is photolyzed, 2-thiabicyclo[3.2.1] octa-3,6-diene (**20**) is obtained *via* a stepwise mechanism involving a homolytic cleavage of the C-S bond.[64]



19 **20**

Triene **21** undergoes a similar rearrangement to afford thiabicycles.[65] Benzothiophene (**23**) was observed when thiirane **22** was heated in refluxing benzene.[66]



21 **22** **23**

Only a few examples in the literature have shown that the C-C bond is cleaved thermally. The formation of dihydrothiepins from thermal rearrangement of 2,3-divinyl

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61 A. Padwa, D. Crumrine, and A. Shubber, *J. Am. Chem. Soc.*, 88, 3064 (1966).

62 R. S. Becker, J. Kolc, R. O. Bost, H. Kietrich, P. Petrellis, and G. Griffin, *J. Am. Chem. Soc.*, 90, 3292 (1968).

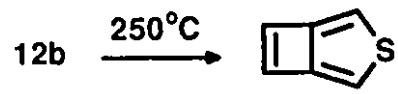
63 A. M. Trozzolo, W. A. Yager, G. W. Griffin, H. Kristinnsson, and I. Sarkar, *J. Am. Chem. Soc.*, 89, 3357 (1967).

64 T. Fujisawa and T. Kobori, *J. Chem. Soc., Chem. Comm.*, 1298 (1972).

65 A. G. Anastassiou and B. Y. H. Chao, *J. Chem. Soc., Chem. Comm.*, 277 (1972).

66 D. Seyferth, W. Tronich, R. S. Marmor, and W. E. Smith, *J. Org. Chem.*, 37, 1537 (1972).

thiirane[51] and Bergman's *cis*-2,3-diethynyl thiirane isomerization to the thienocyclobutadiene (**24**) are believed to take place *via* C-C bond cleavage.[52] Ando[67] reported that in the reaction of palladium(0) with allene episulfide, a bicyclo thiahexane derivative was isolated and that this compound can be rationalized by a C-C bond breaking in an intermediate step.



24

1.8.4 Polymerization

Another common reaction pathway for thiiranes involves polymerization under influence of heat or light. Polymerization reactions of alkene sulfides appear in a review article by Sander.[4] At room temperature, both the parent molecule and 2-phenyl thiirane polymerize and 2-methyl thiirane polymerizes on exposure to light.[4] Most thermal and photochemical polymerizations probably proceed by diradical intermediates which may be trapped by various acceptors. In the thermolysis of cyclohexene sulfide, desulfurization occurs with the formation of cyclohexene. Six other products were also observed which may be derived either from the diradical intermediate (homolytic cleavage of C-S bond) or reactions with elemental sulfur.[68]

1.9 Non-Thermal Reactions of Thiiranes

1.9.1 Electrophilic Reactions on Sulfur

Electrophilic reactions involving thiiranes usually yield sulfonium salts or ring-opened cations (Scheme 4). Depending on which isomer exists, two products can result. In the open-form, product A would be formed if substituent R can stabilize the cation. If the sulfonium salt predominates then an S_N2 mechanism predicts product B would be formed due to the nucleophilic attack at the least hindered site. Thiiranes are more reactive than oxiranes due to the lower C-S bond energy and almost all reactions of thiiranes involve ring openings similar to oxiranes.

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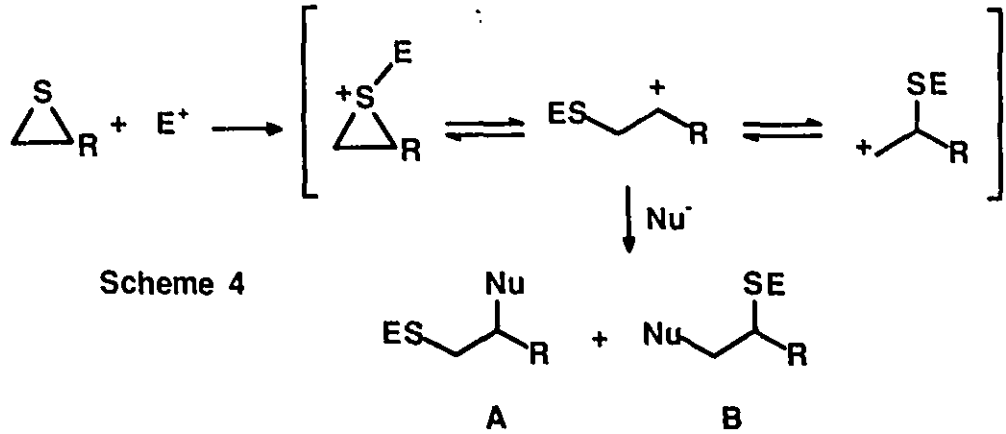
67 N. Choi, Y. Kabe, and W. Ando, *Tetrahedron Lett.*, 32, 4573 (1991).

68 S. Inoue and S. Oae, *Bull. Chem. Soc. Jpn.*, 48, 1665 (1975). See also a) D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, 18 (1951); b) A. Noshay and C. C. Price, *J. Poly. Sci.*, 54, 533 (1961).



Scheme 4

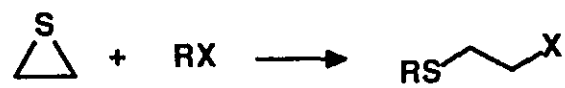
A B

1.9.1.1 Protonation and Behaviour with Lewis Acids

In the presence of acids, thiiranes usually are protonated and polymerization takes place. With the acid-catalyzed addition of nucleophiles, ring opening products are observed and polymerization occurs when another molecule of thiirane acts as the nucleophile. Polymerization is often observed in the presence of Lewis acids whereas thiiranes form complexes with many metals. However, desulfurization is observed with molybdenum,[69] rhodium,[70] ruthenium,[71] and osmium[72] metal complexes. Palladium(0) in the reaction with allene episulfide gave rearrangement products.[67]

1.9.1.2 Alkyl and Acyl Halides

Ring opening products are usually observed in the presence of alkyl or acyl halides. The sulfonium salt is formed in the intermediate but halide attack results in ring opening. Treatment of thiiranes with alkyl chlorides or bromides, gives 2-chloro or 2-bromo ethyl sulfides (Scheme 5). For weak or non-nucleophilic anions, the *S*-alkyl thiiranium salt can be isolated but they are frequently unstable and result in polymeric materials.



Scheme 5

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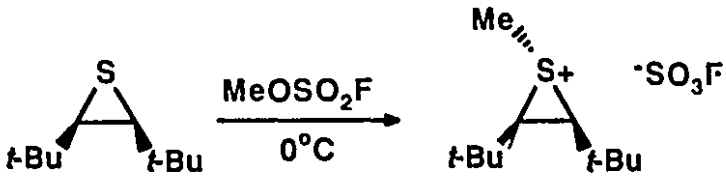
69 J. T. Roberts and C. M. Friend, *J. Am. Chem. Soc.*, **109**, 7899 (1987).

70 S. Calet and H. Alper, *Tetrahedron Lett.*, **27**, 3573 (1986).

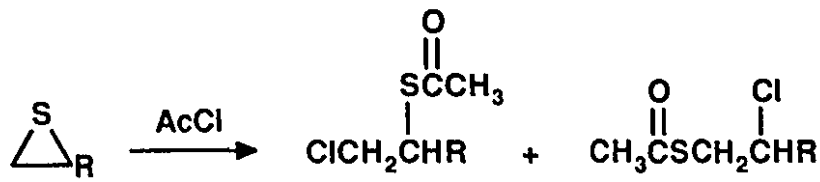
71 C. R. Brulet, S. S. Isied, and H. Taube, *J. Am. Chem. Soc.*, **95**, 4758 (1973).

72 R. D. Adams, G. Chen, S. Sun, and T. A. Wolfe, *J. Am. Chem. Soc.*, **112**, 868 (1990).

The *S*-methyl thiirane salt **26** was isolated when *cis*-1,2 di-*t*-butyl thiirane (**25**) is treated with $MeOSO_2F$ at 0°C. *S*-acetyl derivatives result when thiiranes are reacted with acetyl chloride (Scheme 6).



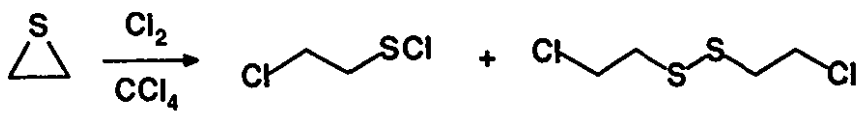
25 **26**



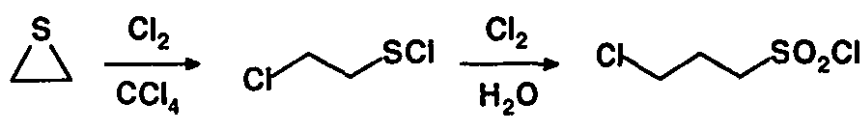
Scheme 6

1.9.1.3 Halogens

In many cases, halogenation reactions of thiiranes give sulfenyl halides or disulfides such as in the case of chlorination of ethylene sulfide (Scheme 7). The iodination reaction gives only disulfide but it can also be used to desulfurize thiiranes. Chlorination reactions carried out in hydroxylic solvents result in sulfonyl chlorides as the sulfenyl chlorides are further oxidized (Scheme 8).



Scheme 7

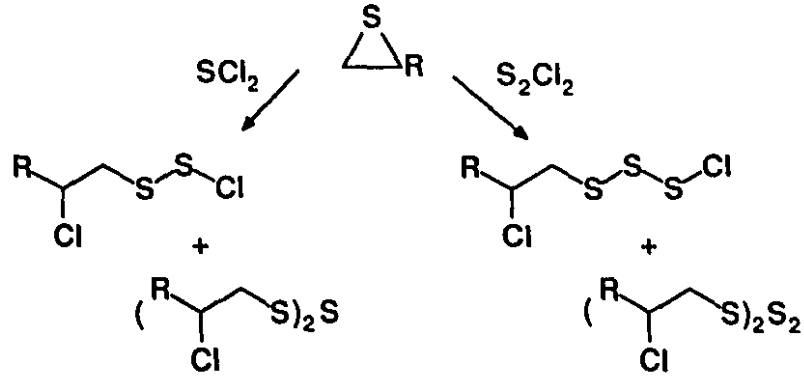


Scheme 8

1.9.1.4 Sulfur, Nitrogen, and Phosphorus Containing Reagents

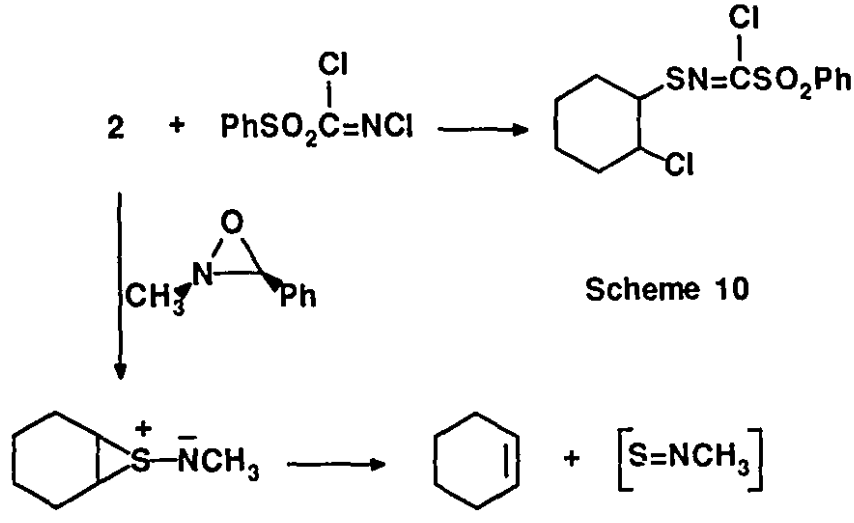
Scheme 9 shows the general behaviour of thiiranes when treated with sulfur monochloride or sulfur dichloride. With sulfur dichloride, a chloro disulfide is obtained

and a chloro trisulfide is obtained with sulfur monochloride. A 2:1 ratio of sulfur halide to thiirane results in tri or tetrasulfides.



Scheme 9

The reaction of 2 with *N*-chlorobenzene sulfonylformimidoyl chloride (Scheme 10) from electrophilic attack by nitrogen on the sulfur atom forms thionitrosomethane as evidenced by trapping experiments.[73] Desulfurization may also occur by using 2-methyl-3-phenyl oxaziridine.[74] Some phosphorus compounds are also known to react electrophilically with the thiirane sulfur.[75]



Scheme 10

1.9.2 Nucleophilic Attack on Sulfur

The most widely used nucleophilic reaction of thiiranes is the desulfurization by trivalent phosphorus compounds to give the alkene and phosphine sulfide.

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73 M. S. A. Vrijland, *Tetrahedron Lett.*, 837 (1974).

74 Y. Hata and M. Watanabe, *J. Org. Chem.*, 45, 1691 (1980).

75 R. Appel and V. I Gläsel, *Z. Naturforsch.*, Teil B, 447 (1981).

Triphenylphosphine[76] is most commonly used although triethylphosphine,[77] triethyl phosphite,[78] tributylphosphine,[79] and tris(alkylamino)phosphines[80] have been employed. Sulfur[81] and nitrogen[82] nucleophiles also attack the sulfur atom of thiiranes. Oxygen nucleophiles usually attack at the carbon atom on the ring but it was reported that desulfurization of thiirane (**27**) occurs by nucleophilic attack by the oxygen of the dimethyl sulfoxide solvent (Scheme 11).[83] Wittig reagents are also known to desulfurize thiiranes.[84] Other desulfurization methods have also been reported.[85]

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76 a) R. E. Davis, *J. Org. Chem.*, **23**, 1767 (1958); b) C. E. Diebert, *J. Org. Chem.*, **35**, 1501 (1970); c) D. H. R. Barton and B. J. Willis, *J. Chem. Soc., Perkin Trans. I*, 305 (1972); d) D. H. R. Barton, F. S. Guziec, Jr., and I. Shahak, *J. Chem. Soc., Perkin Trans. I*, 1794 (1974); e) B. F. Bonini, G. Maccagnani, G. Mazzanti, and P. Piccinelli, *Tetrahedron Lett.*, 3987 (1979); f) G. Barbaro, A. Battaglia, P. Giorgianni, G. Maccagnani, D. Macciantelli, B. F. Bonini, G. Mazzanti, and P. Zani, *J. Chem. Soc., Perkin Trans. I*, 381 (1986); g) W. Freund and S. Hünig, *Helv. Chim. Acta.*, **70**, 929 (1987).

77 C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 282 (1949).

78 a) N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, **81**, 578 (1959); b) R. D. Schuetz and R. L. Jacobs, *J. Org. Chem.*, **26**, 3467 (1961); c) A. I. Meyers and M. E. Ford, *J. Org. Chem.*, **41**, 1735 (1976); d) R. J. Bushby and M. D. Pollard, *J. Chem. Soc., Perkin Trans. I*, 2401 (1979); e) J. E. McMurry, G. J. Haley, J. R. Matz, J. C. Clardy, G. Van Duyne, R. Gleiter, W. Schaefer, and D. H. White, *J. Am. Chem. Soc.*, **108**, 2932 (1986).

79 a) D. B. Denney and M. J. Boskin, *J. Am. Chem. Soc.*, **82**, 4736 (1960); b) W. Ando, Y. Hanyu, Y. Kumamoto, and T. Takata, *Tetrahedron*, **42**, 1989 (1986).

80 a) D. H. R. Barton and B. J. Willis, *J. Chem. Soc., Chem. Comm.*, 1225 (1970); b) A. G. Hortmann, A. Bhattacharjya, *J. Am. Chem. Soc.*, **98**, 7081 (1976).

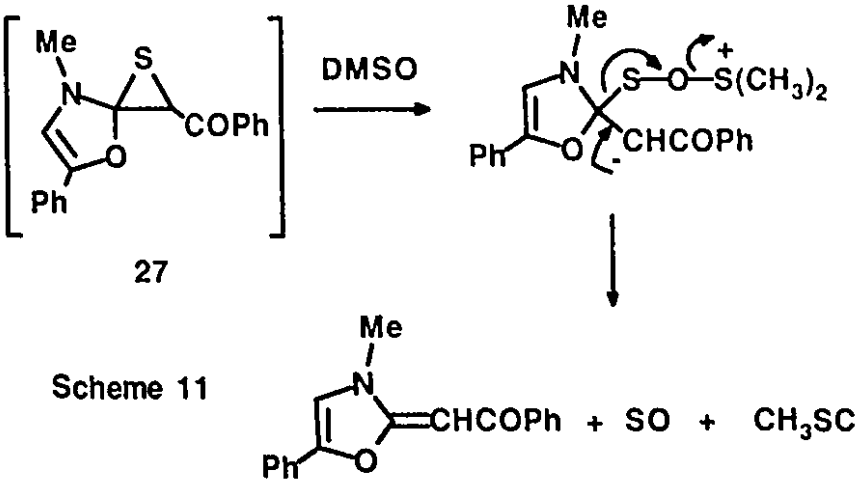
81 A. S. Gybin, W. A. Smit, M. Z. Krimer, N. S. Zefirov, L. A. Novgorodtseva, and N. K. Sadovaya, *Tetrahedron*, **36**, 361 (1980).

82 J. Bolster and R. M. Kellogg, *J. Chem. Soc., Chem. Comm.*, 630 (1978).

83 Y. Ueno and M. Okawara, *Bull. Chem. Soc. Jpn.*, **45**, 1797 (1972).

84 K. Okuma, Y. Tachibana, J. Sakata, T. Komiya, I. Kaneko, Y. Komiya, Y. Yamasaki, S. Yamamoto, and H. Ohta, *Bull. Chem. Soc. Jpn.*, **61**, 4323 (1988).

85 a) J. R. Schauder, J. N. Denis, and A. Krief, *Tetrahedron Lett.*, **24**, 1657 (1983); b) I. Zeid, S. Yassin, I. El-Sakka, and A. Abass, *Liebigs Ann. Chem.*, 191 (1984); c) J. Nakayama, S. Takeue, and M. Hoshino, *Tetrahedron Lett.*, **25**, 2679 (1984); d) F. Capozzi, G. Capozzi, and S. Menichetti, *Tetrahedron Lett.*, **29**, 4177 (1988).

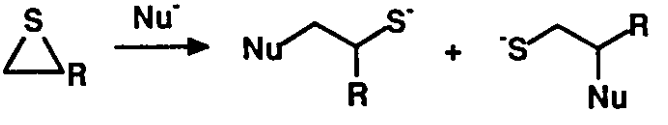


27

Scheme 11

1.9.3 Nucleophilic Attack on Carbon

A variety of nucleophiles attack the carbon atom of thiiranes to give ring opened products (Scheme 4 and 12). The reactivity is higher than in the analogous reaction with oxiranes; hence, thiiranes tend to polymerize more readily than oxiranes. Many different products are obtained from the generated thiolate anion. With oxygen nucleophiles such as hydroxide and alkoxide/aryloxide ions, the mercaptan derivative is usually obtained although polymerization occasionally occurs. Under these conditions, a thiolate anion is formed which is much more reactive than the oxygen anion.[86] In many of these cases, there is no preference for attack at either carbon. The polymeric materials obtained from these reactions have been used as light and water resistant agents.[87]



Scheme 12

Nitrogen nucleophiles also react to give 2-mercaptoethyl amine derivatives. The general feature in reactions of thiiranes with amines is that the attack usually occurs regioselectively at the least hindered position. The thiirane ring is opened easier than the corresponding oxirane ring.[88] Primary and secondary amines react readily whereas

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86 T. V. Vergizova, A. A. Rodin, and K. A. V'yunov, *Zh. Org. Khim.*, 22, 1396 (1986) and references therein.

87 G. Champetier and F. Lucas, *Compt. Rend.*, 252, 2782 (1961).

88 a) H. Kakiuchi, T. Iijima, and H. Horie, *Tetrahedron*, 35, 303 (1979); b) A. Champseix, J. Chanet, A. Étienne, A. Le Berre, J. C. Masson, C. Napierla, and R. Vessière, *Bull. Soc. Chim. Fr.*, 463 (1985); c) R. Luhowy and F. Meneghini, *J. Org. Chem.*, 38, 2405 (1973).

weakly basic and hindered amines are less reactive and require harsher conditions. Polymeric products result when tertiary amines or amide ions are used. The optimal conditions to effect the reaction would be to use polar media with weakly basic amines. This would accelerate nucleophilic opening of the thiirane ring. Unreactive thiiranes can also be made to react with highly basic amines under similar conditions.

Sulfur nucleophiles are more reactive towards thiiranes than oxygen or nitrogen nucleophiles and attack on the least substituted carbon is commonly observed. The thiolate anion reacts rapidly with many functional groups which, in most cases, lead to polymeric products. However, with effective acceptors of thiolates, which inhibit further polymerization, monomeric products can be obtained. Thiols cleave the C-S bond giving 2-alkylethane thiols as well as oligomerization products.

Halogen nucleophiles are also known to react with thiiranes leading to ring opened products. They react preferentially on the most substituted carbon but attacks on the less substituted carbon have also been reported.[89]

Carbanions attack at the least hindered carbon atom of the thiirane.[90] These anions include Grignard[91] and alkyllithium[92] reagents and metal complexes,[93] all which lead to ring-cleaved products. In some cases, desulfurization occurs with the formation of the olefin and metal thiolate.[76c,88b,94]

Although the most common reaction of phosphorus compounds with thiiranes is the elimination of sulfur, there have been some reports where phosphorus compounds react on one of the carbon atoms leading to monomeric and polymeric products.[95]

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89 a) G. K. Helmkamp and D. J. Pettitt, *J. Org. Chem.*, **27**, 2942 (1962); b) P. Raynolds, S. Zonnebelt, S. Bakker, and R. M. Kellogg, *J. Am. Chem. Soc.*, **96**, 3146 (1974); c) Y. Taguchi and Y. Suhara, *Chem. Abs.*, **94**, 174260 (1981).

90 a) C.O. Guss and D. L. Chamberlain, Jr., *J. Am. Chem. Soc.*, **74**, 1342 (1952); b) Y. Taguchi and Y. Suhara, *Bull. Chem. Soc. Jpn.*, **59**, 2321 (1986).

91 a) D. C. Dittmer, J. E. McCaskie, J. E. Babiarz, and M. V. Ruggeri, *J. Org. Chem.*, **42**, 1910 (1977); b) P. K. Claus, W. Rieder, and F. W. Vierhappe, *Monatsh. Chem.*, **109**, 609 (1978).

92 a) F. Lautenschlaeger and H. Schnecko, *J. Poly. Sci. A1*, **8**, 2579 (1970); b) P. Ongona, B. Mauze, and L. Miginiac, *Synthesis*, 1069 (1985).

93 a) L. A. Korotneva, G. P. Belonovskaya, and B. A. Dolgoplosk, *Dokl. Acad. Nauk. SSSR*, **207**(4), 899 (1972); b) B. M. Trost and S. D. Ziman, *J. Org. Chem.*, **38**, 932 (1973); c) A. Mordini, M. Taddei, and G. Seconi, *Gazz. Chim. Ital.*, **116**, 239 (1986).

94 a) F. G. Bordwell, H. M. Andersen, and B. M. Pitt, *J. Am. Chem. Soc.*, **76**, 1082 (1954); b) R. H. Schlessinger, G. S. Ponticello, and A. G. Schultz, *Tetrahedron Lett.*, 3963 (1968); c) B. M. Trost and S. Ziman, *J. Chem. Soc., Chem. Comm.*, 181 (1969); d) B. Rajanikanth and B. Ravindranath, *Ind. J. Chem.*, **23B**, 879 (1984).

95 a) B. E. Jennings, British Patent 1077958, *Chem. Abs.*, **67**, 82542y (1967); b) A. Nicco and B. Boucheron, German Patent 1814640, *Chem. Abs.*, **71**, 81929a (1969).

1.10 Plan of Study

Our main objective is to unequivocally determine a mechanism for the thermally-induced sulfur extrusion of thiiranes. As our model, we have chosen to carefully re-examine the kinetics of 2,2 dichloro-3-[9-fluorenyl] episulfide (**28**) (*cf.* Section 2.1) for several reasons. First, the synthesis of this compound is fairly straightforward and is well-documented in the literature. Second, this particular thiirane can be stored in the refrigerator for several months without noticeable decomposition. Although it is known that thiiranes containing aromatic and electron withdrawing substituents are usually unstable, the stability of this thiirane is ideal as it allows study on its thermal decomposition under suitable conditions. Finally, a detailed kinetic study would allow clarification of the conclusions made by Lutz and Biellman[54] and to provide strong evidence regarding the nature of the desulfurization. It should then be possible to establish a possible general rate law that governs the mechanism of the thermal decomposition of thiiranes.

Another goal of this project is to examine the effect of solvent on the decomposition of **28**. The effect of solvents should distinguish whether the extrusion of sulfur proceeds *via* an ionic or radical mechanism. A possible correlation between rate and a solvent polarity scale could then be made.

We felt it appropriate to synthesize novel derivatives of **28**. This would allow a good test of our mechanistic hypothesis. By studying the structural differences of these derivatives, we can rationalize the reactivity of these compounds. Some general conclusions regarding the mode of decomposition could thus be made.

The possibility of generating singlet diatomic sulfur in thiiranes will also be examined. This would not only provide insight into the overall mechanism of sulfur extrusion from these thiiranes but could also serve as another method to deliver $^1S_2$ from a relatively stable and readily available precursor. Other feasible methods of producing $^1S_2$ will also be investigated.

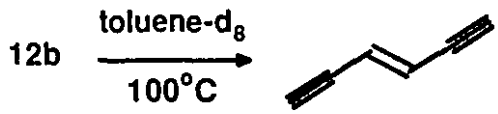
CHAPTER 2

KINETICS OF THE DECOMPOSITION OF 2,2-DICHLORO-3-[9-FLUORENYL] EPISULFIDE

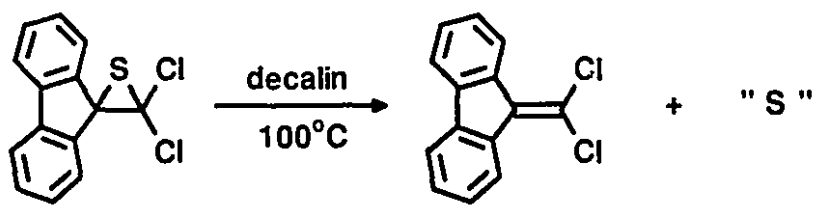
2.1 INTRODUCTION

Detailed kinetic studies on the decomposition of thiiranes have rarely been reported in the literature. In many of these reactions, elemental sulfur is lost but no detailed mention of the mechanism involved in the extrusion is reported. There appear to be three examples in the literature that have dealt with kinetic studies in the thermal decomposition of thiiranes.

Bergman's[52] work suggests that thermal sulfur extrusion from 1,2 diethynyl thiirane (**12b**) occurs in a bimolecular fashion at high concentrations of thiirane. As the concentration of thiirane decreases during the reaction, the bimolecular step changes to a unimolecular process. A simple cheletropic extrusion of a sulfur atom was ruled out as a likely pathway; the authors concluded that the reaction involves a more complicated mechanism.

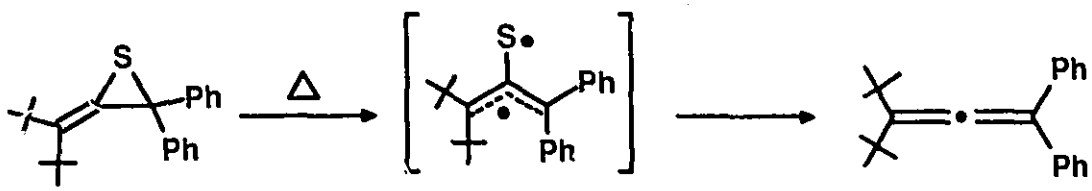


Lutz and Biellmann[54] studied the thermally induced extrusion reaction of 2,2 dichloro-3-[9-fluorenyl] episulfide (**28**) in decalin at 100°C querying whether the loss of sulfur was a unimolecular process (Scheme 13). They concluded that the decomposition of **28** is not a first order reaction. Clean kinetic behaviour was not observed from their results and it was suggested that sulfur loss is not a cheletropic extrusion of a sulfur atom but that a more complex process was involved. It was proposed that an "unknown species" acquires a sulfur atom which reacts further with another molecule of thiirane.



28 **29** **Scheme 13**

Finally, the mechanism of extrusion of a related molecule, an allene episulfide, was examined by Ando and coworkers.[53] The thermally catalyzed desulfurization of **30** in *o*-dichlorobenzene at 150°C led the authors to postulate a thioxyallyl radical intermediate. The observed rate acceleration in diglyme was rationalized by the dipole moment of the C-S bond biradical intermediate with a small contribution of zwitterionic structure. A similar kinetic study was undertaken by the same authors on **31** but only 2,4 dimethyl-3-mercaptopenta-1,3 diene (**32**) was obtained *via* an intramolecular 1,4 hydrogen shift and no allene was recovered.[96]



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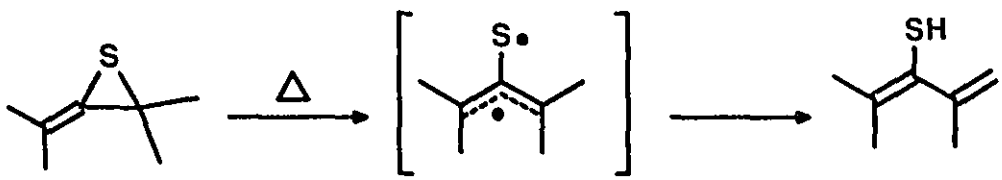

31 **32**

2.2 Rate Law in the Decomposition of 28

According to Scheme 13, the rate of this reaction equals the rate of decrease in the concentration of episulfide or the rate of increase in the concentration of olefin with time. Thus :

$$Rate = -\frac{\partial[E]}{\partial t} = \frac{\partial[O]}{\partial t} \qquad \text{Eq. (1)}$$

$[E]$ = concentration of episulfide

$[O]$ = concentration of olefin

The rate of decomposition of **28** can be conveniently obtained by measuring the increase in absorbance with time of the olefin product **29** at λ = 325 nm. λ_{max} (320 nm) was not used because absorbance values were too high at higher concentration of episulfide. Using the initial rate method, the initial slopes (abs./time) were calculated.

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96 T. Furuhata and W. Ando, *Tetrahedron*, 42, 5301 (1986).

Following the Beer-Lambert Law,

$A = \varepsilon bc$ Eq. (2)

A = absorbance
ε = molar extinction coefficient
b = cell path length (cm)
c = concentration (M)

The concentration/time rates can then be calculated by dividing the calculated slopes by the molar extinction coefficient, ε, a value which is characteristic of the olefin in the medium in which the reaction was conducted. Extinction coefficients were determined by taking the slopes of the plots of absorbance versus concentration of olefin. A typical plot is shown in Figure 1 where the extinction coefficient in decalin was determined. Excellent linear relationships were obtained in all solvents ($r > 0.99$). Errors were obtained by estimating the uncertainty in the absorbances (10%) and using similar equations derived in section 2.4 (*vide infra*). Table 2 shows the experimentally obtained extinction coefficients in the various solvents used in this study.

Figure 1. Plot of Absorbance *vs*. Concentration of olefin **29** in the determination of extinction coefficient. Absorbances were measured at $\lambda = 325$ nm.

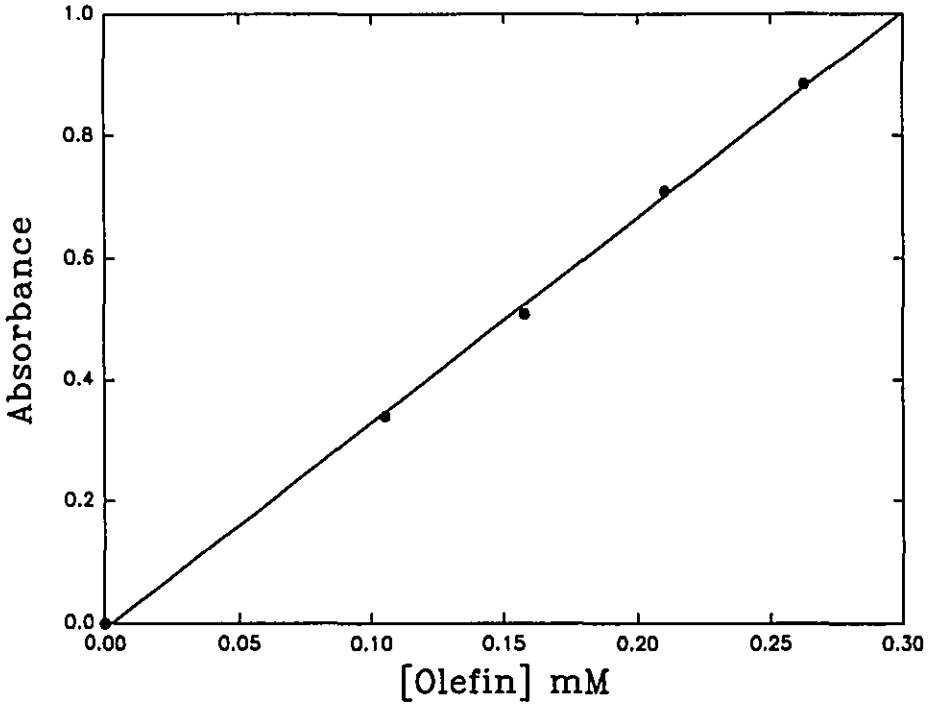

Table 2. Extinction coefficients for **29** in various solvents measured at λ = 325 nm.

Solvent	ε	Solvent	ε
Decalin	3720 ± 381	1:1 Decalin/Toluene	6940 ± 816
DMF	7233 ± 863	Decane	2290 ± 284
DMSO	9368 ± 1084	1,1,2,2-Tetrachloroethane	8476 ± 1087
Isobutanol	2820 ± 342	1,2,4-Trimethylbenzene	8109 ± 1092
2-Chloroethanol	4827 ± 862	*o*-Xylene	13077 ± 1312
Chlorobenzene	7915 ± 989	*m*-Xylene	7743 ± 938
o-Dichlorobenzene	11511 ± 1220	*p*-Xylene	7402 ± 901
Bromobenzene	11121 ± 1301	Ethanol	2894 ± 427
Toluene	6315 ± 770	Ethanol-*d*	3493 ± 768

The thermal decomposition reaction was conducted in 16 different solvents (Table 2) all involving runs at 80°C. Table 3 shows calculated rates at various concentrations. A typical rate profile in toluene is shown in Figure 2.

Figure 2. Rate behaviour in the decomposition of **28** in toluene at 80°C.

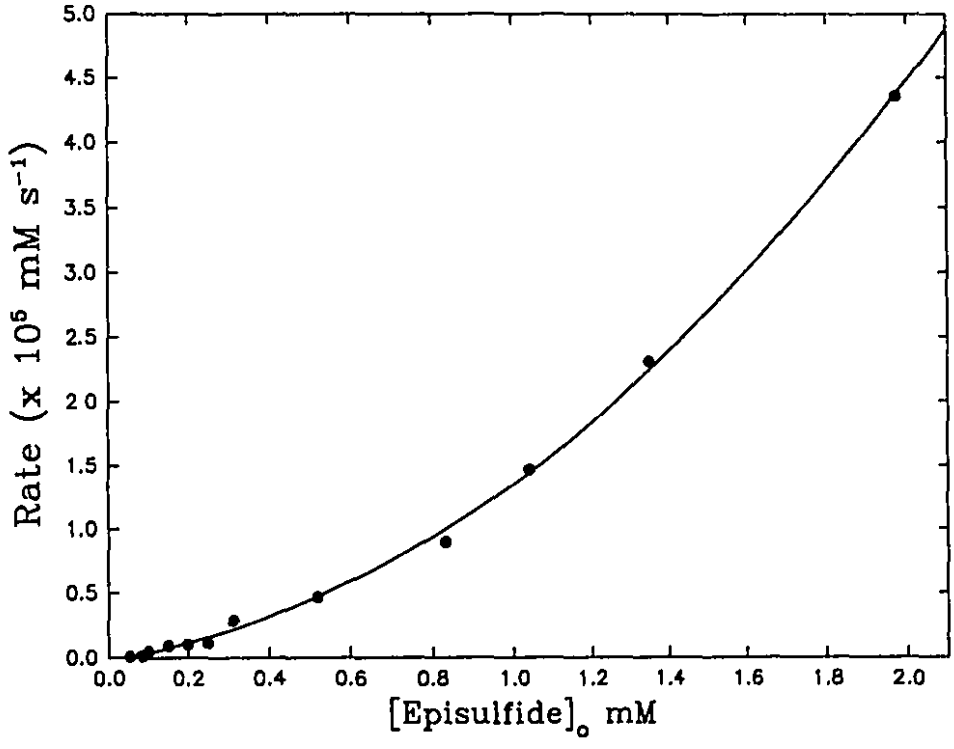

Table 3. Calculated rates of reaction at various concentrations at 80°C.

Decalin		DMF		DMSO	
[episulfide]	[ ] / time[a]	[episulfide]	[ ] / time	[episulfide]	[ ] / time
0.10	0.13	0.001	0.28	0.048	3.4
0.20	0.42	0.005	0.82	0.097	6.4
0.50	1.0	0.01	0.86	0.19	12
1.0	2.9	0.03	3.0	0.48	35
1.2	4.2	0.05	6.1	0.97	113
1.5	5.2	0.08	7.3		
1.8	6.9	0.10	11		
2.0	10	0.15	23		
		0.20	32		
		0.25	34		
		0.30	49		

Isobutanol		2-Chloroethanol		Chlorobenzene	
[episulfide]	[ ] / time	[episulfide]	[ ] / time	[episulfide]	[ ] / time
0.011	0.065	0.031	0.27	0.10	0.023
0.033	0.053	0.083	0.64	0.15	0.040
0.055	0.67	0.31	1.8	0.20	0.084
0.088	0.88	0.52	9.8	0.25	0.11
0.33	1.5	0.83	16	0.32	0.23
0.55	2.9	1.0	20	0.51	0.48
0.88	5.3	1.6	43	0.82	2.0
1.1	6.8			1.1	2.5
1.3	7.4			1.3	3.0
1.7	9.8			1.8	5.8

Table 3. continued

o-Dichlorobenzene		Bromobenzene		Toluene	
[episulfide]	[ ] / time	[episulfide]	[ ] / time	[episulfide]	[ ] / time
0.10	0.043	0.033	0.020	0.052	0.0098
0.15	0.060	0.087	0.072	0.083	0.019
0.20	0.097	0.10	0.037	0.10	0.050
0.25	0.15	0.15	0.072	0.15	0.096
0.33	0.38	0.21	0.099	0.20	0.10
0.54	0.90	0.26	0.15	0.25	0.12
0.87	1.5	0.33	0.31	0.31	0.29
1.1	2.3	0.54	0.87	0.52	0.47
1.4	3.0	0.87	1.3	0.83	0.90
1.9	4.2	1.1	2.4	1.0	1.5
		1.4	3.2	1.4	2.3
		1.8	6.3	2.0	4.4

1:1 Decalin/Toluene		Decane		1,1,2,2 Tetrachloroethane	
[episulfide]	[ ] / time	[episulfide]	[ ] / time	[episulfide]	[ ] / time
0.053	0.041	0.010	0.020	0.11	0.064
0.084	0.043	0.051	0.045	0.23	0.24
0.11	0.081	0.10	0.076	0.57	0.66
0.16	0.12	0.31	0.54	1.2	2.2
0.21	0.21	0.51	0.73	1.4	3.1
0.26	0.31	0.82	0.93	1.7	4.7
0.53	0.32	1.0	1.9		
0.84	0.82	1.6	3.0		
1.1	1.1	2.1	4.4		
1.4	1.9				
1.9	3.3				

Table 3. continued

1,2,4 Trimethylbenzene		*o*-Xylene	
[episulfide]	[ ] / time	[episulfide]	[ ] / time
0.30	0.026	0.05	0.019
0.50	0.11	0.11	0.071
1.0	0.39	0.22	0.15
1.5	0.63	0.55	0.41
2.0	1.1	1.1	1.3
3.0	2.2	2.2	3.4
		2.7	5.4
		3.3	6.5

m-Xylene		*p*-Xylene	
[episulfide]	[ ] / time	[episulfide]	[ ] / time
0.10	0.013	0.10	0.036
0.50	0.081	0.21	0.070
1.0	0.30	0.52	0.31
1.5	0.46	1.0	0.76
2.0	0.97	1.6	2.5
2.5	1.5	1.6	1.8
3.0	2.3	1.8	2.2
		2.1	3.6
		2.2	3.8
		2.4	4.2
		2.6	4.6
		3.1	5.8

[a] All rates are in mM s^{-1} x 10^5

By inspection, the decomposition of **28** is *not* a first order reaction (in agreement with that observed by Lutz and Biellmann[54]) and thus is not a simple unimolecular decomposition. From this detailed kinetic study, four possible rate laws were examined to fit the data :

$$\text{Rate} = k_1[E] + k_2[E]^2 \qquad \text{Eq. (3)}$$

$$\text{Rate} = k_1[E] + k_3[E]^3 \qquad \text{Eq. (4)}$$

$$\text{Rate} = k_2[E]^2 + k_3[E]^3 \qquad \text{Eq. (5)}$$

$$\text{Rate} = k_3[E]^3 \qquad \text{Eq. (6)}$$

[E] = concentration episulfide (mM)

$k_1 = s^{-1}$

$k_2 = mM^{-1}\ s^{-1}$

$k_3 = mM^{-2}\ s^{-1}$

Values of the rate constants, k_1, k_2 and k_3, were obtained by curve-fitting the data using the Marquardt-Lerenberg interactive algorithm[97] and are listed in Tables 4a and 4b. The accuracy of the rate equations were judged by calculated correlation coefficients. These coefficients are shown in Table 5. The best overall correlation value corresponded to Eq. (3). This enables us to conclude that the mechanism of sulfur loss is consistent with the two-term rate expression consisting of the first and second order terms, Eq. (3).[98]

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97 SigmaPlot Scientific Graphing System Version 4.1, Jandel Scientific Corporation.

98 W. Chew and D. N. Harpp, *Tetrahedron Lett.*, 33, 45 (1992).

Table 4a. k_1/k_2 and k_1/k_3 rate constants derived from Eq. (3) and (4) respectively.

	Rate = $k_1[E] + k_2[E]^2$		Rate = $k_1[E] + k_3[E]^3$	
Solvent	k_1[a]	k_2[b]	k_1[a]	k_3[c]
Decalin	0.72 ± 0.51	2.0 ± 1.0	2.1	0.69
DMF	109 ± 32	173 ± 116	133	330
DMSO	36 ± 21	82 ± 29	57	14
Isobutanol	5.6 ± 1.2	0.14 ± 0.82	5.6	0.07
2-Chloroethanol	8.3 ± 5.0	12 ± 4	16	5.0
Chlorobenzene	0.78 ± 0.27	1.3 ± 0.3	2.1	0.35
o-Dichlorobenzene	0.52 ± 0.20	0.99 ± 0.33	2.1	0.08
Bromobenzene	0.50 ± 0.27	2.5 ± 1.0	1.24	0.63
Toluene	0.45 ± 0.17	0.90 ± 0.43	1.2	0.28
1:1 Decalin/Toluene	0.83 ± 0.17	0.61 ± 0.84	1.3	0.20
Decane	1.2 ± 0.4	0.49 ± 0.24	1.5	0.16
1,1,2,2 Tetrachloroethane	1.9 ± 0.3	2.2 ± 0.5	1.2	0.53
1,2,4 Trimethylbenzene	0.11 ± 0.07	0.21 ± 0.05	0.40	0.04
o-Xylene	0.71 ± 0.20	0.41 ± 0.54	1.3	0.07
m-Xylene	0.09 ± 0.08	0.22 ± 0.09	0.22	0.06
p-Xylene	0.63 ± 0.21	0.42 ± 0.20	1.4	0.07

[a] in $s^{-1} \times 10^5$; [b] in $mM^{-1}\ s^{-1} \times 10^5$; [c] in $mM^{-2}\ s^{-1} \times 10^5$

Table 4b. k_2/k_3 and k_3 rate constants derived from Eq. (5) and (6) respectively.

	Rate = $k_2[E]^2 + k_3[E]^3$		Rate = $k_3[E]^3$
Solvent	k_2[a]	k_3[b]	k_3[b]
Decalin	2.2	0.072	1.2
DMF	536	2.0×10^{-5}	1775
DMSO	60	2.9×10^{-7}	46
Isobutanol	3.6	3.0×10^{-8}	2.1
2-Chloroethanol	17	4.6×10^{-8}	11
Chlorobenzene	1.7	4.8×10^{-9}	0.94
o-Dichlorobenzene	1.2	7.4×10^{-9}	0.66
Bromobenzene	1.6	0.11	0.98
Toluene	1.1	2.0×10^{-9}	0.57
1:1 Decalin/Toluene	1.1	4.3×10^{-9}	0.60
Decane	1.0	4.4×10^{-9}	0.49
1,1,2,2 Tetrachloroethane	1.4	0.046	0.89
1,2,4 Trimethylbenzene	0.24	1.5×10^{-10}	0.08
o-Xylene	0.63	1.2×10^{-9}	0.19
m-Xylene	0.17	0.025	0.08
p-Xylene	0.63	1.4×10^{-9}	0.20

[a] in $mM^{-1}\ s^{-1} \times 10^5$; [b] in $mM^{-2}\ s^{-1} \times 10^5$

Table 5. Correlation coefficients obtained in the determination of rate constants for several different rate laws.

	Correlation coefficients			
Solvent	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (6)
Decalin	0.993	0.994	0.989	0.953
DMF	0.993	0.992	0.990	0.928
DMSO	0.997	0.997	0.992	0.960
Isobutanol	0.996	0.996	0.993	0.902
2-Chloroethanol	0.991	0.991	0.989	0.902
Chlorobenzene	0.993	0.993	0.991	0.954
o-Dichlorobenzene	0.998	0.998	0.997	0.928
Bromobenzene	0.996	0.997	0.995	0.983
Toluene	0.999	0.998	0.999	0.968
1:1 Decalin/Toluene	0.998	0.998	0.997	0.947
Decane	0.995	0.994	0.993	0.943
1,1,2,2-Tetrachloroethane	0.998	0.998	0.984	0.942
1,2,4-Trimethylbenzene	0.999	0.999	0.999	0.980
o-Xylene	0.996	0.996	0.992	0.937
m-Xylene	0.998	0.998	0.998	0.992
p-Xylene	0.999	0.997	0.999	0.972

Table 6 shows the relative values of the data obtained from Eq. (3) (Table 4a). In general, the unimolecular rate constants in the solvents do show the expected trends with respect to their polarities (*cf.* Section 2.8.3). DMF and DMSO which are the most polar have higher rates and the alcohols, isobutanol and 2-chloroethanol, which are moderately polar have slightly lower rates. The non-polar aromatic solvents all show similar slow rates with the exception of 1,2,4-trimethylbenzene and *m*-xylene which are even lower contrary to expectation. No explanation can be given to account for these observed rates. However, it has been reported recently that the 9-fluorenyl cation can undergo electrophilic aromatic substitution reactions with benzene, toluene, and mesitylene.[99]

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[99] a) R. A. McClelland, N. Mathivanan, and S. Steenken, *J. Am. Chem. Soc.*, **112**, 4857 (1990); b) R. A. McClelland, J. Li, and F. Cozens, *3rd European Symposium on Organic Reactivity*,

Strong evidence was provided for capture of the fluorenyl cation with these solvents. Our observation of the slower rates in the methylbenzenes (Table 6) could possibly be linked to the trapping of the fluorenyl cation by these solvents since our proposed intermediate involves a fluorenyl cation (*cf.* Section 2.6). Electrophilic substitution would inhibit formation of olefin **29** and thus the rate of reaction would diminish. We explored this possibility further by conducting product studies on the desulfurization of thiirane **28** in toluene, 1,2,4-trimethylbenzene and the xylenes. Unfortunately, no indication of trapping of the fluorenyl cation with these solvents was observed and only the olefin **29** plus elemental sulfur was obtained. The failure to detect any other products does not discount the proposed dipolar mechanism but perhaps it is likely that the linking of sulfur atoms and subsequent extrusion of elemental sulfur is much faster than electrophilic reaction with the solvent molecules. The relative rates in the bimolecular term also show the expected trends with the exception of decalin and decane, both non-polar solvents, and bromobenzene. All show somewhat higher rates than either 1,2,4-trimethylbenzene and *m*-xylene. The rationale for these higher rates in these solvents is not clear. It will be shown later that the rate is slowest in isobutanol perhaps due to the near exclusive unimolecular pathway observed.

Göteborg, Sweden, July 7-12, 1991, Abstract B5; c) F. Cozens, J. Li, R. A. McClelland, and S. Steenken, *Angew. Chem. Int. Ed. Engl.*, **31**, 743 (1992).

Table 6. Relative rates calculated from rate constants using Eq. (3).

Solvent	k_{rel} (k_1)	k_{rel} (k_2)
DMF	1211	1236
DMSO	400	586
2-Chloroethanol	92	86
Isobutanol	62	1
1,1,2,2-Tetrachloroethane	21	16
Decane	13	4
1:1 Decalin/Toluene	9	4
Chlorobenzene	9	9
o-Xylene	8	3
Decalin	8	14
p-Xylene	7	3
o-Dichlorobenzene	6	7
Bromobenzene	6	18
Toluene	5	6
1,2,4-Trimethylbenzene	1	2
m-Xylene	1	2

In each solvent at low concentration of episulfide, the reaction follows a unimolecular, first order process, but at higher concentrations a bimolecular pathway becomes more important. The unimolecular term in Eq. (3) predominates at low concentration levels and as the concentration increases the second order or bimolecular term becomes more important. Table 7 shows the percentage of the unimolecular pathway calculated from Eq. (3) and rate data in Table 3 showing the importance of the unimolecular term at low concentrations and the significance of the bimolecular term at high concentrations. Thus in toluene, over a 400-fold increase (*cf.* Table 3) in the rate of desulfurization is observed when the concentration is increased 38-fold, thus reflecting the contribution of the bimolecular term. At low concentration levels (*ca.* 0.10-0.15 mM) the nearly exclusive pathway is a unimolecular decomposition while at higher concentrations (*ca.* 2.0 mM), the bimolecular path is actually followed by *ca.* 4:1. The bimolecular term predominates at higher concentrations in the majority of the solvents. In the case of DMF, at low concentrations, the exclusive pathway is unimolecular and at higher concentrations the unimolecular pathway is favored by *ca.* 2:1. In decane, the

unimolecular and bimolecular pathways become competitive at higher concentrations (*ca.* 1:1). One interesting feature is observed in the behaviour of isobutanol. In the entire concentration range studied, experimental results indicate that the decomposition is exclusively unimolecular. While we expect isobutanol and 2-chloroethanol to behave in a similar fashion since they are both alcohols, our results indicate otherwise. A typical plot of the ratio of the relative contribution of each term in Eq. (3) *vs.* concentration is shown in Figure 3 (toluene solvent). It clearly shows the decrease in the unimolecular contribution as the concentration of episulfide increases.

Table 7. Ratio of unimolecular to bimolecular terms in rate equation (3) shown as percentages. Calculated from rate data in Table 3.

Decalin		DMF		DMSO	
[episulfide]	uni/bimol	[episulfide]	uni/bimol	[episulfide]	uni/bimol
0.10	78	0.001	100	0.048	90
0.20	64	0.005	99	0.097	82
0.50	48	0.01	98	0.19	69
1.0	26	0.03	95	0.48	48
1.2	22	0.05	93	0.97	31
1.5	19	0.08	89		
1.8	17	0.10	86		
2.0	15	0.15	81		
		0.20	76		
		0.25	72		
		0.30	68		

Isobutanol		2-Chloroethanol		Chlorobenzene	
[episulfide]	uni/bimol	[episulfide]	uni/bimol	[episulfide]	uni/bimol
0.011	100	0.031	96	0.10	86
0.033	100	0.083	89	0.15	80
0.055	100	0.31	68	0.20	75
0.089	100	0.52	56	0.25	70
0.33	99	0.83	45	0.32	65
0.55	99	1.0	39	0.51	54
0.88	98	1.6	30	0.82	42
1.1	97			1.1	36
1.3	97			1.3	31
1.7	96			1.8	24

Table 7. continued

o-Dichlorobenzene		Bromobenzene		Toluene	
[episulfide]	uni/bimol	[episulfide]	uni/bimol	[episulfide]	uni/bimol
0.10	84	0.033	86	0.052	91
0.15	78	0.087	70	0.083	86
0.20	72	0.10	66	0.10	83
0.25	68	0.15	57	0.15	77
0.33	62	0.21	50	0.20	71
0.54	49	0.26	44	0.25	67
0.87	38	0.33	38	0.31	62
1.1	32	0.54	27	0.52	49
1.4	27	0.87	19	0.83	38
1.9	22	1.1	16	1.0	32
		1.4	13	1.4	27
		1.9	10	2.0	20

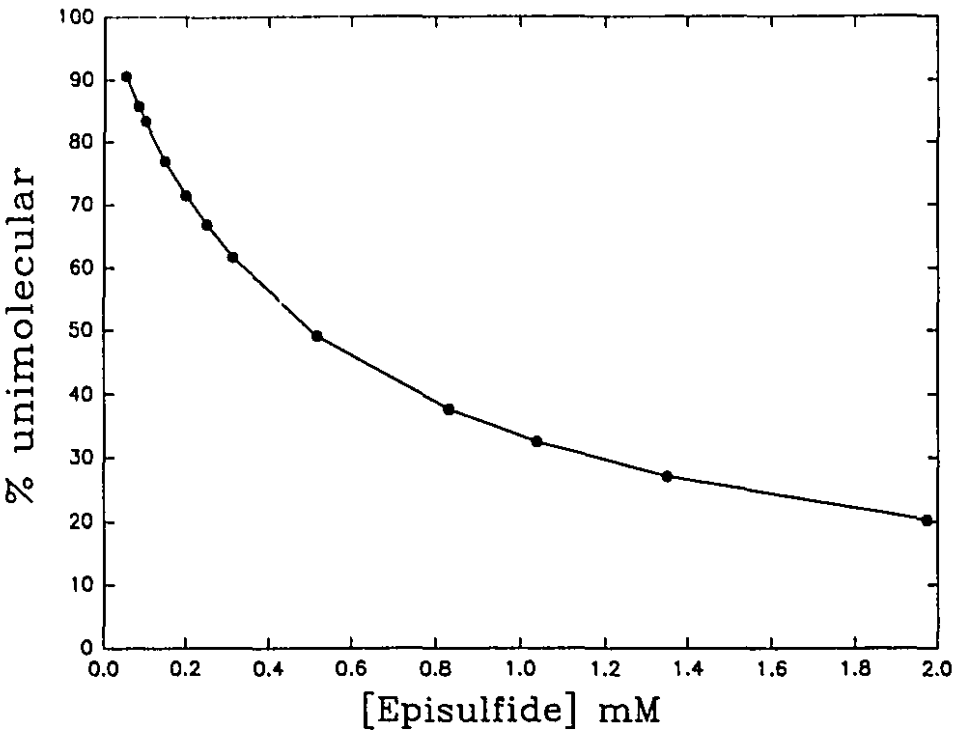
1:1 Decalin/Toluene		Decane		1,1,2,2 Tetrachloroethane	
[episulfide]	uni/bimol	[episulfide]	uni/bimol	[episulfide]	uni/bimol
0.053	96	0.010	99	0.11	88
0.084	94	0.051	98	0.23	79
0.11	93	0.10	96	0.57	60
0.16	90	0.31	88	1.2	43
0.21	86	0.51	82	1.4	37
0.26	84	0.82	74	1.7	33
0.53	72	1.0	70		
0.84	62	1.6	60		
1.1	56	2.1	53		
1.4	50				
1.9	42				

Table 7. continued

1,2,4 Trimethylbenzene		*o*-Xylene	
[episulfide]	uni/bimol	[episulfide]	uni/bimol
0.30	64	0.05	97
0.50	51	0.11	94
1.0	34	0.22	89
1.5	26	0.55	76
2.0	21	1.1	61
3.0	15	2.2	44
		2.7	39
		3.3	34

m-Xylene		*p*-Xylene	
[episulfide]	uni/bimol	[episulfide]	uni/bimol
0.10	79	0.10	94
0.50	44	0.21	88
1.0	28	0.52	74
1.5	20	1.0	59
2.0	16	1.6	49
2.5	13	1.6	48
3.0	11	1.8	45
		2.1	42
		2.2	40
		2.4	38
		2.6	37
		3.1	32

Figure 3. Plot of the ratio of the unimolecular to the bimolecular term of Eq. (3) *vs.* episulfide concentration in toluene solvent.



2.3 Arrhenius Parameters

It is well-known that the rates of almost all chemical reactions increase with increasing temperature. The rate can commonly increase a factor of 2 to 4 for every 10 K rise in temperature. The activation energy or the minimum energy required for a reaction to occur is much higher than the average energy of the colliding molecules and only a small fraction of collisions lead to reaction. If the activation energy is low then the reaction becomes faster. Therefore, the rate constant depends on the activation energy of the reaction. Increasing the temperature increases the number of collisions and for most reactions the rate generally increases. The Arrhenius equation, Eq. (7), shows how the rate constant of a reaction depends on the temperature.

$$k = Ae^{-\frac{E_{act}}{RT}} \qquad \text{Eq. (7)}$$

k = rate constant
A = Arrhenius constant
E_{act} = activation energy
R = gas constant
T = temperature (K)

The Arrhenius parameter, A, is the total number of collisions per second that have the correct orientation. Taking natural logarithms of both sides gives :

$$\ln k = \ln A - \frac{E_{act}}{RT} \qquad \text{Eq. (8)}$$

A plot of ln k *vs.* 1/T should give a straight line with a slope equal to $-E_{act}/R$. Such a plot gives a method for determining the activation energy of a reaction from values of the rate constants at different temperatures.

The thermal decomposition of episulfide **28** was conducted at four temperatures for 15 solvents used in the study. The rates at various concentrations in different solvents are shown in Table 8. Using our proposed rate law, Eq. (3), rates were curve fitted[97] to obtain the first and second order rate constants, k_1 and k_2, and these are shown in Table 9. From these rate constants in Table 9, the activation energies, E_{act}, for the unimolecular and bimolecular terms in Eq. (3) can be calculated independently for each solvent using Eq. (8). Good linear correlation was found in most of the Arrhenius plots.

Table 8. Decomposition rates of **28** in the specified solvent at different temperatures.

Decalin							
[E]	70°C	[E]	80°C[c]	[E]	90°C	[E]	100°C
0.10[a]	0.11[b]	0.10	0.13	0.15	0.32	0.10	0.42
0.20	0.12	0.20	0.42	0.23	0.60	0.14	0.56
0.51	0.39	0.50	1.0	0.30	0.87	0.19	0.69
0.73	0.69	1.0	2.9	0.38	1.3	0.24	1.1
0.85	1.1	1.2	4.2	1.0	5.7	1.0	11
0.97	1.6	1.5	5.2	1.5	10	1.5	19
1.3	2.0	1.8	6.9	1.8	14	1.8	24
1.3	2.4	2.0	10	2.0	19	2.0	28
1.5	2.6						
1.8	3.8						

Table 8. continued

DMF					
[E]	37.5°C	50°C	65°C	[E]	80°C
0.0011	-	0.092	0.23	0.001	0.28
0.0054	-	0.14	0.87	0.005	0.82
0.010	0.13	0.62	1.7	0.01	0.86
0.050	0.35	0.84	5.1	0.03	3.0
0.10	0.41	2.0	7.4	0.05	6.1
0.16	0.58	3.9	28	0.08	7.3
0.25	0.78	5.3	29	0.10	11
0.32	1.3	5.7	32	0.15	23
				0.20	32
				0.25	35
				0.30	49

DMSO							
[E]	40°C	[E]	75°C	[E]	80°C	[E]	100°C
0.050	0.22	0.034	2.1	0.048	3.4	0.034	6.8
0.10	0.68	0.057	2.5	0.097	6.4	0.057	8.5
0.18	1.2	0.092	4.4	0.19	12	0.10	10
0.25	1.6	0.18	5.9	0.48	35	0.18	17
0.34	1.8	0.25	6.8	0.97	113	0.25	23
0.57	3.6	0.34	26			0.34	89
0.92	6.0	0.57	41			1.2	275
1.2	12	0.92	90				
1.5	17	1.2	134				

2-Chloroethanol							
[E]	70°C	[E]	80°C	[E]	90°C	[E]	100°C
0.031	0.10	0.031	0.27	0.030	0.50	0.030	8.1
0.082	0.21	0.083	0.64	0.050	1.1	0.050	13
0.31	0.66	0.31	1.8	0.080	1.5	0.080	19
0.51	2.1	0.52	9.8	0.10	1.9	0.30	53
0.82	3.0	0.83	16	0.15	2.8	0.50	55
1.0	3.8	1.0	20	0.25	5.0	0.80	69
1.5	6.2	1.6	43	0.30	6.6	1.2	131
2.0	11			0.50	17	1.8	202
				1.2	55		
				1.8	99		

Table 8. continued

Chlorobenzene							
[E]	70°C	[E]	80°C	[E]	90°C	[E]	100°C
0.30	0.15	0.10	0.023	0.10	0.068	0.10	0.13
0.51	0.32	0.15	0.040	0.15	0.088	0.15	0.25
0.79	0.63	0.20	0.084	0.20	0.13	0.20	0.39
1.0	1.1	0.25	0.11	0.25	0.22	0.25	0.47
1.3	1.6	0.32	0.23	0.51	1.1	0.51	2.1
1.8	2.7	0.51	0.48	1.0	3.5	1.0	6.7
		0.82	2.0	1.3	5.9	1.3	9.7
		1.1	2.5	1.8	8.2	1.8	14
		1.3	3.0				
		1.8	5.8				

o-Dichlorobenzene							
[E]	70°C	[E]	80°C	[E]	90°C	[E]	100°C
0.10	0.011	0.10	0.043	0.10	0.080	0.10	0.24
0.15	0.020	0.15	0.060	0.15	0.15	0.20	0.64
0.32	0.043	0.20	0.097	0.20	0.16	0.30	0.93
0.50	0.13	0.25	0.15	0.32	0.34	0.50	1.7
0.60	0.27	0.33	0.38	0.53	0.55	0.64	2.8
0.70	0.38	0.54	0.90	0.85	1.1	0.75	3.3
0.80	0.46	0.87	1.5	1.1	2.3	0.80	4.0
1.0	0.77	1.1	2.3	1.4	2.9	0.86	4.9
1.5	1.6	1.4	3.0	1.8	4.2	1.0	5.0
2.0	2.9	1.9	4.2			1.2	8.6
						1.5	6.8
						2.0	16

Table 8. continued

Bromobenzene							
[E]	70°C	[E]	80°C	[E]	90°C	[E]	100°C
0.11	0.021	0.033	0.020	0.033	0.094	0.10	0.24
0.17	0.035	0.087	0.072	0.089	0.11	0.16	0.41
0.22	0.086	0.10	0.037	0.10	0.12	0.21	0.62
0.28	0.12	0.15	0 072	0.15	0.20	0.26	0.77
0.33	0.36	0.21	0.099	0.20	0.31	0.34	1.6
0.56	0.48	0.26	0.15	0.25	0.39	0.56	3.2
0.89	1.4	0.33	0.31	0.33	1.1	0.90	4.7
1.1	2.6	0.54	0.87	0.56	1.8	1.1	6.9
1.4	3.8	0.87	1.3	0.90	3.2	1.9	18
1.9	5.9	1.1	2.4	1.1	4.1		
		1.4	3.2	1.5	5.7		
		1.8	6.3	1.9	8.3		

Toluene							
[E]	70°C	[E]	80°C	[E]	90°C	[E]	100°C
0.10	0.026	0.052	0.0098	0.10	0.062	0.10	0.11
0.15	0.054	0.083	0.019	0.15	0.096	0.15	0.13
0.20	0.072	0.10	0.050	0.20	0.17	0.20	0.25
0.25	0.093	0.15	0.096	0.25	0.18	0.25	0.27
0.30	0.16	0.20	0.10	0.30	0.47	0.30	0.79
0.81	0.43	0.25	0.12	0.81	1.6	0.81	2.5
1.3	0.99	0.31	0.29	1.3	2.8	1.3	5.3
2.0	1.6	0.52	0.47	2.0	5.3	2.0	7.6
		0.83	0.90				
		1.0	1.5				
		1.4	2.3				
		2.0	4.4				

Table 8. continued

1:1 Decalin/Toluene							
[E]	70°C	[E]	80°C	[E]	90°C	[E]	100°C
0.050	0.0034	0.053	0.041	0.053	0.042	0.053	0.092
0.080	0.026	0.084	0.043	0.084	0.043	0.084	0.14
0.10	0.032	0.11	0.081	0.11	0.081	0.11	0.20
0.16	0.047	0.16	0.12	0.16	0.12	0.16	0.34
0.21	0.070	0.21	0.21	0.21	0.21	0.21	0.40
0.26	0.092	0.26	0.31	0.26	0.31	0.26	0.55
0.50	0.12	0.53	0.32	0.54	0.32	0.54	0.61
0.80	0.22	0.84	0.82	0.84	0.82	0.84	1.4
1.0	0.33	1.1	1.1	1.1	1.1	1.1	3.0
1.3	0.51	1.4	1.9	1.4	1.9	1.4	4.4
1.8	0.96	1.9	3.3	1.9	3.3	1.9	6.7

Decane							
[E]	70°C	[E]	80°C	[E]	90°C	[E]	100°C
0.31	0.13	0.010	0.020	0.31	0.83	0.31	1.0
0.52	0.10	0.051	0.045	0.52	1.2	0.52	1.6
0.83	0.23	0.10	0.076	0.83	1.9	0.83	3.1
1.03	0.78	0.31	0.54	1.03	3.5	1.03	7.0
1.6	1.3	0.51	0.73	1.6	7.2	1.6	15
2.1	1.8	0.82	0.93	2.1	8.9	2.1	21
		1.0	1.9				
		1.6	3.0				
		2.1	4.4				

Table 8. continued

1,1,2,2 Tetrachloroethane							
[E]	70°C	[E]	80°C	[E]	90°C	[E]	100°C
0.10	0.024	0.11	0.064	0.10	0.18	0.10	0.40
0.20	0.089	0.23	0.24	0.20	0.47	0.20	2.1
0.50	0.31	0.57	0.66	0.51	1.7	0.50	3.0
0.60	0.51	1.1	2.2	1.0	4.4	1.0	15
0.70	0.92	1.4	3.1	1.5	7.6	1.5	20
1.0	1.1	1.7	4.7	2.0	13		
1.1	1.2						
1.2	1.8						
1.5	2.5						
1.8	4.0						
2.0	4.4						

1,2,4 Trimethylbenzene							
[E]	70°C	[E]	80°C	[E]	90°C	[E]	100°C
0.10	0.018	0.30	0.026	0.10	0.018	0.25	0.20
0.30	0.041	0.50	0.11	0.25	0.10	0.30	0.27
0.50	0.068	1.0	0.39	0.30	0.13	1.2	2.5
1.0	0.16	1.5	0.63	1.2	1.1	1.8	4.6
1.5	0.26	2.0	1.1	1.8	1.9	2.0	7.1
2.0	0.62	3.0	2.2	2.0	3.3	3.0	14
3.0	1.2			3.0	6.4		

o-Xylene							
[E]	70°C	[E]	80°C	[E]	90°C	[E]	100°C
0.051	0.013	0.05	0.019	0.051	-	0.10	0.39
0.10	0.038	0.11	0.071	0.10	0.15	0.15	0.46
0.15	0.061	0.22	0.15	0.15	0.18	0.20	0.51
0.31	0.11	0.55	0.41	0.31	0.52	0.25	0.73
0.51	0.21	1.1	1.2	0.51	0.78	0.30	0.77
0.82	0.38	2.2	3.4	0.82	1.6	0.50	1.7
1.0	0.52	2.7	5.4	1.0	2.5	0.80	3.7
1.3	0.84	3.3	6.5	1.3	3.4	1.0	5.4
1.7	1.3			1.7	5.3	1.3	7.3
2.0	1.7			2.0	7.1	1.7	11
						2.0	14

Table 8. continued

m-Xylene							
[E]	70°C	[E]	80°C	[E]	90°C	[E]	100°C
0.50	0.046	0.10	0.013	0.50	0.14	0.10	0.035
1.0	0.20	0.50	0.081	1.0	0.53	0.50	0.26
1.5	0.32	1.0	0.30	1.6	0.83	1.0	2.6
2.0	0.58	1.5	0.46	1.8	1.4	1.6	5.4
2.5	0.70	2.0	0.97	2.0	4.1	1.8	6.0
3.0	0.90	2.5	1.5	2.2	7.1	2.0	7.2
		3.0	2.3			2.2	8.3
						2.4	9.7
						2.5	12
						3.0	17

p-Xylene							
[E]	70°C	[E]	80°C	[E]	90°C	[E]	100°C
0.10	0.031	0.10	0.036	0.10	0.038	0.10	0.071
0.49	0.15	0.21	0.070	0.50	0.50	0.50	0.90
0.98	0.59	0.52	0.31	0.80	0.88	0.80	1.5
1.2	0.93	1.0	0.76	1.2	2.1	1.0	1.9
1.6	1.8	1.5	2.5	1.5	2.5	1.2	3.6
1.8	1.9	1.6	1.8	1.6	2.6	1.5	4.4
2.0	2.3	1.8	2.2	1.8	3.4	1.6	8.5
2.2	2.6	2.1	3.6	2.0	5.9	1.8	9.7
2.4	3.1	2.2	3.8	2.2	6.1	2.0	10
2.5	3.7	2.4	4.2	2.5	7.6	2.2	13
3.0	4.3	2.6	4.6	3.0	9.2	2.4	14
		3.1	5.8			2.5	14
						3.0	16

[a] in mM; [b] in mM s^{-1} x 10^{5}; [c] all rate values at 80°C were taken from Table 3 and included here for completeness.

Table 9. k_1 and k_2 rate constants derived from Eq. (3).

Decalin		DMF		DMSO	
Temp. (°C)	k_1[a]; k_2[b]	Temp. (°C)	k_1; k_2	Temp. (°C)	k_1; k_2
70	0.53 ± 0.23	37.5	3.7 ± 0.6	40	3.1 ± 1.2
	0.87 ± 0.56		4.8[d] ± 4.3		5.6 ± 1.6
80[c]	0.72 ± 0.51	50	22 ± 4.9	75	31 ± 23
	2.0 ± 1.0		2.2[d] ± 26		74 ± 22
90	1.6 ± 0.9	65	100 ± 23	80	36 ± 21
	3.7 ± 1.4		12 ± 83		82 ± 29
100	7.1 ± 1.5	80	109 ± 32	100	95 ± 44
	3.5 ± 3.4		173 ± 16		126 ± 52

2-Chloroethanol		Chlorobenzene		*o*-Dichlorobenzene	
Temp. (°C)	k_1; k_2	Temp. (°C)	k_1; k_2	Temp. (°C)	k_1; k_2
70	2.2 ± 1.0	70	0.44 ± 0.17	70	2.0[d,e] ± 0.1
	1.6 ± 0.6		0.57 ± 0.19		0.72 ± 0.12
80	8.3 ± 5.0	80	0.78 ± 0.27	80	0.52 ± 0.20
	12 ± 4		1.3 ± 0.3		0.99 ± 0.33
90	23 ± 11	90	1.9 ± 0.4	90	0.90 ± 0.24
	18 ± 7		1.5 ± 0.6		0.84[e] ± 0.65
100	110 ± 23	100	4.0 ± 0.8	100	3.1 ± 0.8
	0.42[e] ± 16		2.2 ± 1.4		2.2 ± 1.6

Table 9. continued

Bromobenzene		Toluene		1:1 Decalin/Toluene	
Temp. (°C)	k_1; k_2	Temp. (°C)	k_1; k_2	Temp. (°C)	k_1; k_2
70	0.39 ± 0.26	70	0.45 ± 0.09	70	0.12 ± 0.05
	1.5 ± 0.3		0.18 ± 0.26		0.22 ± 0.28
80	0.50 ± 0.27	80	0.45 ± 0.17	80	0.83 ± 0.17
	2.5 ± 1.0		0.90 ± 0.44		0.61 ± 0.85
90	2.6 ± 0.9	90	1.2 ± 0.2	90	1.0 ± 0.5
	0.93[e] ± 0.52		0.69 ± 0.62		0.71 ± 0.27
100	2.3 ± 0.8	100	2.8 ± 0.8	100	1.2 ± 0.7
	3.7 ± 2.0		0.53[e] ± 0.54		1.3 ± 0.4

Decane		1,1,2,2-Tetrachloroethane		1,2,4-Trimethylbenzene	
Temp. (°C)	k_1; k_2	Temp. (°C)	k_1; k_2	Temp. (°C)	k_1; k_2
70	0.28 ± 0.10	70	0.13 ± 0.21	70	0.03 ± 0.04
	0.30 ± 0.12		1.1 ± 0.24		0.12 ± 0.11
80	1.2 ± 0.4	80	0.31 ± 0.29	80	0.11 ± 0.07
	0.49 ± 0.24		1.4 ± 0.5		0.21 ± 0.05
90	2.2 ± 0.6	90	1.9 ± 0.7	90	0.11 ± 0.19
	1.1 ± 0.7		2.2 ± 1.5		0.66 ± 0.20
100	2.3 ± 1.1	100	9.2 ± 3.0	100	0.25 ± 0.42
	4.0 ± 1.1		3.3 ± 2.4		1.5 ± 0.4

Table 9. continued

o-Xylene		*m*-Xylene		*p*-Xylene	
Temp. (°C)	k_1; k_2	Temp. (°C)	k_1; k_2	Temp. (°C)	k_1; k_2
70	0.22 ± 0.08	70	0.15 ± 0.04	70	0.39 ± 0.16
	0.31 ± 0.35		0.05 ± 0.02		0.37 ± 0.17
80	0.71 ± 0.21	80	0.09 ± 0.07	80	0.63 ± 0.21
	0.41 ± 0.54		0.22 ± 0.08		0.42 ± 0.20
90	1.1 ± 0.3	90	0.86 ± 0.20	90	0.56 ± 0.33
	1.1 ± 0.9		0.24 ± 0.20		0.90 ± 0.27
100	2.9 ± 0.7	100	0.19 ± 0.56	100	2.2 ± 0.7
	2.1 ± 2.3		1.7[e] ± 0.3		1.3 ± 0.5

[a] in mM^{-1} s^{-1} x 10^5; [b] in mM^{-2} s^{-1} x 10^5; [c] all rate constants at 80°C were taken from Table 4a and included here for completeness; [d] these rate constants were very small to be of any significance; [e] these irregular rate constants were omitted in the calculation of the activation parameters.

In several cases, notably in the k_2 values, the uncertainties become exceedingly large. We will see later that this is caused by the small concentrations employed in the derivation of the rate constants (*cf.* Section 2.4). In some cases, the uncertainties are slightly greater than the rate constants themselves. This suggests that, statistically, from the available rate data, the rate constant could not be obtained accurately.

From the transition state theory, the Eyring equation is defined as :

$$k = \frac{k_b T}{h} e^{-\frac{\Delta G^{\neq}}{RT}}$$

k = rate constant

k_b = Boltzmann's constant (1.38 x 10^{-23} J/ K)

h = Planck's constant (6.63 x 10^{-34} J s)

T = temperature (K)

R = gas constant (1.987 cal/ K mole)

$\Delta G^{\neq}$ = free energy of activation.

Solving for $\Delta G^{\neq}$ one obtains,

$$\Delta G^{\neq} = T(4.576 \log \frac{k}{T} + 47.21)$$

The activation parameters can thus be computed from the following :

$$\Delta H^{\neq} = E_{act} - RT \qquad \text{Eq. (9)}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad \text{Eq. (10)}$$

$$\Delta G^{\neq} = E_{act} - RT - T\Delta S^{\neq}$$

So that,

$$\Delta S^{\neq} = 4.576 \log(\frac{k}{T}) + \frac{E_{act}}{T} - 49.21$$

or from Eq. (7),

$$\Delta S^{\neq} = 4.576 \log(\frac{A}{T}) - 49.21 \qquad \text{Eq. (11)}$$

The values of the activation parameters E_{act}, $\Delta H^{\neq}$, $\Delta G^{\neq}$, and $\Delta S^{\neq}$ can be calculated from Eqs. (8), (9), (10), and (11) respectively. These are included in Tables 10a and 10b in increasing $\Delta G^{\neq}$.

The standard deviations were determined by applying a similar method in the determination of standard deviations in the rate constants. An estimated 15% error in the values of the slopes and intercepts of the ln k *vs.* 1/T plots were used. The σs in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the same as for E_{act} and the σs in $\Delta G^{\neq}$ were determined by taking the square root of the sum of the squares of the σs in E_{act} and $\Delta S^{\neq}$ (*cf.* Section 2.4).

Table 10a. Activation parameters derived from k_1 rate constants.

Solvent	E_{act}[a,b]	$\Delta H^{\neq}$[c]	$\Delta S^{\neq}$[d]	$\Delta G^{\neq}$[e]
DMSO	17.9 ± 0.5	17.3 ± 0.5	-22.5 ± 1.5	24.0 ± 1.6
DMF	12.4 ± 0.5	11.8 ± 0.5	-47.3 ± 1.4	25.9 ± 1.5
Bromobenzene	10.5 ± 0.7	9.9 ± 0.7	-53.5 ± 2.0	25.9 ± 2.1
1,1,2,2 Tetrachloroethane	14.0 ± 0.7	13.4 ± 0.7	-45.4 ± 2.0	26.9 ± 2.1
Toluene	16.4 ± 0.7	15.8 ± 0.7	-37.6 ± 2.0	27.0 ± 2.1
o-Dichlorobenzene	19.0 ± 0.8	18.4 ± 0.8	-29.7 ± 2.1	27.3 ± 2.2
p-Xylene	17.1 ± 0.7	16.5 ± 0.7	-36.2 ± 2.0	27.3 ± 2.1
1:1 Decalin/Toluene	16.7 ± 0.7	16.2 ± 0.7	-37.4 ± 2.1	27.3 ± 2.2
Decane	18.0 ± 0.7	17.4 ± 0.7	-34.1 ± 2.0	27.6 ± 2.1
Decalin	21.7 ± 0.7	21.1 ± 0.7	-21.9 ± 1.9	27.7 ± 2.0
m-Xylene	20.9 ± 0.8	20.3 ± 0.7	-25.4 ± 2.4	27.8 ± 2.5
Chlorobenzene	30.4 ± 0.7	29.8 ± 0.7	6.6 ± 2.0	27.8 ± 2.1
2-Chloroethanol	32.6 ± 0.5	32.0 ± 0.5	13.0 ± 1.5	28.1 ± 1.6
1,2,4 Trimethylbenzene	15.3 ± 0.9	14.7 ± 0.9	-45.2 ± 2.4	28.2 ± 2.6
o-Xylene	21.9 ± 0.7	21.3 ± 0.7	-23.9 ± 2.0	28.5 ± 2.1

[a] Activation parameters derived from k_1 rate constants; [b] in kcal mol^{-1}; [c] kcal mol^{-1}; [d] cal mol^{-1} $^{o}K^{-1}$; [e] kcal mol^{-1}.

Table 10b. Activation parameters derived from k_2 rate constants.

Solvent	E_{act}[a,b]	$\Delta H^{\neq}$[c]	$\Delta S^{\neq}$[d]	$\Delta G^{\neq}$[e]
DMF	12.7 ± 1.2	12.1 ± 1.2	-39.1 ± 3.8	23.7 ± 4.0
Decalin	13.4 ± 0.7	12.8 ± 0.7	-38.3 ± 1.9	24.2 ± 2.0
DMSO	11.6 ± 0.5	11.0 ± 0.5	-47.2 ± 1.3	25.0 ± 1.4
Bromobenzene	7.4 ± 0.7	6.8 ± 0.7	-60.8 ± 2.0	25.0 ± 2.1
1,1,2,2 Tetrachloroethane	8.8 ± 0.7	8.2 ± 0.7	-57.0 ± 1.9	25.2 ± 2.0
Chlorobenzene	9.4 ± 0.7	8.8 ± 0.7	-56.6 ± 2.0	25.7 ± 2.2
p-Xylene	11.4 ± 0.7	10.8 ± 0.7	-52.4 ± 2.1	26.4 ± 2.2
m-Xylene	12.9 ± 0.8	12.3 ± 0.8	-48.0 ± 2.2	26.6 ± 2.3
o-Dichlorobenzene	17.8 ± 0.7	17.2 ± 0.7	-33.5 ± 2.1	27.2 ± 2.2
Toluene	17.8 ± 0.8	17.2 ± 0.8	-33.4 ± 2.3	27.2 ± 2.4
1:1 Decalin/Toluene	21.8 ± 0.7	21.2 ± 0.7	-22.7 ± 2.1	28.0 ± 2.2
2-Chloroethanol	23.0 ± 0.6	22.5 ± 0.6	-19.6 ± 1.8	28.3 ± 1.9
1,2,4 Trimethylbenzene	20.9 ± 0.8	20.3 ± 0.8	-27.0 ± 2.2	28.4 ± 2.3
Decane	34.9 ± 0.7	34.3 ± 0.7	16.8 ± 2.0	29.3 ± 2.1
o-Xylene	27.1 ± 0.7	26.5 ± 0.7	-10.4 ± 2.1	29.6 ± 2.2

[a] Activation parameters derived from k_2 rate constants; [b] in kcal mol^{-1}; [c] kcal mol^{-1}; [d] cal mol^{-1} $^{o}K^{-1}$; [e] kcal mol^{-1}.

Relatively few articles in the literature have *thoroughly* dealt with the overall effect of changing the medium upon the activation energy (or enthalpy) and entropy. The variation in these kinetic activation parameters is frequently so unpredictable that no generalizations can be easily made. In some ionization studies, certain regularities in the activation parameters do exist and these data are consistent with the theory of absolute reaction rates.[100] The high $\Delta H^{\neq}$ value of chlorobenzene in the k_1 determinations indicate some desolvation in the transition state which is consistent with a dipolar transition state. Solvent interaction in the ground state by chlorobenzene might be attributed to the greater polarizability of the aromatic π electrons.[101] DMF, a strong solvating agent, would experience little desolvation in the transition state and consequently have a lower $\Delta H^{\neq}$ albeit we do not observe the same behaviour in DMSO. All non-polar solvents should, therefore, have high $\Delta H^{\neq}$ values but our data indicate otherwise.

The somewhat large negative values of the entropy of activation suggest a highly ordered transition state in which the solvent plays a strong stabilizing role. The ground state would have less ordering of solvent molecules. This further strengthens our proposed mechanism involving ionized intermediates (*cf.* Section 2.6). Ionization reactions usually accompany a large negative $\Delta S^{\neq}$ because of the loss of entropy of the solvent when going to the transition state. Large negative entropies have been observed in the unimolecular thermolysis reaction of α-chloroalkyl ethers in aprotic solvents.[102] For the majority of the solvents, the molecules are somewhat unordered in the ground state but on solvation in the transition state they experience a reduction in the number of degrees of freedom available to them and, therefore, suffer from a greater loss in entropy. Solvents which are already ordered in the ground state will suffer a smaller loss in entropy upon solvation in the transition state. In two solvents, chlorobenzene and 2-chloroethanol, the positive values of $\Delta S^{\neq}$ (Table 10a) suggest a highly unordered transition state but become negative in the bimolecular mechanism (Table 10b) as expected. On the contrary, the reverse is observed for decane. The value of $\Delta S^{\neq}$ becomes positive in the bimolecular mechanism. No rationale can be offered for this unusual behaviour. It is interesting to note that numerical values for $\Delta S^{\neq}$ of the bimolecular term are almost uniformly more negative than the $\Delta S^{\neq}$ in the unimolecular

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100 a) G. Salomon, *Helv. Chem. Acta.*, **16**, 1361 (1933); b) N. J. T. Pickles and C. N. Hinshelwood, *J. Chem. Soc.*, 1353 (1936); c) B. L. Archer and R. F. Hudson, *J. Chem. Soc.*, 3259 (1950); d) J. W. Hackett and H. C. Thomas, *J. Am. Chem. Soc.*, 72, 4962 (1950).

101 R. E. Pincock, *J. Am. Chem. Soc.*, **86**, 1820 (1964).

102 H. Kwart and P. A. Silver, *J. Org. Chem.*, **40**, 3019 (1975).

term. This is consistent with the fact that a bimolecular reaction usually involves more ordering of solute and solvent molecules as two reacting species must come together for reaction to occur. The fact that some of the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are inconsistent within a series of solvents of similar structure or polarity (*ie.* xylenes, haloaromatic solvents, polar/non-polar solvents) implies solvent interactions, in both the ground and transition states, are too complicated for simple interpretation. The values of $\Delta G^{\neq}$ are all relatively constant which is consistent with the compensating effect of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ (*cf.* Section 2.5) and which satisfies Eq. (10).

2.4 Error Analysis of Rate Constants and Activation Parameters

In evaluating rate constants and kinetic activation parameters, it is necessary to examine the accuracy of the experimental data in the rate profiles. This would not only allow us to strengthen our proposed mechanism of decomposition but it also gives an indication of the validity of our experimental approach and procedures.

A typical rate profile for the decomposition of **28** is shown in Figure 2 (toluene at 80°C). An arbitrary deviation of ±15% in any of the first seven data points along the rate profile does not affect the calculated rate constants to a significant extent. However, it will be seen that a rate deviation of ±15% in the higher concentration region produces a slight variation in the rate constants with the largest change at the highest concentration. A simultaneous -15% change in the observed rate for the eleventh data point and a +15% change in the observed rate for the last value while keeping the first 10 points unchanged gives a first order rate constant that is diminished 7-fold (Table 11). The estimated ± 15% range originates from standard deviations obtained from multiple experimental runs. In the majority of the two or more experimental runs at the same concentration, standard deviations were not greater than 15%. In only a few cases, notably the lower concentration levels, the standard deviations were above 25%. Figure 4 shows the comparison of the experimental observed data with a hypothetical 15% deviation for the last two data values. Thus, the most sensitive portion of the rate profile is in the higher concentration range. Although the shape of the curves are very similar, the derived rate constants from curve-fitting are *different*. Conversely, the first and second order rate constants are slightly changed if one varies the eleventh point by +10% while varying the last point by -10%. Table 11 shows the variation in rate constants at different temperatures when the eleventh data point is increased or decreased (with a simultaneous decrease or increase in the last data point) by different percentages.

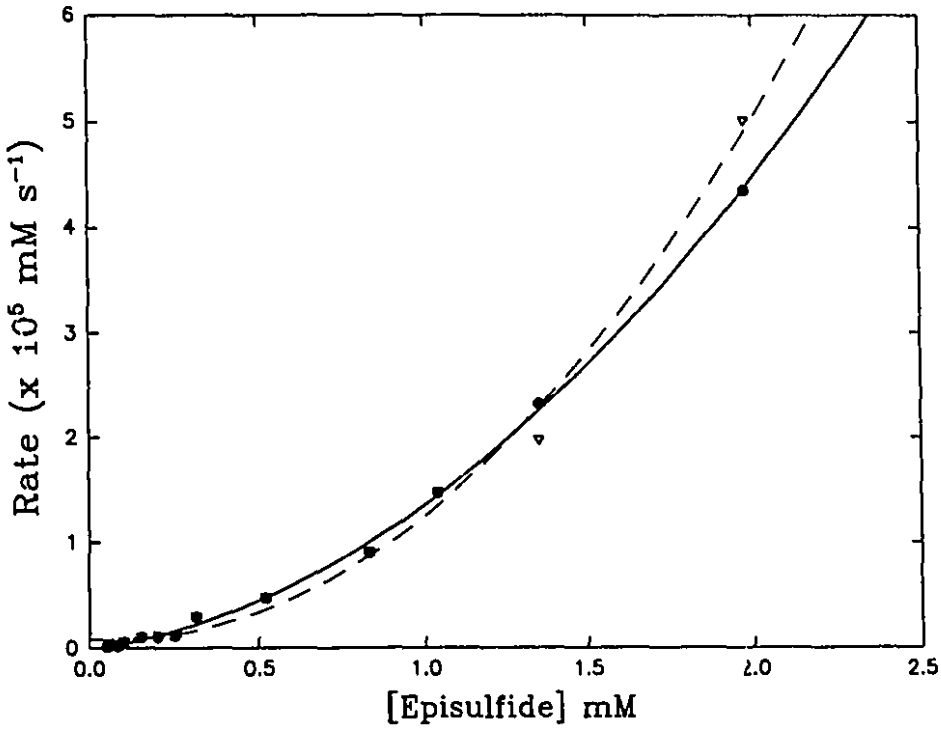
Table 11. Calculated rate constants obtained by variation of experimental rate values in toluene at different temperatures.

70°C			80°C		
% deviation from expt'l	k_1[a]	k_2[b]	% deviation from expt'l	k_1[a]	k_2[b]
15	0.65	0.034	15	0.83	0.57
10	0.58	0.083	10	0.70	0.68
5	0.52	0.13	5	0.58	0.79
2	0.48	0.16	2	0.50	0.85
-	0.45[c]	0.18	-	0.45[c]	0.90
2	0.42	0.20	2	0.40	0.94
5	0.38	0.23	5	0.32	1.0
10	0.32	0.28	10	0.19	1.1
15	0.25	0.33	15	0.066	1.2

90°C			100°C		
% deviation from expt'l	k_1[a]	k_2[b]	% deviation from expt'l	k_1[a]	k_2[b]
15	1.8	0.23	15	2.8	0.53
10	1.6	0.38	10	2.7	0.62
5	1.4	0.53	5	2.5	0.76
2	1.3	0.63	2	2.2	1.0
-	1.2[c]	0.69	-	1.8[c]	1.2
2	1.1	0.75	2	3.0	0.43
5	1.0	0.84	5	3.1	0.29
10	0.82	1.0	10	3.5	0.050
15	0.62	1.2	15	3.5	1.8×10^{-9}

[a] in $mM^{-1} s^{-1} \times 10^5$; [b] in $mM^{-2} s^{-1} \times 10^5$; [c] experimental observed value

Figure 4. Comparison of experimental data with a hypothetical deviation of 15% in the higher concentration range. Plot shows data from toluene at 80°C. • experimental data (see also Figure 2); ∇ 15% deviation data.



Based upon the deviations observed in toluene, it prompted us to determine an error range where our experimental rate constants, which lie within this range, can be taken as valid and accurate data and any experimental rate constants that lie below or above the range can be assumed simply as a bad experimentally derived rate constant. The tolerance range was determined by taking the uncertainty in the rate constants by estimating the errors in evaluating the rates. An estimate of ±15% was obtained. By treating the uncertainties in both k_1 and k_2 independently, the variance in the rate constants can be obtained from Eqs. (12a) and (12b).[103]

$$\sigma_{k_1}^2 = \frac{1}{N-1}\Sigma\frac{\sigma_y^2}{x^2} \qquad \text{Eq. (12a)}$$

$$\sigma_{k_2}^2 = \frac{1}{N-1}\Sigma\frac{\sigma_y^2}{x^4} \qquad \text{Eq. (12b)}$$

$\sigma_{k_1}^2$ = variance in k_1

$\sigma_{k_2}^2$ = variance in k_2

σ_y = estimated error in rates
= 15% of rate values

x = [episulfide]

N = number of data points

Thus, the uncertainties or standard deviations are easily obtained by taking the square root of the variance. From this 15% error in the determination of the rate constants, we can assume that a similar 15% variance interval exists in the evaluation of the activation energy, enthalpy, entropy and free energy. The activation parameter ranges for both the unimolecular and bimolecular portions of Eq. (3) are included in Tables 10a and 10b. As mentioned previously, large σs were obtained for some of the second order rate constants (*eg.* DMF, DMSO, and 2-chloroethanol). This is ascribed to the small values of x (low concentrations) employed in Eqs. (12a) and (12b). Small values of x would magnify into a much larger value in σ. Since x should define the error in the unimolecular term (k_1), we decided to apply only the higher concentration values in the evaluation of the error in the bimolecular term (k_2). This improved the value of σ for k_2.

In many instances where experimental runs were repeated, the derived rate constants were acceptable within the prescribed error limits. The differences in these rate constants are not likely to be due to systematic error but by random error which could not

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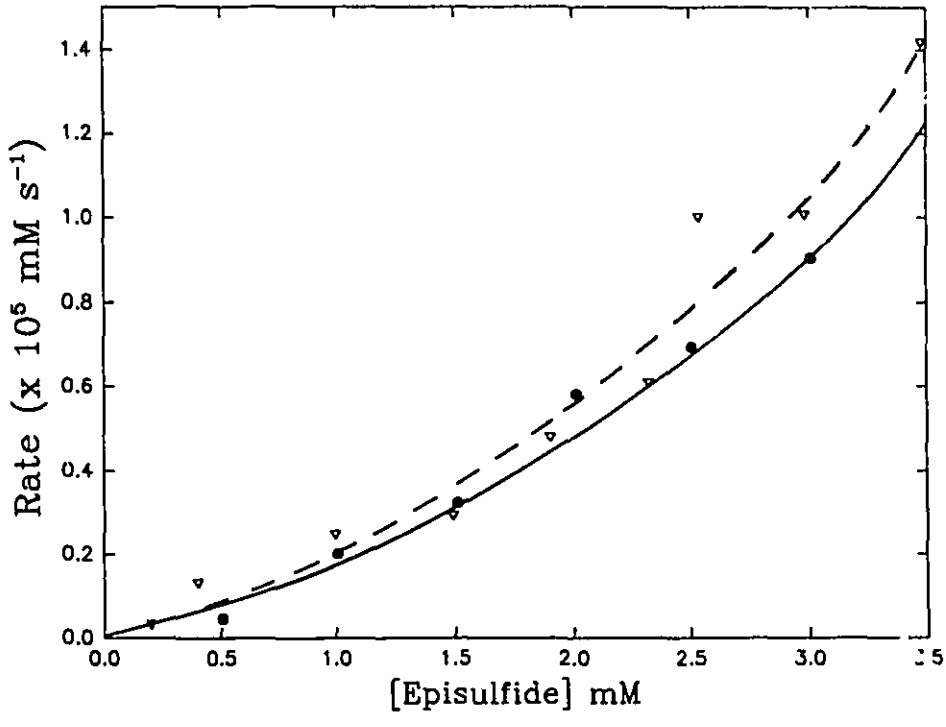
103 D. C. Harris, *Quantitative Chemical Analysis*, 2nd ed., W. H. Freeman and Co., New York, 1987, pp. 31, 43.

be avoided. Under the experimental conditions employed, the rates can be measured quite accurately. A good indication of this can be seen in the rate profile for *m*-xylene at 70°C shown in Figure 5 along with the same rate profile re-acquired after one year. The experimental runs are duplicable. The computed rate constants are similar; hence our experimental procedures appear to be quite accurate and valid. By derivation of the rate constants from Eq. (3), we see that the observed rate constants provide solid evidence of a dipolar mechanism consistent with our proposed mechanism of sulfur extrusion in thiiranes.

Figure 5. Rate profiles for the decomposition of **28** in *m*-xylene at 70°C shows data collected under identical experimental conditions at different times.
• experimental data taken March 23/91; ∇ experimental data taken March 13/92.



The experimental derived rate constants should thus be accepted only as a good approximation to the real values (*cf.* Table 4a). These values should be viewed with caution, as shown, from the possible large variations in the rate constants from the small deviations (random errors) in the observed rates. Although the error range is somewhat narrow, the activation parameters should also be treated with discretion as they are also obtained from approximate rate constants. An important feature that should be noted

invariably lower than the unimolecular first order entropy values as expected. This observation is a good indication that the activation parameters are reasonably accurate.

To further recognize how favorably the rate data fits Eq. (3), we calculated for each datum value, the number of standard deviations, σ, from the proposed parabolic rate law. We decided to use the rate data accumulated from all solvents at 80°C (*cf.* Table 3) to test the fit. From the determined k_1 and k_2 rate constants in Table 4a, we first replace their values back into Eq. (3) and calculate the rates at each concentration. To determine the number of standard deviations or how much deviation from Eq. (3) there is for each value, we subtract the calculated rates from the experimentally obtained rates and divide by σ_y. σ_y is obtained from the experimental rate multiplied by the estimated error in the determination of the rate. This estimate is 15% as shown above. Table 12 shows the calculated number of standard deviations for each rate and solvent. We immediately notice that in each solvent, the magnitude of the majority of the points are within 2σ. This suggests that we can be certain by statistical analysis that to a 95% confidence level, the determined rates at any particular concentration of episulfide will fall within 15% from the theoretical value obtained from Eq. (3). It is interesting to note that in some solvents (chlorobenzene, toluene, 1:1 decalin/toluene, 1,2,4-trimethylbenzene, *o*-xylene, and *p*-xylene), the first or lowest concentration levels resulted in large σs. This is not coincidental in view of the narrow range of variance at the low concentrations *vs.* the higher concentration levels. At low concentration, a 15% error in the rate gives a much smaller spread in the error range than at higher concentrations. This, consequently, produces a larger overall σ if the best fit curve from Eq. (3) does not include or go through those points. It is also interesting to point out that the number of positive σs is approximately equal to the number of negative σs which implies a reliable fit of the data with no apparent irregularity in them.

Table 12. Calculated number of standard deviations, σ, from Eq. (3).

Decalin	DMF	DMSO	Isobutanol	2-ClEtOH[a]	Clbenz[b]
-2.0	-4.1	-2.8	-0.32	0.081	21
-3.1	-2.2	-2.2	16	1.4	18
-0.95	1.9	-1.1	-3.5	7.0	9.8
-0.41	0.81	0.35	-2.9	-1.6	9.2
-0.25	-0.21	-0.09	1.5	-0.45	4.3
0.47	2.3		0.65	0.50	3.4
0.53	1.1		-0.28	-0.17	-1.7
-0.33	-0.90		-0.40		-0.53
	-0.63		0.31		0.70
	0.66		-0.02		-0.03
	-0.12				

DiClbenz[c]	Brbenz[d]	Toluene	Dec/tolu[e]	Decane	4ClEthane[f]
2.8	-0.53	11	7.0	-2.7	-1.1
4.4	-0.88	8.8	5.3	2.2	-2.7
3.2	7.2	0.50	7.5	4.1	-0.31
1.9	6.1	-0.62	10	-1.8	-0.08
-0.24	7.5	1.25	5.3	-0.09	0.34
3.5	6.6	2.8	2.3	2.4	-0.16
1.9	2.5	-1.4	1.5	-0.76	
0.37	1.0	0.10	-1.7	-0.12	
1.1	0.07	0.71	-0.74	0.04	
-0.56	-1.2	-0.14	0.67		
1.2	-0.36	-0.19	0.02		
-1.4	0.28	0.06	-0.30		
-0.62			0.05		
0.32					

Table 12. continued

124 Mebenz[g]	*o*-Xylene	*m*-Xylene	*p*-Xylene
6.5	7.3	-1.2	6.4
-0.12	1.0	1.5	7.4
-0.45	1.0	0.25	2.7
0.21	1.6	2.5	3.0
0.06	0.11	-1.0	-1.2
0.05	0.31	-0.1	1.4
	-0.53	0.08	1.0
	0.20	-0.03	-0.80
			-0.47
			-0.29
			-0.24
			0.29

[a] 2-chloroethanol; [b] chlorobenzene; [c] dichlorobenzene; [d] bromobenzene; [e] 1:1 decalin/toluene; [f] 1,1,2,2-tetrachloroethane; [g] 1,2,4-trimethylbenzene.

We conclude that Eq. (3) can be regarded as a likely fit to the overall kinetic observations in all solvents. If, however, we delete the values that are greater than 2σ units and recalculate the rate constants, we find that k_1 and k_2 do not change to any significant extent. For example, the value of 16σ in isobutanol was removed perhaps it could very well be a bad experimental point. However, after recalculating the rate constants, no change from the previous values was observed. In cases where the data are greater than 7σ, if we vary the rates by as much as 15% no noticeable change in the overall rate constants was observed. Hence, the rates at the lower concentration levels do not contribute to any critical degree to the overall determination of k_1 and k_2.

2.5 Isokinetic Relationship

The variation in rate due to a change in solvent may be caused by changes in either, or both, enthalpy or entropy of activation. Changes in rate can be chiefly caused by changes only in the enthalpy of activation, which is most commonly observed, or changes only in entropy of activation. Rate changes in both entropy and enthalpy are also observed but these quantities are often linearly correlated. This correlation is known as the isokinetic relationship, Eq. (13).

$$\delta\Delta H^{\ddagger} = \beta\delta\Delta S^{\ddagger} \qquad \text{Eq. (13)}$$

This phenomenon was first recognized by Leffler[104] who discussed its scope and significance. In simple terms, it states that at the isokinetic temperature, β, all the reactions in a given series have identical rates, or that $\delta\Delta G^{\neq} = 0$. The significance of this relationship lies within the rates of reaction in a reaction series. A reaction series consists of either substituent or solvent effects on the reaction rate. A reaction that is the fastest below β becomes the slowest above β and vice versa. Below the isokinetic temperature, the fastest reaction will have a lower $\Delta H^{\neq}$ and it is in the region of control by $\Delta H^{\neq}$. Above the isokinetic temperature, the fastest reaction will have a higher $\Delta S^{\neq}$ and it is in the region of control by $\Delta S^{\neq}$. Such an enthalpy-entropy relationship is well precedented in the literature.[105] An interesting feature in our study is an observed isokinetic relationship. The isokinetic plots for both unimolecular and bimolecular terms are shown in Figures 6a and 6b respectively using the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values from Tables 10a and 10b resulting in a linear relationship. A compensating effect of $\Delta S^{\neq}$ is observed as values of $\Delta H^{\neq}$ increase. It should be emphasized that this linearity is a requirement of Eq. (10). The isokinetic temperatures are 45°C and 93°C respectively for the first and second order terms with good correlations of 0.983 and 0.988 respectively. The linearity of the isokinetic plots also provides an indication that the reaction series in these solvents proceed with the same mechanism. Any noticeable deviation from the isokinetic function is attributed to different solvent interactions and possibly a different reaction mechanism. It has been debated that the apparent isokinetic relationship is a result of indiscriminate experimental error.[106] However, the spread of *ca.* 20 kcal in $\Delta H^{\neq}$ and *ca.* 45 eu in $\Delta S^{\neq}$ argue for the authenticity of our relationship.

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104 J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

105 a) M. G. Alder and J. E. Leffler, *J. Am. Chem. Soc.*, **76**, 1425 (1954); b) M. D. Cohen, J. E. Leffler, and L. M. Barbato, *J. Am. Chem. Soc.*, **76**, 4169 (1954); c) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958); d) C. D. Cook and B. E. Norcross, *J. Am. Chem. Soc.*, **81**, 1176 (1959); e) E. S. Huyser and R. M. VanScoy, *J. Org. Chem.*, **33**, 3524 (1968); f) Y. Matsumoto and R. Ueoka, *J. Org. Chem.*, **55**, 5797 (1990); g) R. M. Hassan, *Can. J. Chem.*, **69**, 2018 (1991); h) Y. Inoue, N. Yamasaki, T. Yokoyama, and A. Tai, *J. Org. Chem.*, **57**, 1332 (1992).

106 a) R. C. Petersen, J. H. Markgraf, and S. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961); b) W. Good, D. B. Ingham, and J. Stone, *Tetrahedron*, **31**, 257 (1975).

Figure 6a. Isokinetic plot from activation parameters derived from k_1 values. Isokinetic temperature = 45°C.

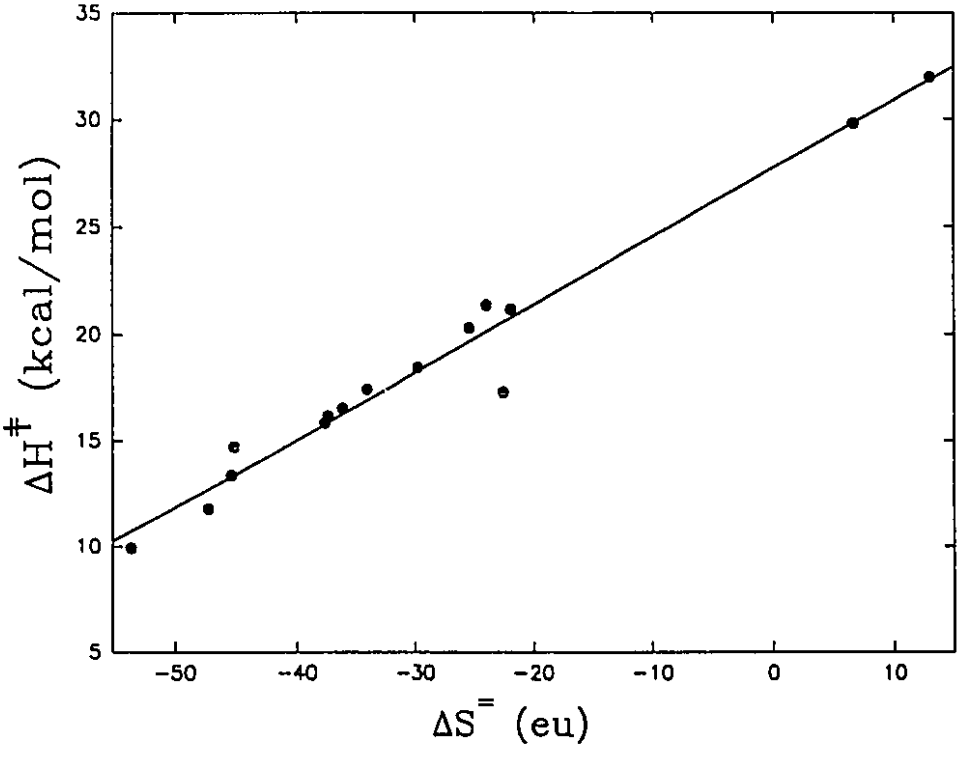
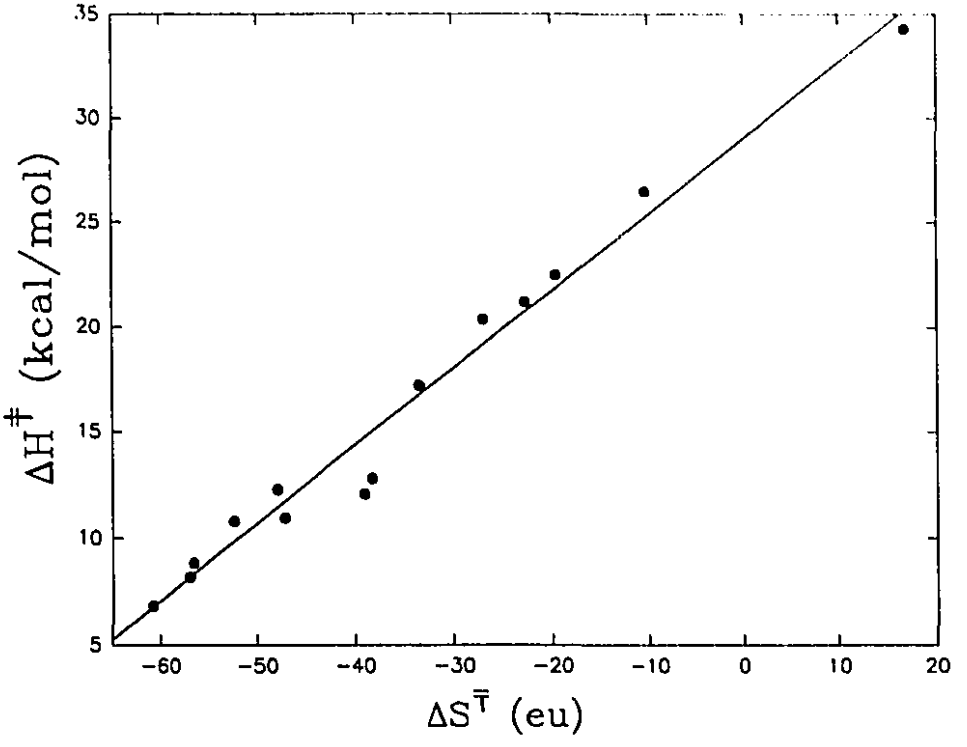


Figure 6b. Isokinetic plot from activation parameters derived from k_2 values. Isokinetic temperature = 93°C.



Since the isokinetic temperature for k_2 lies within our experimental temperature range, we should expect a reversal in rates above and below the isokinetic temperature. A reversal in the rates above and below the isokinetic temperature has been demonstrated from substituent effects on the thermal isomerization of triphenylformazans.[107] An attempt to show the reversal in rates above and below the isokinetic temperature was, however, unsuccessful. The lack of observed reversal in rates can be attributed to the fact that our rates were determined near the isokinetic temperature. A number of cases are reported where the isokinetic temperature falls within the experimental temperatures and reactions carried out at or near the isokinetic temperatures could lead to erroneous conclusions about the nature of the reaction.[108] Thus, interpretation of rate data from any reaction series should therefore be regarded with care. The failure to find a true linear correlation between the rate constants and some characteristic of the solvent (*ie.* dipole moment, internal pressure, etc. *cf.* Section 2.8.3) could also lead to the unobserved

107 N. Nishimura, Y. Sucishi, and S. Yamamoto, *Chem. Lett.*, 429 (1979).

108 a) J. F. Bunnett and R. J. Morath, *J. Am. Chem. Soc.*, 77, 5165 (1955); b) W. H. Saunders, Jr. and J. C. Ware, *J. Am. Chem. Soc.*, 80, 3328 (1958); See also ref. 104 and references cited therein.

reversal in rates. Plots of log k_1 *vs.* μ (dipole moment) or δ_H (internal pressure) are shown in Figures 7a and 7b respectively. They illustrate the significant scattering of the points.

Figure 7a. Plot of log k_1 *vs.* μ (dipole moment) showing the significant scatter with k_1. The k_1 values were taken from all solvents at 80°C.

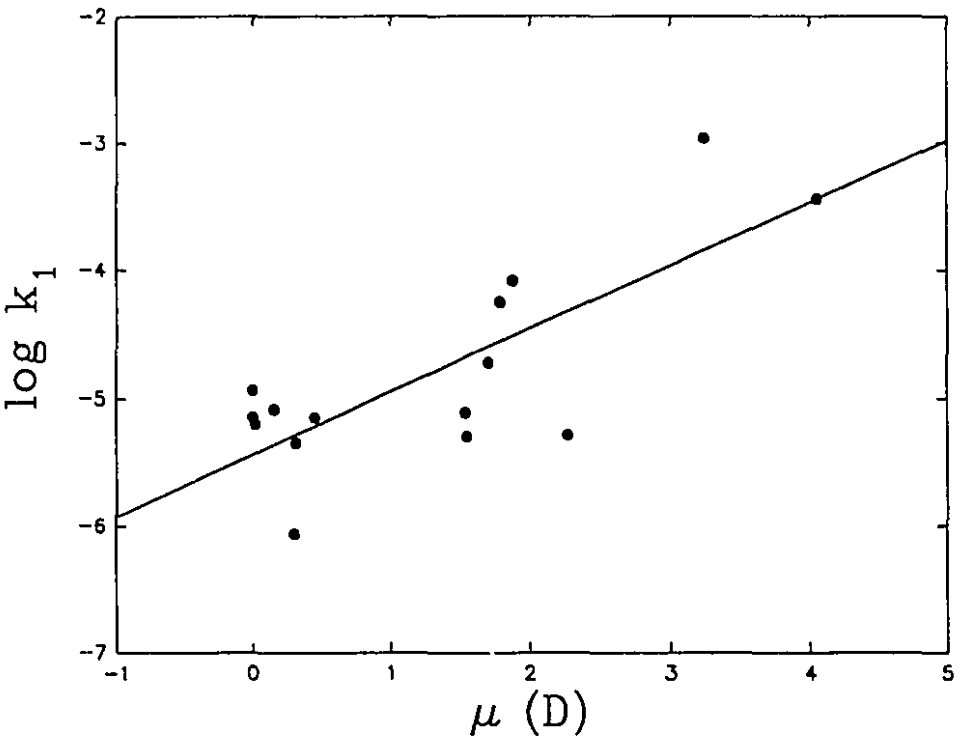
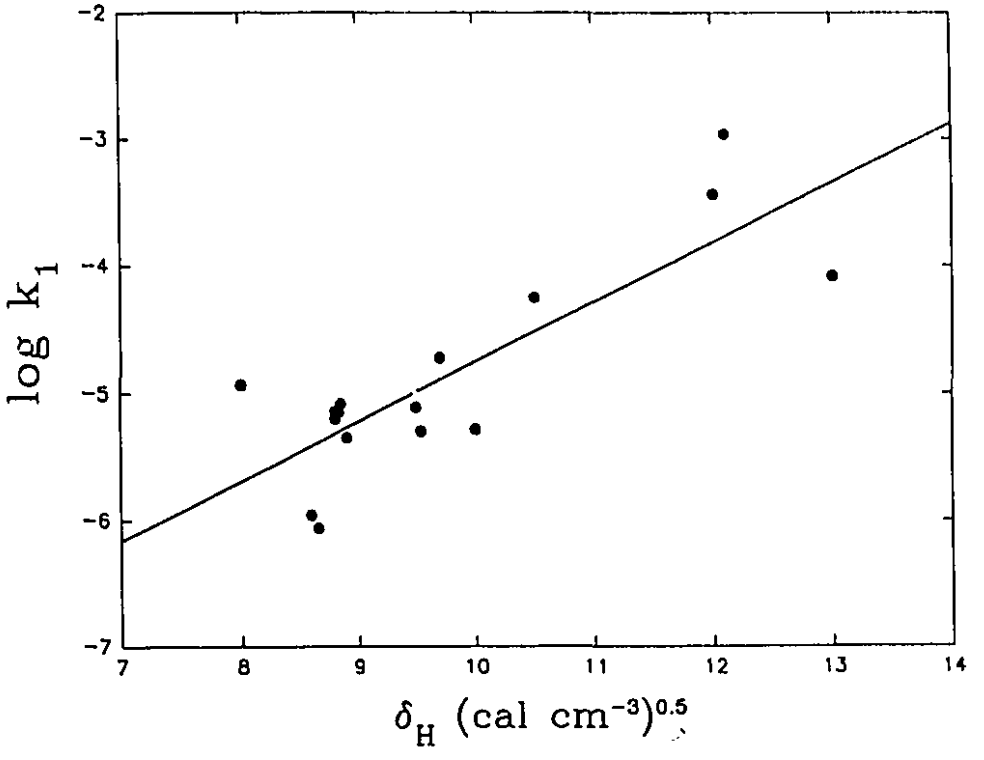
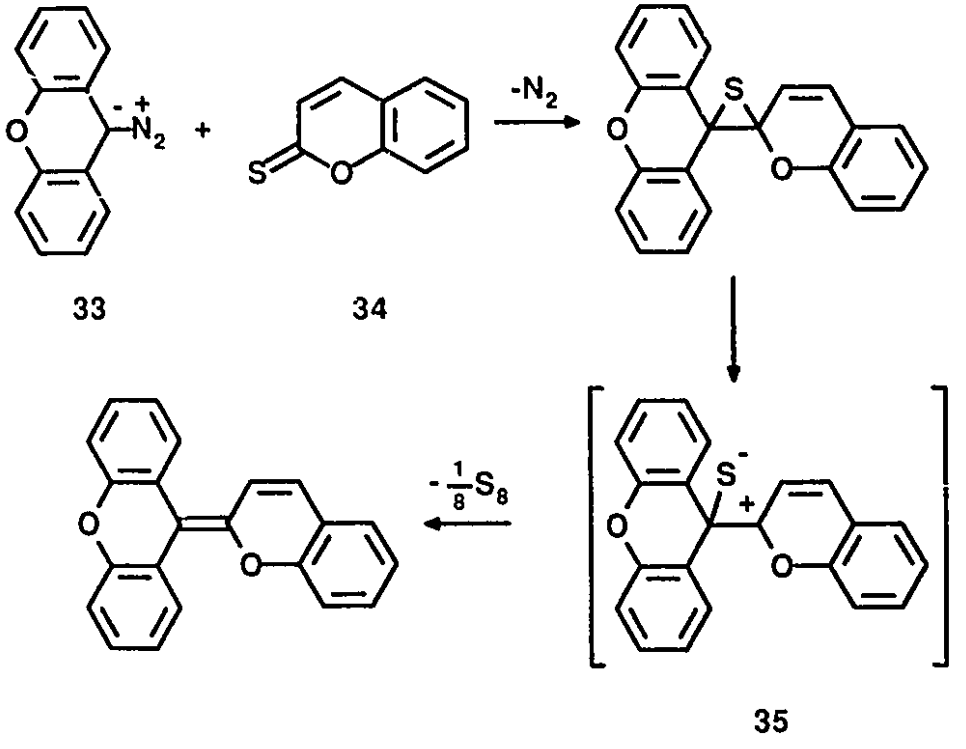


Figure 7b. Plot of log k_1 *vs.* δ_H (internal pressure) showing the scattering with k_1. The k_1 values were taken from all solvents at 80°C.



2.6 Plausible Mechanism of Sulfur Extrusion

From the desulfurization kinetics of episulfide **28**, the following mechanism is proposed to account for the observations. At low concentrations, thermal ionization of the C-S bond in **28** (Scheme 14) likely occurs as the first and rate determining step. Such an intermediate **35** has been suggested, as in the reaction between 9-diazoxanthene (**33**) and coumarin 2-thione (**34**).[109] A thiirane is isolated but which loses sulfur quickly.



33 **34** **35**

Cleavage of the C-S bond of **28** at the carbon bearing the two chlorines would be unfavorable due to their electron-withdrawing effect. The positive charge on the carbon bearing the fluorene substituent would be stabilized by resonance. The fast step would involve the subsequent attack of the sulfur anion species **36** on another molecule of episulfide **28**, giving intermediate **37**. This species would acquire sulfur atoms sequentially until an S_8 cycle is formed along with **29**.

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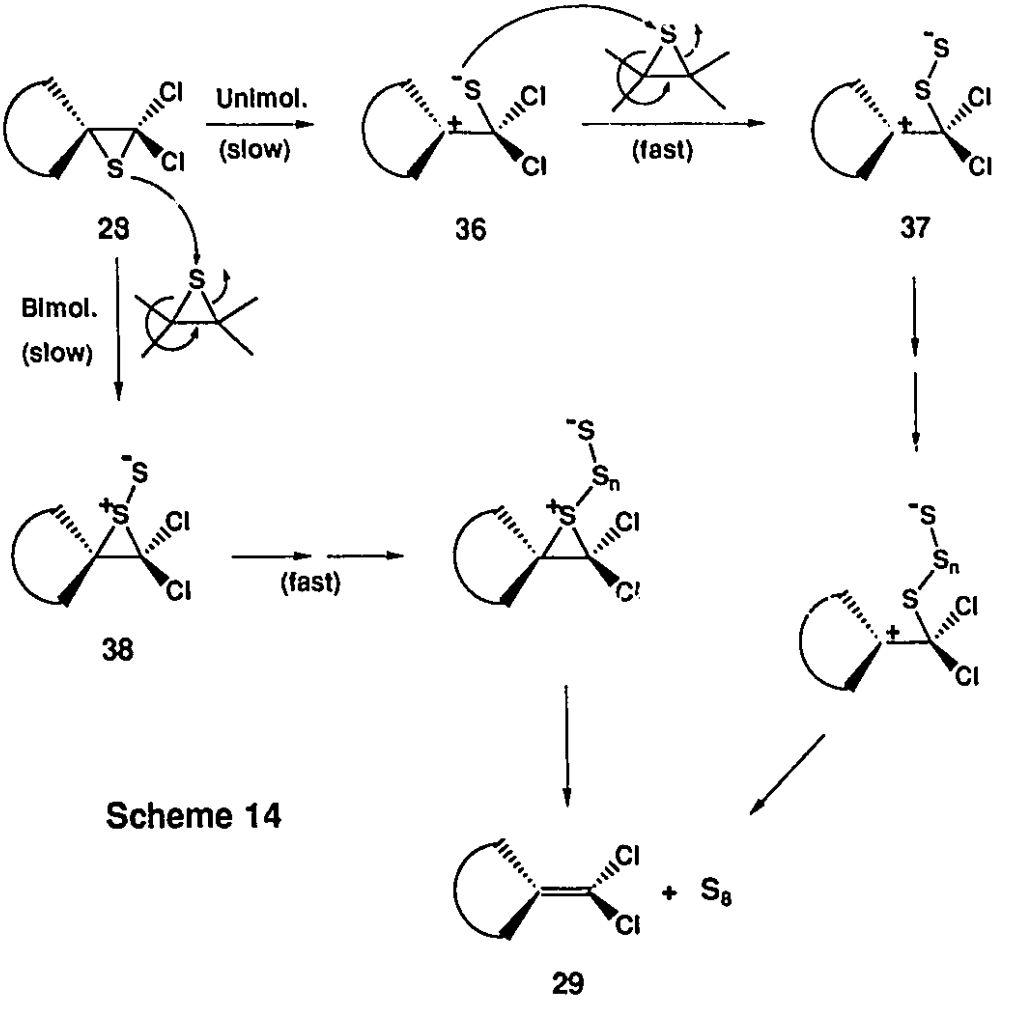
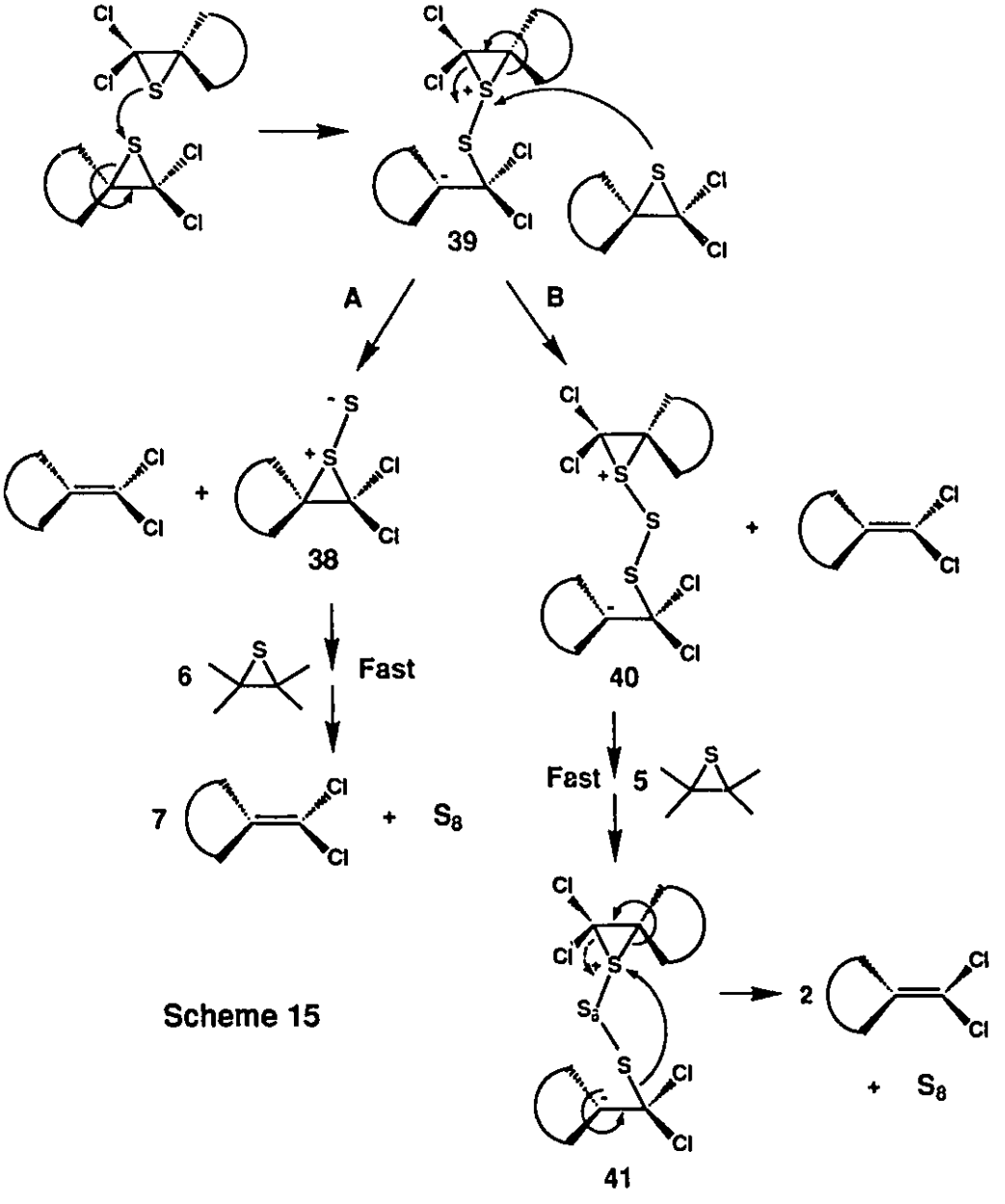
109 a) N. Latif and I. Fathy, *Can. J. Chem.*, **44**, 1075 (1966); b) M. Kamata, K. Murayama, and T. Miyashi, *Tetrahedron Lett.*, **30**, 4129 (1989).



Scheme 14

As the concentration of episulfide **28** increases, the second term in the rate equation becomes more important and a competing bimolecular mechanism is followed (Scheme 14). The sulfur atom from one episulfide molecule abstracts the sulfur atom from another in the rate determining step, giving intermediate **38**. The fast step is the subsequent concatenation of more sulfur atoms until S_8 is formed. At even higher concentration levels in thirteen solvents, the bimolecular route actually becomes the rate-determining step.

We have also found that rate equations 4, 5, and 6 fit the experimental data reasonably well and therefore they cannot be completely ruled out as possible rate laws. A mechanism that can be envisioned for the third order term in the equations is the following (Scheme 15). The initial step would be the formation of adduct **39**. Adduct **39** could either lose the olefin product (path A) and give **38** or react with a third molecule of episulfide in the rate determining step giving **40** (path B). Subsequent acquisition of more episulfide molecules in the fast step would give **41**. Elemental sulfur is eventually extruded *via* recyclization of intermediate **41** to give the olefin **29**.



Scheme 15

2.7 Stereochemical Aspects in the Decomposition of Thiiranes

We have convincing evidence that the mechanism of thermal decomposition of **28**, and perhaps thiiranes in general, is concentration dependent. Such an observation for episulfide was initially made by Bergman but little proof was provided.[52] Both a unimolecular and bimolecular mechanism play an important role in the extrusion of sulfur. One vital aspect that one should address is the stereochemical outcome in these desulfurization reactions.

It is known that the higher oxidized analogues of thiiranes, episulfoxides and episulfones, extrude sulfur monoxide and sulfur dioxide respectively under thermolytic and pyrolytic conditions. Furthermore, the stereochemistry of the substituents is preserved. Vollhardt examined the sulfur monoxide extrusion reaction of 2,3-dideuterio thiirane oxide and found that there was greater than 90% retention of stereochemistry.[110] It was concluded that the mechanism follows a partial biradical pathway but with a significant contribution from the concerted process in which SO is expelled. A biradical intermediate was proposed to account for the loss of stereoselectivity and it may be the exclusive mode of decomposition if C-C bond rotation is slow compared to the extrusion of SO. On the other hand, non-stereoselective extrusion reactions have also been reported in the thermolysis of stilbene and 2-butene episulfoxides.[111] These are thought to involve rupture of the C-S bond in the first step forming a diradical followed by an internal rotation around the C-C bond. Evidence for the diradical intermediate was demonstrated by kinetic studies in solvents of different polarity where little effect on the decomposition rates was observed with increasing solvent polarity. The stereoselectivity was also found to be lowered with increasing temperature.[111b]

Stereochemical integrity is usually observed in the decomposition of episulfones.[112] A concerted cheletropic expulsion of SO_2 is the favored pathway although a biradical mechanism where SO_2 extrusion occur faster than C-C bond rotation cannot be excluded.[113] However, the decomposition of 2-phenyl and *cis*- or *trans*-2,3

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110 a) W. G. L. Aalbersberg and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 99, 2792 (1977); b) W. G. L. Aalbersberg and K. P. C. Vollhardt, *Israel J. Chem.*, 21, 145 (1981).

111 a) G. E. Hartzell and J. N. Paige, *J. Org. Chem.*, 32, 459 (1967); b) K. Kondo, M. Matsumoto, and A. Negishi, *Tetrahedron Lett.*, 2131 (1972).

112 a) N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, 85, 1209 (1963); b) L. A. Carpino and L. V. McAdams, III, *J. Am. Chem. Soc.*, 87, 5804 (1965); c) N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, 88, 558 (1966); d) N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, 31, 349 (1966).

113 N. H. Fisher, *Synthesis*, 393 (1970).

diphenyl episulfones was believed to progress by a non-concerted pathway leading to stereoselective products. From solvent studies, both a diradical and ionic mechanism was proposed.[114]

There are several reported cases in the literature that discuss the stereochemical aspects in the degradation of thiiranes. In reactions of thiiranes with certain reagents, desulfurization occurs non-stereospecifically as evidenced by yielding mixtures of *cis* and *trans* olefins.[85a,94c,d] By contrast, reactions with a number of reagents gave olefins stereospecifically.[70,74,76e,78a,79a,89a,115] In these reactions, the reagents are believed to attack the sulfur atom followed by ring opening to give the olefin.

Thermally induced desulfurizations, in general, can be classified as non-stereospecific (*cf.* Section 1.8.2). Pommelet[51b] suggested that a competition between C-C and C-S bond cleavage occurs upon thermolysis of **12a** to rationalize the formation of the different isomers. A similar conclusion was also adapted by Schneider.[51a] The mixture of *cis*- or *trans*-2,3-divinyl thiiranes (**12a**) gave the same proportion of 20% *cis* and 80% *trans* isomers. Both ionic and biradical intermediates were postulated to account for other products. Bergman[52] emphasized a strong dependence of stereochemistry on temperature and he classifies these reactions as non-stereospecific. Nevertheless, Strausz argues that low temperature thermolysis of *cis*- or *trans*- 2-butene thiiranes is stereospecific with greater than 90% retention of configuration.[116] In cases where thiiranes undergo photolysis, formation of the diradical from C-S bond cleavage would most likely give non-stereospecific products.[62] Padwa,[61] however, claims that the photodesulfurization of **18** is stereoselective and the loss of sulfur is best explained by cleavage of the C-S bond forming a diradical which is then followed by loss of atomic sulfur. It was also suggested that the non-stereoselectivity in the thermolysis was attributed to photoisomerization of the thiirane.

One can clearly see that the steric outcome of these reactions is unpredictable. Several different mechanisms have been postulated to account for the observed products. Although our substrate cannot be used to investigate stereochemical aspects, we can

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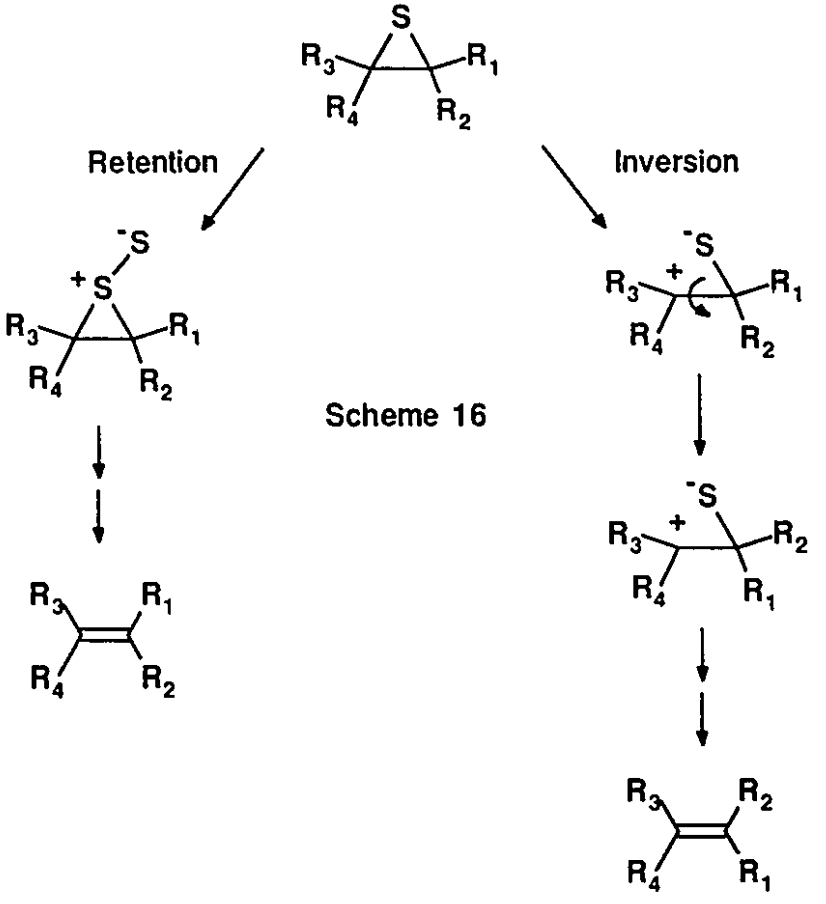
114 F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *J. Am. Chem. Soc.*, **90**, 429 (1968).

115 V. Calò, L. Lopez, A. Mincuzzi, and G. Pesce, *Synthesis*, **3**, 200 (1976).

116 E. M. Lown, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *J. Am. Chem. Soc.*, **90**, 7164 (1968).

speculate from our proposed mechanism of sulfur extrusion from thiiranes that, in general, stereoselectivity can be predicted. Our mechanism is dependent on concentration and at low concentration of thiirane, one should expect to see non-stereoselectivity in these reactions (Scheme 16). A unimolecular C-S bond fission giving a dipolar intermediate followed by C-C bond rotation would give a mixture of stereoisomers. At higher concentration levels, one should expect retention of configuration of the olefin. A bimolecular mechanism comes into play and a stepwise abstraction of sulfur atoms predominates which would give stereospecific products.



2.8 Solvent Effects

2.8.1 Introduction

It has long been known that solvents play a paramount role in reaction rates, chemical equilibria, and spectral properties of compounds. One of the most important factors in performing a chemical reaction is choosing the appropriate solvent. A change in solvent can considerably alter the rates of most chemical reactions in which ions are formed from neutral molecules. Several monographs and articles have been published emphasizing solvent effects in organic chemistry.[117] A recent book providing a comprehensive description of solvents effects in organic chemistry was written by Reichardt.[118] One of the earliest examples of solvent effects was demonstrated by Menschutkin[119] where the reaction of triethylamine with iodoethane showed rate acceleration depending on what solvent was chosen. He found that the reaction in methanol was 280 times faster than in *n*-hexane and 742 times faster in benzyl alcohol. An increase in the solvating power of the solvent leads to an increase in the rate of reaction. By careful selection of solvents, the rate of a chemical reaction can be controlled.

The influence of solvent on reaction rates is best treated by the transition state theory developed by Eyring. A one dimensional Gibbs energy diagram (Figure 8) is useful in describing this theory. The activated complex exists at the top of the energy barrier and represents that point in the reaction coordinate where the molecular species has an equal chance to reform into reactants or form its products. The overall reaction rate is the rate in which the activated complex passes over the energy barrier towards the formation of the products.

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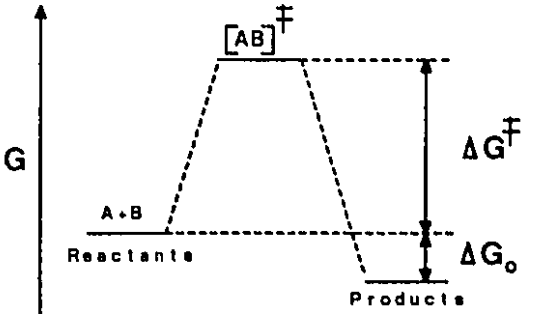
117 a) E. S. Amis and J. F. Hinton, *Solvent Effects on Chemical Phenomenon*, Vol. 1, Academic Press, New York, 1973; b) V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum Press, New York, 1978; c) C. Reichardt, *Pure Appl. Chem.*, **54**, 1867 (1982); d) M. H. Abraham, *Pure Appl. Chem.*, **57**, 1055 (1985).

118 C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed., VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1988.

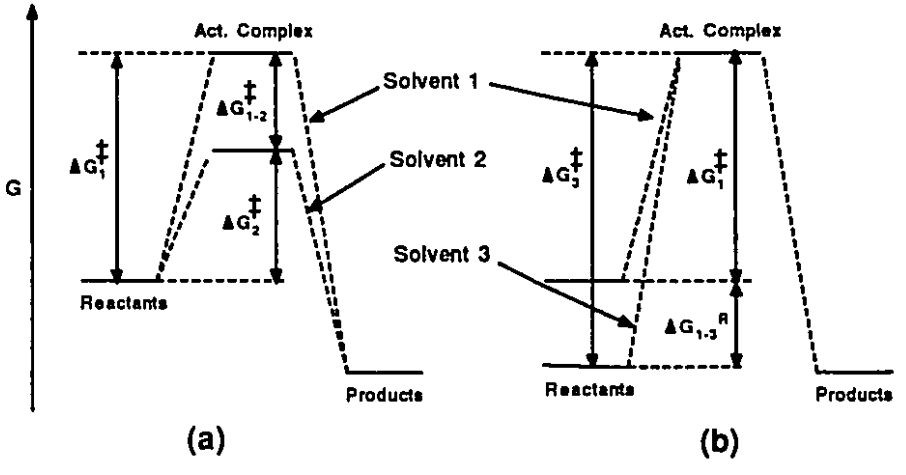
119 N. Menschutkin, *Z. Phys. Chem.*, **34**, 157 (1900).

Figure 8. One dimensional Gibbs energy diagram showing relative standard molar Gibbs energy of reactants, transition state, and products.



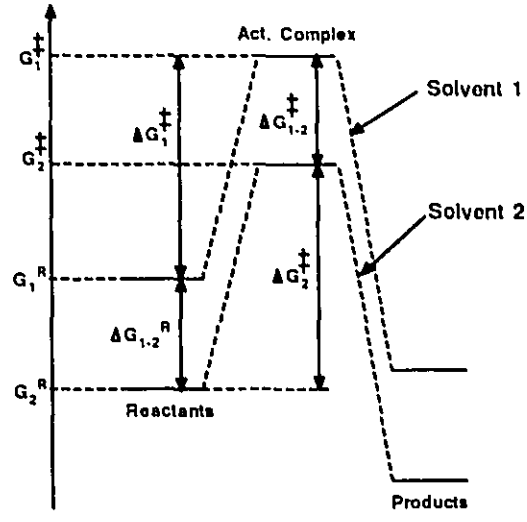
The initial reactants and activated complex will, however, be solvated to a different extent according to the solvating power of the solvent and this would retard or accelerate a reaction (Figure 9). In Figure 9(a), solvent 1 represents an ideal solvent in which neither the reactants or the activated complex are solvated and it has a Gibbs energy of activation, $\Delta G_1^{\neq}$. Solvent 2 is shown to solvate the activated complex preferentially and it has a Gibbs energy of activation $\Delta G_2^{\neq}$. The Gibbs energy of transfer is reduced by a value $\Delta G_{1\text{-}2}^{\neq}$ thus giving a rate acceleration. In Figure 9(b), solvent 3 is shown to solvate the initial reactants and thus the Gibbs energy of transfer is increased by $\Delta G_{1\text{-}3}^{\neq}$ resulting in rate retardation.

Figure 9. One dimensional Gibbs energy diagram showing (a) Solvent 2 solvating activated complex preferentially and (b) Solvent 3 solvating initial reactants preferentially. Solvent 1 is an ideal solvent, solvating neither the reactants nor activated complex.



In reality, both initial reactants and activated complex are solvated and it is the difference in Gibbs energy of transfer which determines the net rate. Such a solvation scheme is represented in Figure 10.

Figure 10. One dimensional Gibbs energy diagram for two different solvents.



The difference in the Gibbs energy of activation for the reaction in the 2 solvents is :

$$\begin{aligned}\Delta\Delta G^{\neq} &= \Delta G_1^{\neq} - \Delta G_2^{\neq} \\ &= G_1^{\neq} - G_1^{R} - G_2^{\neq} + G_2^{R} \\ &= \Delta G_{1\text{-}2}^{\neq} - \Delta G_{1\text{-}2}^{R}\end{aligned}$$

Hence, $\Delta G_{1\text{-}2}^{\neq}$ can be evaluated by obtaining $\Delta\Delta G^{\neq}$ from measured kinetic activation parameters and $\Delta G_{1\text{-}2}^{R}$ from Eq. (14) where γ refers to the activity coefficients of reactants in solvent 1 and 2.

$$\Delta G_{1\text{-}2}^{R} = -RT\ln\left(\frac{\gamma_1}{\gamma_2}\right) \qquad \text{Eq. (14)}$$

If both $\Delta G_{1\text{-}2}^{\neq}$ and $\Delta G_{1\text{-}2}^{R}$ are positive, then there is a destabilizing effect. If both are negative, then there is a stabilizing effect, and if they are both zero, then there is no solvent effect. A large solvent effect is expected if one term is positive and the other negative since they reinforce each other.

2.8.2 Hughes - Ingold Rules

In studying the effect of solvents on reaction rates, many different factors come into play and it is often difficult to provide a complete explanation of these effects. One must therefore treat experimental data in a qualitative fashion. One of the more successful qualitative theories was that developed by Hughes and Ingold.[120] They investigated solvent effects on nucleophilic substitution and elimination reactions. Only pure electrostatic interactions between ions and solvent molecules in the initial and transition state were considered so that solvation will increase if there is an increase in magnitude of charge. A decrease in solvation results if charge is dispersed or destroyed. The following rules were thus defined :[120]

a) An increase in solvent polarity will increase the rate of reaction in which there is a greater charge in the activated complex relative to the initial reactants.

b) An increase in solvent polarity will decrease the rate of reaction in which the charge density in the activated complex is lower than in the initial reactants.

c) If there is little or no charge developing on going from the initial reactants to the activated complex, then a change in solvent polarity will have negligible effect on the rate.

Table 13 summarizes the effect of increasing solvent polarity on nucleophilic substitution type reactions. A vast number of examples in the literature demonstrate the application of the Hughes-Ingold rules.[121]

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120 C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, 2nd ed., Cornell University Press, Ithaca, New York, 1969.

121 a) S. Fukuzumi and J. K. Kochi, *J. Am. Chem. Soc.*, **102**, 2141 (1980); b) Y. Kondo, M. Ituh, and S. Kusabayashi, *J. Chem. Soc., Faraday Trans. I*, **78**, 2793 (1982); c) A. R. Katritzky and B. Brycki, *J. Am. Chem. Soc.*, **108**, 7295 (1986); d) G. A. Jones, C. J. M. Stirling, and N. G. Bromby, *J. Chem. Soc., Perkin Trans. II*, 385 (1987); e) P. M. E. Mancini, R. D. Martinez, L. R. Vottero, and N. S. Nudelman, *J. Chem. Soc., Perkin Trans II*, 951 (1987).

Table 13. Predicted solvent effects on rates of nucleophilic substitution reactions (taken from reference 120).

Reaction Type	Initial Reactants	Activated Complex	Charge alteration during activation	Effect of increased solvent polarity on rate
S_Ni	R-X	$R^{\delta+}...X^{\delta-}$	Separation of unlike charges	Large Increase
S_N1	$R\text{-}X^+$	$R^{\delta+}...X^{\delta+}$	Dispersal of charge	Small Decrease
S_N2	Y + R-X	$Y^{\delta+}...R...X^{\delta-}$	Separation of unlike charges	Large Increase
S_N2	$Y^- + R\text{-}X$	$Y^{\delta-}...R...X^{\delta-}$	Dispersal of charge	Small Decrease
S_N2	$Y + R\text{-}X^+$	$Y^{\delta+}...R...X^{\delta+}$	Dispersal of charge	Small Decrease
S_N2	$Y^- + R\text{-}X^+$	$Y^{\delta-}...R...X^{\delta+}$	Destruction of charge	Large Decrease

2.8.3 Attempt to Correlate Reaction Rate with Solvent Polarity

Organic chemists have attempted to understand solvent effects in terms of the polarity of the solvent. The polarity of a solvent is a term used to relate the capacity of a solvent to solvate reactants and activated complexes. Qualitatively, it is easy to understand but quantitatively it is more difficult. Many have tried to express experimental rates with such properties as dielectric constant, dipole moment, refractive index, or Hildebrand's solubility parameter (internal pressure) and some have found these solvent parameters successful.[101,122] Because of the highly complicated interactions between solvents and reactants or activated complexes, the correlation of these effects with solvent properties is often difficult and inadequate. For example, the dielectric constant does not take into account hydrogen bonding or electron pair donor/electron pair acceptor (EPD/EPA) interactions, both which often play a major role in solute/solvent interactions nor does it take into account solvents which are highly structured.

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122 a) E. Tommila and P. Kauranen, *Acta. Chem. Scand.*, 8, 1152 (1954); b) M. Watanabe and R. M. Fuoss, *J. Am. Chem. Soc.*, 78, 527 (1956); c) K. F. Wong and C. A. Eckert, *J. Chem. Soc., Trans. Faraday I*, 66, 2313 (1970); d) J. P. Snyder and D. N. Harpp, *J. Am. Chem. Soc.*, 98, 7821 (1976); e) G. Desimoni, G. Faita, P. P. Righetti, and L. Toma, *Tetrahedron*, 46, 7951 (1990).

There have been attempts to evolve an empirical scale of solvent polarity based on solvent-sensitive reference processes. Such a reference would serve as a model that covers a wide variety of possible intermolecular interactions. With this model, it could be assumed that the process reflects all possible interactions which are present in related solvent-sensitive actions. These empirical parameters would then constitute a more reliable measure of solvent polarity. Empirical solvent polarity scales are reviewed by Reichardt,[123] Abraham,[124] and recently by Pytela.[125] The most comprehensive scales are briefly described here.

Grunwald and Winstein[126] defined a solvent ionizing power parameter, Y, based on a standard reaction namely the S_N1 solvolysis of *t*-butyl chloride in 4:1 aqueous ethanol as a reference solvent. This standard reaction was given a value of zero as the Y parameter. The model was chosen because it was believed to occur by a pure S_N1 mechanism where ionization of the C-Cl bond is the rate determining step. The authors defined Eq. (15) :

$$Log\frac{k_a}{k_o} = mY \qquad \text{Eq. (15)}$$

k_o = first order rate constant in reference solvent

k_a = rate constant in another solvent

m = substrate parameter

Y = parameter characteristic of a solvent

Y values were obtained from a number of solvents and in a large number of cases, good linear relationships were found.[127] Less satisfactory results were obtained in reactions that go through S_N2 type mechanisms or in reactions where nucleophilic solvent participation becomes relevant.

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123 C. Reichardt, *Angew. Chem. Int. Ed. Engl.*, 4, 29 (1965).

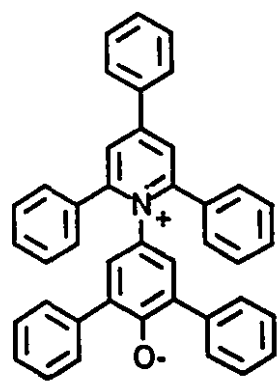
124 M. H. Abraham, *Progress in Physical Organic Chemistry*, 11. 7 (1974).

125 O. Pytela, *Collect. Czech. Chem. Comm.*, 53, 1333 (1988).

126 E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 70, 846 (1948).

127 a) M.-F. Ruasse and B.-L. Zhang, *J. Org. Chem.*, 49, 3207 (1984); b) C. A. Bunton, M. M. Mhala, and J. R. Moffatt, *J. Org. Chem.*, 49, 3639 (1984); c) T. W. Bentley, M. Christl, and S. J. Norman, *J. Org. Chem.*, 56, 6238 (1991); d) M. Fujio, N. Tomita, Y. Tsuno, S. Kobayashi, H. Taniguchi, J. Kaspi, and Z. Rappoport, *Tetrahedron Lett.*, 33. 1309 (1992).

Dimroth and Reichardt[128] proposed a E_T solvent polarity parameter based on the transition energy for the longest-wavelength solvatochromic absorption band of pyridinium *N* phenoxide betaine dye (**42**). E_T values are a measure of the amount of energy (kcal) necessary to bring one mole of dye from the electronic ground state to the first excited state. Since the ground state is an ion pair, E_T values for polar solvents will be higher due to stronger stabilizing effects. This would require more energy to promote the electron to the excited state. E_T values for more than 270 organic solvents have been determined and many examples in the literature show strong correlation between E_T values and rate constants; a few are cited.[102,129,130,131,132] One major drawback of these E_T values is that they cannot be measured in acidic solvents due to direct protonation of the phenolic oxygen atom **42**, which results in no absorption bands. A recent article showed that **42** forms hydrogen bonds with proton donors and thus the E_T scale is a reasonable measure of solvent hydrogen-bond donor ability.[133] Nevertheless, solvents of different polarity can indeed provide useful information concerning solute-solvent interactions because of the differences in position, intensity, and shape of absorption bands measured in the different medium.



42

There have been many other approaches in proposing a solvent polarity scale but in these cases they are restricted because of the limited number of solvents used to establish the polarity scales.[134] A recent article indicated that the solvent polarity

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128 K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Liebigs Ann. Chem.*, **661**, 1 (1963); **752**, 64 (1971). For improved synthesis of betaine dyes see C. Reichardt and S. Asharin-Fard, *Angew. Chem. Int. Ed Engl.*, **30**, 558 (1991).

129 R. Tang and K. Mislow, *J. Am. Chem. Soc.*, **92**, 2100 (1970).

130 M. H. Abraham and P. C. Grellier, *J. Chem. Soc., Perkin Trans. II*, 1735 (1976).

131 F. Mao, D. R. Tyler, M. R. M. Bruce, A. E. Bruce, A. L. Rieger, and P. H. Rieger, *J. Am. Chem. Soc.*, **114**, 6418 (1992).

132 X. Creary, H. N. Hatoum, A. Barton, and T. E. Aldridge, *J. Org. Chem.*, **57**, 1887 (1992).

133 C. A. Coleman and C. J. Murray, *J. Org. Chem.*, **57**, 3578 (1992).

134 a) Z-scale : E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958); b) Ω-scale : J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962); c) X-scale : M. Gielen and J.

parameter, a_N (^{14}N isotropic hyperfine splitting constant), can be linearly correlated with rate constants in the kinetics of nitroxide radical trapping of carbon centered radicals.[135] On the other hand, all these parameters constitute a somewhat better measure of solvent polarity than the single physical characteristics since they reflect the intermolecular forces between solute and solvent molecules more reliably.

Despite the observation that single empirical parameters serve as good approximations of solvent polarity, many solvent-sensitive processes do not correlate well with these parameters; our work appears to fall into this category. Plots of either log k_1 or log k_2 *vs.* several polarity scales including dipole moment, Hildebrand's solubility parameter, Dimroth's E_T values, and refractive index, showed no apparent correlation (Figures 7a, 7b, 11a, 11b).

Nasielski, *J. Organomet. Chem.*, 1, 173 (1963); d) DN scale : V. Gutmann, *"The Donor-Acceptor Approach to Molecular Interactions"*, Plenum Press: New York, 1978; e) AN scale : A. J. Parker, U. Mayer, R. Schmid, and V. Gutmann, *J. Org. Chem.*, 43, 1843 (1978).

135 A. L. J. Beckwith, V. W. Bowry, and K. U. Ingold, *J. Am. Chem. Soc.*, 114, 4983 (1992).

Figure 11a. Plot of log k_1 *vs.* E_T showing the non-linearity with k_1. The k_1 values were taken from those solvents at 80°C and which have an E_T value that was measured.

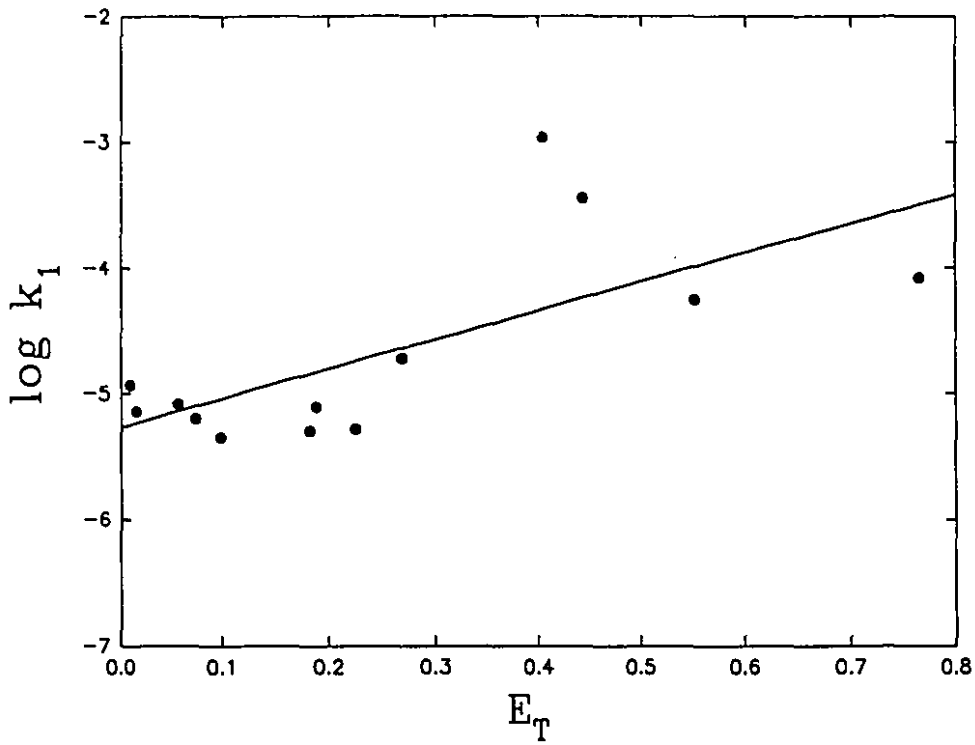
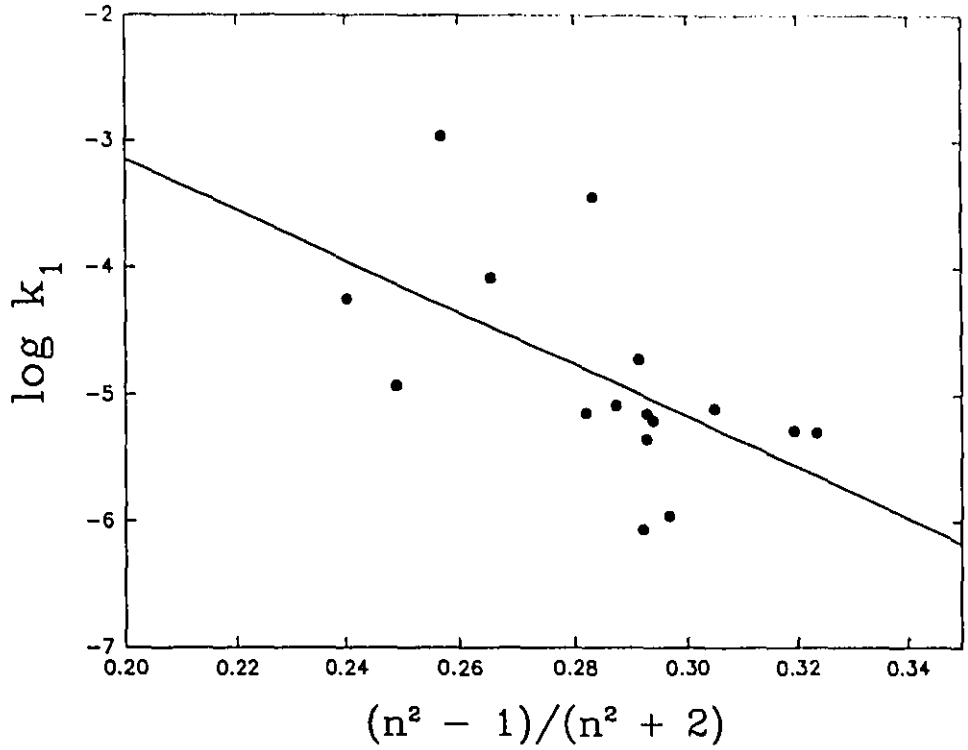


Figure 11b. Plot of log k_1 *vs.* $(n^2-1)/(n^2+2)$ showing the non linearity with k_1. The k_1 values were taken from those solvents at 80°C.



Log k_1 (or log k_2) against Grunwald's Y values were not plotted because of unavailable Y parameters for the solvents used in our study. An enticing characteristic is found when we plot log k_1 or log k_2 *vs.* $(D_c-1)/(2D_c+1)$, where D_c is the dielectric constant (Figures 12a and 12b). Table 14 shows the dielectric constants and log k_1 and log k_2 values for the solvents used in this study. The quantitative correlation ($r = 0.72$ and 0.61 respectively) is not ideal but, in general and with the exception of a few irregular data points, an increase in rate with dielectric constant is shown. This is direct evidence for the existence of an ionized transition state in agreement with our proposals. Several cases in the literature have shown log k *vs.* $f(D_c)$ plots with few scattered points but a general increase in rate with dielectric constant (positive slope) is observed.[136] This is demonstrated in Figure 13 ($r = 0.82$). A similar trend is also observed in other polarity scales (Figures 7a,. 7b, and 11a). These also support the existence of ionized transition states. We serve to point out that any single physical quantity cannot effectively be used as a measure of solvent polarity in our system perhaps due to the multitude and complex

136 a) M. Auriel and E. de Hoffmann, *J. Am. Chem. Soc.*, 97, 7433 (1975); b) M. H. Abraham and P. L. Grellier, *J. Chem. Soc., Perkin Trans. II*, 1735 (1976).

nature of solute/solvent processes. There are many different kinds of interaction mechanisms between solute and solvent molecules which may act simultaneously.

Table 14. Dielectric and rate constants used in this study. Rate constants were obtained at 80°C. Dielectric constants were taken from *Handbook of Chemistry and Physics*, 73rd ed., D. R. Lide, Ed., CRC Press, 1992-93, p 9-51.

Solvent	$(D_c-1)/(2D_c+1)$	log k_1[a]	log k_2[a]
Decane	0.19	-4.9	-5.3
Decalin	0.22	-5.1	-4.7
p-Xylene	0.23	-5.2	-5.4
1:1 Decalin/Toluene	0.23	-5.1	-5.2
m-Xylene	0.24	-6.0	-5.7
Toluene	0.24	-5.3	-5.0
o-Xylene	0.25	-5.1	-5.4
Bromobenzene	0.37	-5.3	-4.6
Chlorobenzene	0.38	-5.1	-4.9
1,1,2,2-Tetrachloroethane	0.41	-4.7	-4.7
o-Dichlorobenzene	0.43	-5.3	-5.0
Isobutanol	0.46	-4.3	-5.9
2-Chloroethanol	0.47	-4.1	-3.9
DMF	0.48	-3.0	-2.8
DMSO	0.48	-3.4	-3.1

[a] rate constants taken from Table 4a.

Figure 12a. Plot of log k_1 against a function of dielectric constant showing the general increase in rate with dielectric constant.

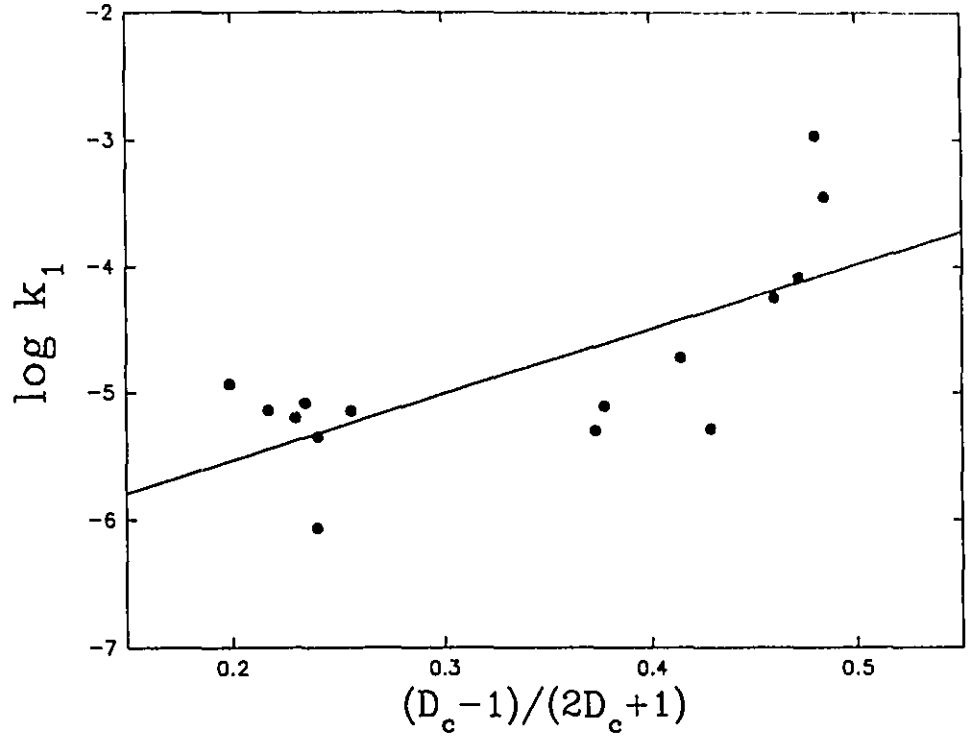


Figure 12b. Plot of log k_2 against a function of dielectric constant showing the general increase in rate with dielectric constant.

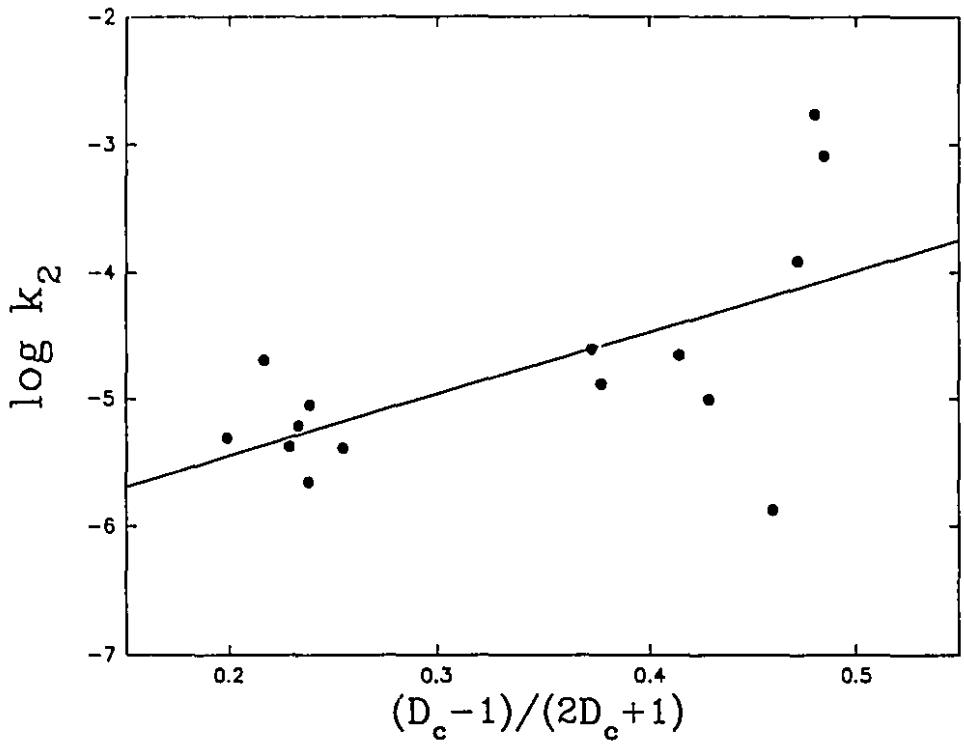
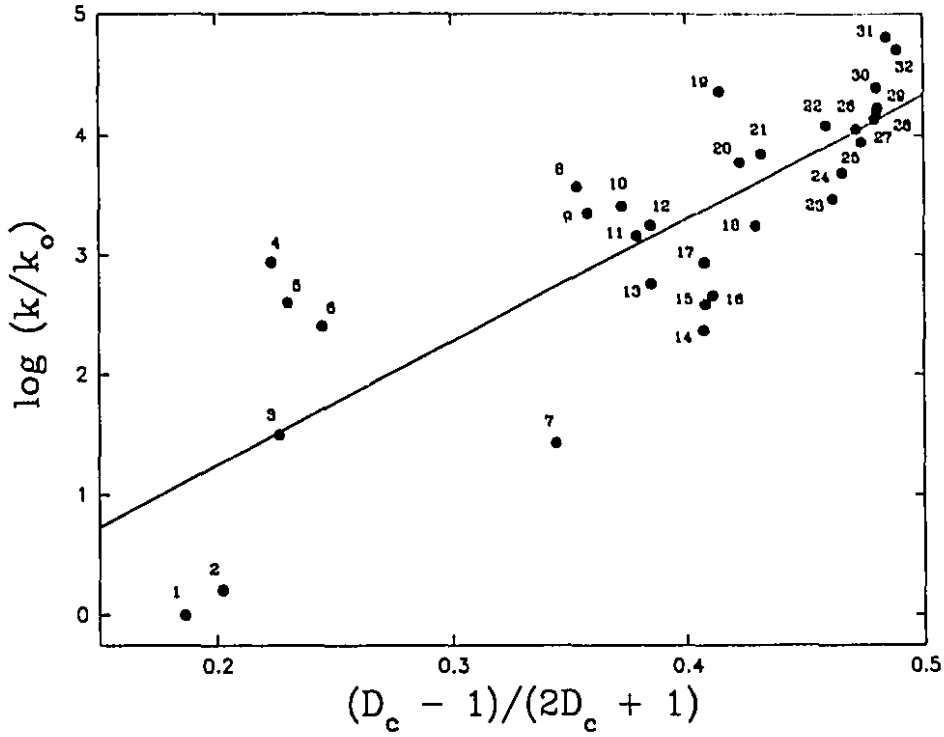


Figure 13. Plot of log (k/k_0) *vs.* $(D_c-1)/(2D_c+1)$ for the Menschutkin reaction between triethylamine and iodoethane showing the scattering of points. A general increase in rate with dielectric constant is also illustrated. Rate constants were taken from reference 136 and are relative to *n*-hexane as the slowest solvent.



1. *n*-hexane; 2. cyclohexane; 3. carbon tetrachloride; 4. 1,4-dioxane; 5. benzene; 6. toluene; 7. diethyl ether; 8. iodobenzene; 9. chloroform; 10. bromobenzene: 11. chlorobenzene; 12. ethyl benzoate; 13. ethyl acetate; 14. 1,1,1-trichloroethane; 15. chlorocyclohexane; 16. bromocyclohexane; 17. tetrahydrofuran; 18. 1,1-dichloroethane; 19. 1,1,2,2-tetrachloroethane; 20. dichloromethane; 21. 1,2-dichloroethane; 22. acetophenone; 23. 2-butanone; 24. acetone; 25. propionitrile; 26. benzonitrile; 27. nitrobenzene; 28. *N,N* dimethylformamide; 29. acetonitrile; 30. nitromethane: 31. dimethylsulfoxide; 32. propylene carbonate.

2.8.4 Multiparameter Approaches

The quantitative treatment of the effect of solvents requires inclusion of all solvation effects and self-association of the solvents, determined by the solubility parameter. Particularly significant is the role of nonspecific solvation of the reaction complex, due to the polarizability (or polarity) of the medium. To account for two or more aspects of solvation, multiparameter approaches were developed.

Katritzky et al.[137] employed a linear combination of E_T values and the Kirkwood dielectric function, $(D_c-1)/(2D_c+1)$, where they assumed the dielectric function represents dipole/dipole interactions and where the E_T values represent dipolar interactions and hydrogen bonding factors. Correlations with rates show significant improvements with their multiparameter treatment.

Koppel and Palm[138] argued that a complete description of solute/solvent interactions should include specific and non-specific effects. A 4-term equation was derived consisting of two specific and two non-specific solvent interaction terms, Eq. (16).

$$A = A_0 + yY + pP + eE + bB \qquad \text{Eq. (16)}$$

A = solvent dependent property
A_0 = solvent property in inert solvent
Y, P = non-specific parameter
E, B = specific parameter

The basis for the Y values is the dielectric constants, for P the refractive index, for E, the Lewis acidity parameter, is based on Dimroth's E_T values, and B, the Lewis basicity parameter is based on the O-D IR stretching bands of CH_3OD.[139] Over 70 solvent-sensitive processes correlated well[140] with Eq. (16) and in 50 of them, parameter E showed the most importance which reflects the dominance of E_T values (electrophilic solvation) in these processes.[138] Thus, the authors showed that it is necessary to take into account all four possible solvent-solute interactions in dealing with solvent effects.

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137 F. W. Fowler, A. R. Katritzky, and R. J. D. Rutherford, *J. Chem. Soc.*, Part B, 460 (1971).

138 A. Koppel and V. A. Palm, *"Advances in Linear Free Energy Relationships"*, N. B. Chapman and J. Shorter, Eds., Plenum Press: New York, 1972, Chapter 5, p 203.

139 T. Kayiya, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Jpn.*, 41, 767 (1968).

140 The validity of Eq. (16) was characterized by the standard deviations of the regression coefficients, the correlation coefficient, r, and the relative standard deviation of the correlation.

Kamlet and Taft's[141] treatment of multiple solvent effects were similar to Koppel and Palm's treatment. They proposed the multiparameter Eq. (17)

$$A = A_o + s(\pi^* + d\delta) + a\alpha + b\beta + h\delta_H^2 + e\xi \qquad \text{Eq. (17)}$$

where π^* measures the ability of the solvent to stabilize a charge by its dielectric effect, δ is the polarizability correction term which is 0 for non-chlorinated aliphatic solvents, 0.5 for polychlorinated aliphatic solvents, and 1.0 for aromatic solvents, α and β are similar to Koppel and Palm's Lewis acidity and basicity terms, δ_H^2 is the Hildebrand solubility parameter squared which is a measure of the solute/solvent interactions that are interrupted in creating a cavity for the solute, and the ξ parameter is the coordinate covalency measure which is equal to -0.20 for P=O bases, 0 for C=O, S=O, and N=O bases, 0.20 for single-bonded oxygen bases, 0.60 for pyridine bases, and 1.0 for sp^3 amines. s, d, a, b, h, and e are the regression coefficients that dictate the importance of that parameter in the overall reaction. As the authors explained, by rationally choosing specific solvents, the multiparameter equation can be reduced to 1, 2, or 3 terms involving different combinations of the parameters.

The parameter, π^*, which is an index of solvent dipolarity/polarizability measuring the ability of the solvent to stabilize a charge by virtue of the solvent dielectric effect, should effectively correlate better than the dielectric constant, D_c, itself. This can be explained by the way the parameters are derived. The term D_c is a macroscopic property of the bulk solvent and does not probe the cybotactic region, whereas π^* values are obtained from probing electronic transitions occurring in the solute organized cybotactic region or solvation shell. The distinction between the cybotactic region and the bulk solvent is shown in Figure 14. The cybotactic region is defined as the region where the solvent is highly organized around the solute molecules. This suggests that in order to describe solvent effects on reaction rates, the solvent polarity scale should reflect or be based on the cybotactic region since the reaction of interest would be most influenced by the cybotactic region rather than the bulk solvent.[142] Grunwald-Winstein's Y values and Dimroth-Reichardt's E_T values are also derived from experiments which probe the cybotactic region of the solvent.

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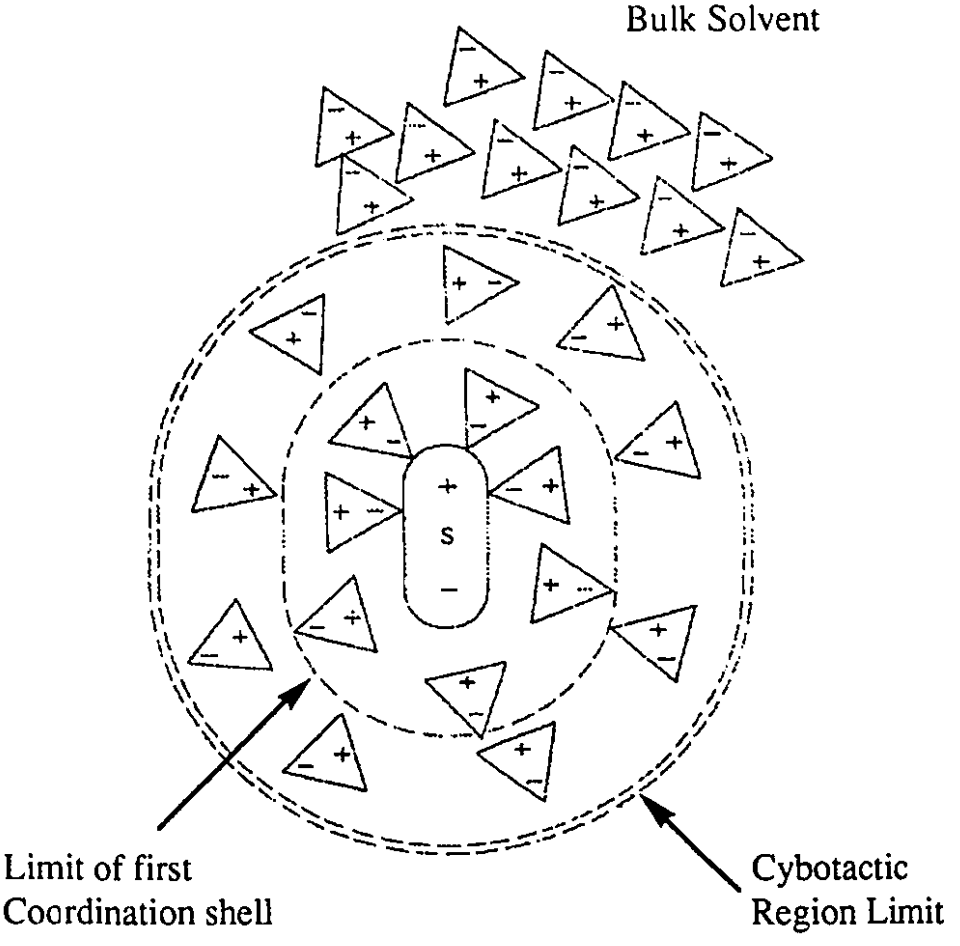
141 M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham, and R. W. Taft, *J. Org. Chem.*, 48, 2877 (1983). Application of the Kamlet equation has been shown in Diels-Alder reactions : See reference 122e.

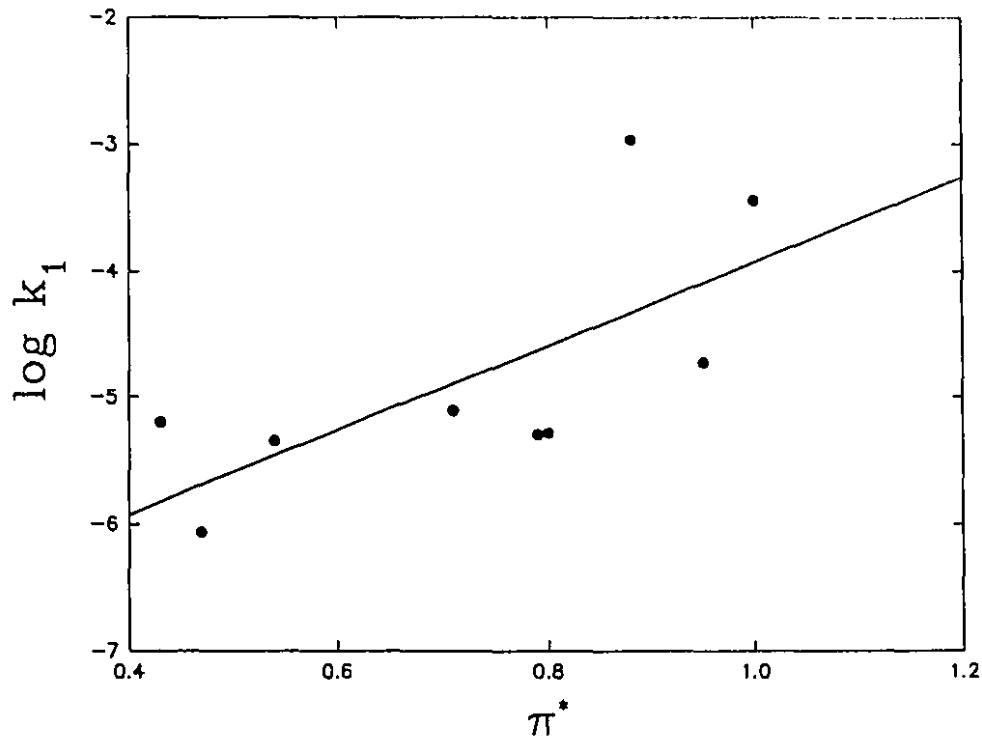
142 B. R. Knauer and J. J. Napier, *J. Am. Chem. Soc.*, 98, 4395 (1976).

Figure 14. Distinction between the bulk solvent and the cybotactic region.



Our attempt to correlate π^* values alone with log k_1 or log k_2 was met with some success. We observe a prevailing increase in rate with the π^* solvent polarity parameter which is indicative of a dipolar mechanism (Figure 15). The lack of good correlation ($r = 0.75$) of log k_1 or log k_2 with π^* (or even E_T as shown in Figure 12a) can be attributed to the fact that these parameters stem from a particular effect the solvent polarity has on a certain model (reference) chemical process of a certain compound (*cf.* Section 2.8.3). These model processes do not bear any resemblance to our decomposition reaction and hence the parameters do not correlate well with our reaction rates.

Figure 15. Plot of log k_1 *vs.* π^* solvent polarity parameter showing a general increase in rate with π^*. The k_1 values were taken from Table 4 and which have a π^* value that was measured.



Nevertheless, the rate of reaction correlates reasonably well with the non-specific parameters of Koppel and Palm. Since our reaction involves neither acidity or basicity effects of solvents we can neglect the specific parameters in Eq. (16). The equation, therefore, reduces to three terms comprising of the dielectric and refractive index parameters. Multiple regression provides Eqs. (18) and (19) where $f(D_c) = (D_c-1)/(2D_c+1)$ and $f(n^2) = (n^2-1)/(n^2+2)$.

$$\log k_1 = -1.83 + 4.80f(D_\epsilon) - 16.15f(n^2) \qquad \text{Eq. (18)}$$

$$\log k_2 = -6.12 + 4.92f(D_\epsilon) - 1.11f(n^2) \qquad \text{Eq. (19)}$$

We see that the dielectric term plays a dominant role and the refractive index term plays a negative role in the overall reaction rate. If we increase the polarity of the solvent (*ie.* dielectric constant) the rate increases which is in agreement with our proposed ionic mechanism.

Similarly, we can simplify Kamlet and Taft's equation, Eq. (17), by eliminating the acidity and basicity terms as well as the coordinate covalency parameter. Multiple regression analysis shows that the solubility parameter, δ_H^2, plays a very minor role in the rate of reaction and therefore we can neglect that term altogether thus arriving at Eqs. (20) and (21) :

$$\log k_1 = -3.88 + 0.83\pi^* - 1.79\delta \qquad \text{Eq. (20)}$$

$$\log k_2 = -3.47 + 0.18\pi^* - 2.05\delta \qquad \text{Eq. (21)}$$

As with the pronounced effect of dielectric constant in the Koppel and Palm treatment, the reaction rate is directly proportional to the π^* parameter here. The greater the value π^* the greater the reaction rate which supports our mechanism involving dipolar intermediates.

We should also note that in the Koppel and Palm approach we used the dielectric constants which are ground-state properties of the bulk solvent and in the Kamlet and Taft illustration we used π^* values which are derived from probing the cybotactic region. Overall, this suggests that although the rates of reactions are mainly influenced by the cybotactic region more than the bulk solvent, we show here that the bulk solvent is meaningful in our system.

2.9 Solvent Isotope Effect

The solvent isotope effect in the study of reaction kinetics is used to describe changes in a kinetic process when a solvent is replaced by its isotopically substituted counterpart. In most cases, hydrogen is substituted by deuterium but carbon, sulfur, and nitrogen isotopes have also been used. The isotope effect for reactions is used to indicate whether there is a direct or indirect solvent participation in the reaction. A combination of three factors are involved when observing these effects :[118]

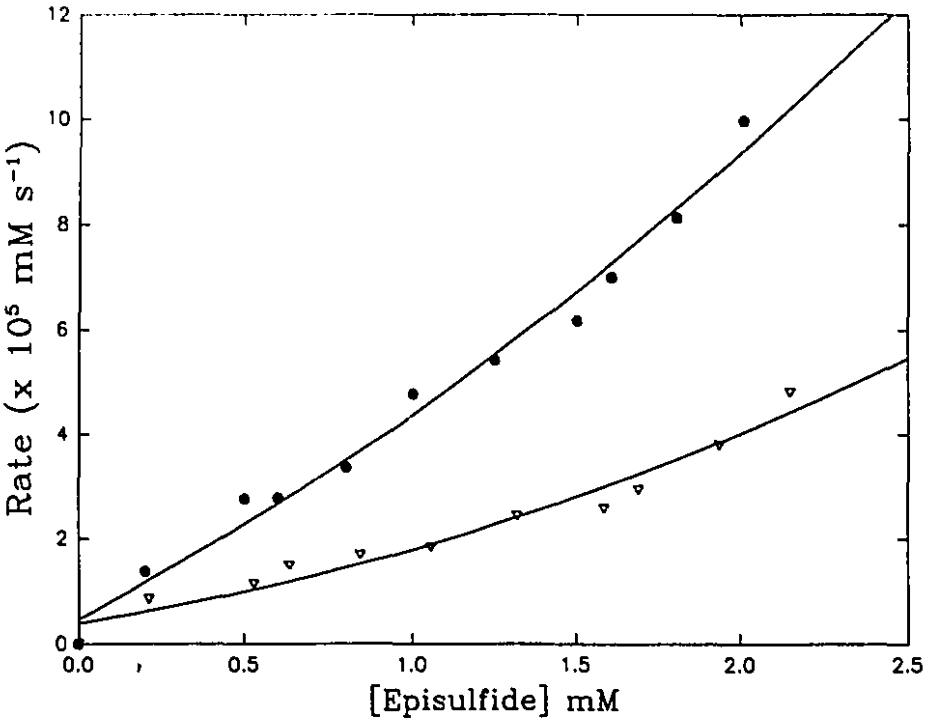
a) Primary isotope effect where in the rate determining step the bond to the isotopically-labelled atom is broken;
b) Secondary isotope effect in a solute/solvent interaction where bonds to the isotopically labelled atoms are not broken in the reaction;
c) The reactants become labelled by fast exchange and the newly labelled molecules cleave in the rate determining step.

Unfortunately, these three factors all operate simultaneously and is thus difficult to differentiate between them.

In general, a reaction shows an increase in rate with unlabelled solvent relative to the labelled solvent if the activated complex becomes charged. Conversely, a reaction that disperses or destroys charge will exhibit an enhanced rate in labelled solvent relative to the unlabelled solvent. The different behaviours are most likely attributed to the difference in polarization of the X-H and X-D bonds where the X-H is more polarizable than X-D. In a charged activated complex, the more polarizable unlabelled solvent will increase the rate of reaction whereas labelled solvent, being less polarizable, will decrease the rate of reaction.

Our study focused on the difference in the observed rate constant in the decomposition of episulfide **28** when ethanol is substituted with ethanol-*d*. The rate profiles were obtained at 50°C starting with an initial concentration of 1.00 mM of episulfide **28**. Figure 16 shows the rate profiles for the two solvent systems.

Figure 16. Rate profile in the decomposition of **28** in ethanol (•) and ethanol-*d* (▽).



By curve-fitting[97] the rate *vs.* concentration of episulfide to Eq. (3) k_1 and k_2 values were determined and are listed in Table 15. We observe that the rate of appearance of olefin **29** is faster in the protonated solvent than in the deuterated solvent. This is not inconsistent with our mechanism involving a charged activated complex as it appears the rate determining step in deuterated ethanol is altered, the O-D bond being stronger than the O-H bond. According to our proposed dipolar mechanism, it is possible for the sulfur anion from the unimolecular or bimolecular pathways to abstract the deuterium atom from the labelled solvent. If this is now rate-determining, the production of the alkene would be retarded.

Table 15. Rate constants derived from Eq. (3) in ethanol and ethanol-*d* solvents.

Solvent	k_1 ($\times 10^5$ s^{-1})	k_2 ($\times 10^5$ mM^{-1} s^{-1})
Ethanol	4.2	0.21
Ethanol-*d*	1.7	0.17

The solvent isotope effect can be calculated from taking the ratio of the second order rate constants of the unlabelled and labelled solvent :

$$\frac{k_2(unlabelled)}{k_2(labelled)}$$

An isotope ratio of 2.5 and 1.2 is obtained from k_1 and k_2 rate constants respectively which is indicative of a primary isotope effect. The magnitude of the isotope ratio is not uncommon in other studies with ethanol and ethanol-*d* solvents.[143]

Further evidence of hydrogen transfer within this system can be seen from the addition of acetic acid. The rate profile shown in Figure 17 was obtained starting with an initial concentration of episulfide **28** of 1.0 mM and varying the concentration of acetic acid. As the concentration of acetic acid is increased, the rate of decomposition in toluene at 80°C is reduced dramatically. A 6-fold decrease in rate is observed when the concentration of acetic acid is increased by 1.5 times. This is compatible with the abstraction of hydrogen by the sulfur anion intermediates which inhibits further decomposition.

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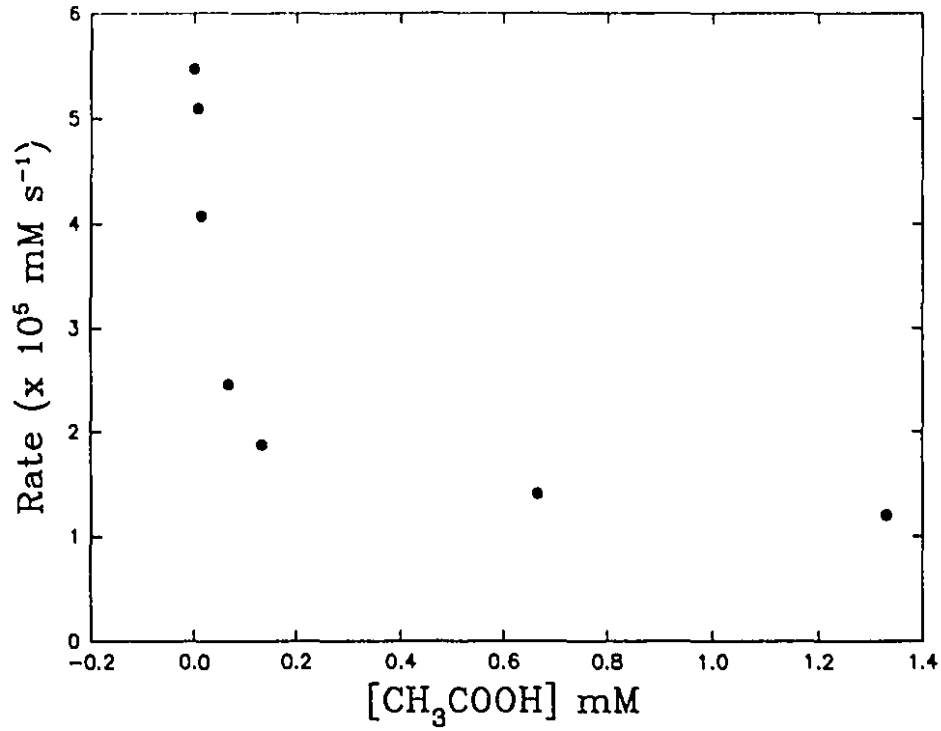
143 a) J. D. Roberts, W. Watanabe, and R. E. McMahon, *J. Am. Chem. Soc.*, 73, 760 (1951); b) J. D. Roberts, C. M. Regan, and I. Allen, *J. Am. Chem. Soc.*, 74, 3679 (1952).

Figure 17. Effect of adding acetic acid in the decomposition of **28**.



2.10 Effect of Radical Inhibitor

We extended our mechanistic efforts by studying the effect of radical inhibitors on the decomposition of thiirane **28.** If the rate is slowed, then we could conclude that the reaction possibly follows a radical-type mechanism. Rates were determined by ^{1}H NMR by following the increase in the appearance of alkene **29** in toluene-d_8 at 80°C with and without addition of a radical inhibitor. The bimolecular rate constants were used for comparison of reaction rates and are shown in Table 16 for two different radical inhibitors, acetanilide and styrene. The addition of either inhibitor, even at 2.2-2.7 times more concentrated than **28**, showed no significant change in the rate thus demonstrating the unlikelihood of a radical mechanism. Thus, it can be concluded that an ionic mechanism is likely operative in the decomposition of **28**.

Table 16. Second order rate constants obtained from appearance of **29** in toluene-d_8 at 80°C with and without addition of radical inhibitor.

	k_2 (x 10^5 mM^{-1} s^{-1})
No inhibitor	0.38 ± 0.09
Acetanilide	0.34 ± 0.07
Styrene	0.33 ± 0.07

2.11 Effect of Added Sulfur

Huisgen demonstrated that the desulfurization of triphenylthiirane by sodium thiophenoxide is inhibited by the interaction of the eliminated sulfur.[144] Kinetic analysis by ^1H NMR showed that the addition of sulfur suppresses the rate of decomposition of the thiirane. In the presence of sulfur, the thiophenoxide anion reacts with sulfur forming polythiolate anions; hence diminishing active thiophenoxide which would otherwise desulfurize the thiirane. There was no mention of the possibility that the thiirane could also react with the added sulfur presumably because the thiophenoxide would be a better nucleophile. In our kinetic studies, no external nucleophile was employed and we therefore, decided to see if our particular thiirane would interact with sulfur which would be present in the early stages of the reaction.

We compared the rate of increase of olefin **29** with an experiment in which elemental sulfur was added prior to the addition of thiirane and we measured the rate of increase of **29**. Our studies on the effect of adding sulfur in the decomposition of thiirane **28** indicated that sulfur did not inhibit the rate of decomposition. Figure 18 shows the effect of adding 0.2 mM of sulfur to the reaction while monitoring the increase in concentration of olefin **29** in chlorobenzene at 80°C. It is clearly seen that sulfur has no effect on the rate and therefore does not seem to interact with **28**.

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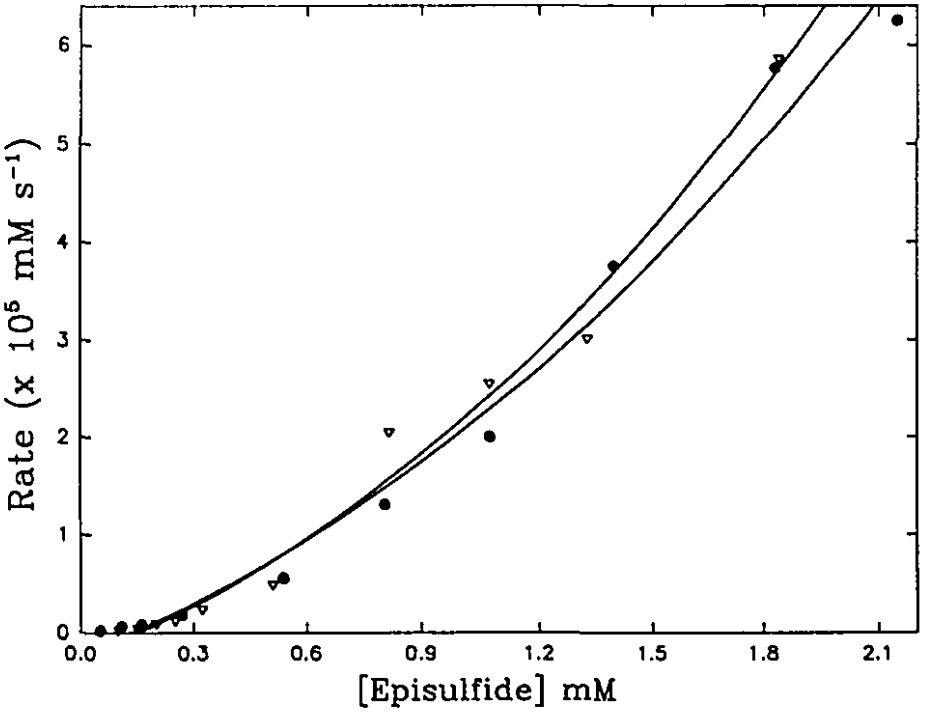
144 R. Huisgen, *"Developments in the Organic Chemistry of Sulfur", Proceedings of the XIII International Symposium on the Organic Chemistry of Sulfur*, Odense, Denmark, C.T. Pedersen and J. Becher, Eds., Gordon and Breach Science Publishers, 1989, p 63.

Figure 18. The increase in olefin **29** in the thermolysis of thiirane **28** in chlorobenzene at 80°C. • 0.2 mM sulfur added; ∇ no sulfur added.



Moreover, no significant change in rate is observed if one varies the concentration of sulfur added. We see that the rate changes by only two-fold if we vary the concentration of sulfur by 62-fold (Table 17). The small difference in rate can be attributed to the random errors in the determination of the rates.

Table 17. Rate of appearance of olefin **29** at various concentrations of added sulfur. Initial concentration of thiirane **28** = 0.20 mM.

Conc. S_8 (mM)	Rate ($\times 10^5$ mM s^{-1})
0.021	0.11
0.063	0.12
0.10	0.12
0.21	0.14
0.26	0.15
0.52	0.16
0.78	0.20
1.04	0.20
1.31	0.21

It is known that elemental sulfur reacts with alkenes to give sulfurated products as well as episulfides.[145] The synthesis of stable episulfides, however, resulted from reacting the alkene with elemental sulfur in refluxing DMF. Under these conditions we would expect to favor formation of olefin **29** rather than thiirane **28** which is thermally unstable.

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145 a) R. Sato, M. Nakayama, Y. Yuzawa, T. Goto, and M. Saito, *Chem. Lett.*, 1887 (1985); b) P. D. Bartlett and T. Ghosh, *J. Org. Chem.*, **52**, 4937 (1987); c) W. Ando, H. Sonobe, and T. Akasaka, *Tetrahedron Lett.*, **28**, 6653 (1987); d) J. Nakayama, Y. Ito, and A. Mizumura, *Sulfur Lett.*, **14**, 247 (1992). See also W. A. Pryor, *"Mechanisms of Sulfur Reactions,"* McGraw-Hill, 1962, Chapter 5.

CHAPTER 3

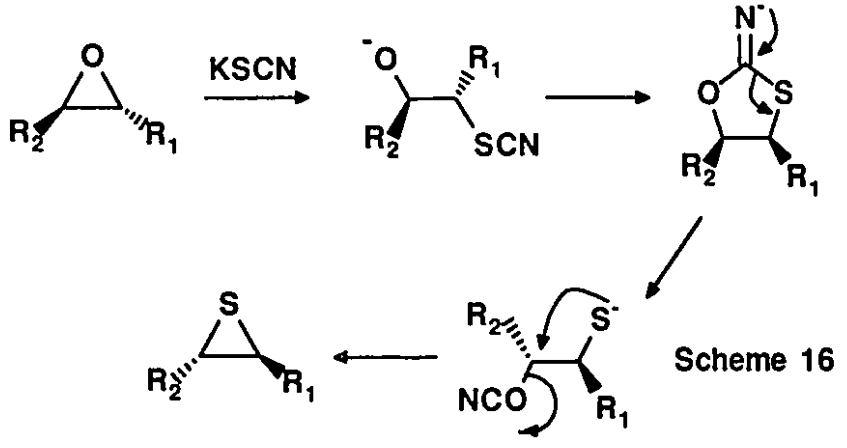
SYNTHESIS, STRUCTURE AND REACTIVITY

3.1 INTRODUCTION

The majority of synthetic studies on thiiranes is devoted not only to develop novel methods of synthesis but also to modify the classical methods in order to improve the range of reagents used and to improve the yields. There have been numerous studies on the effect of reaction conditions in the formation and yields of thiiranes. With the discovery of new thiolating agents, it has been possible to design new non-traditional methods of synthesis.

3.1.1 CONVERSION FROM OXIRANES

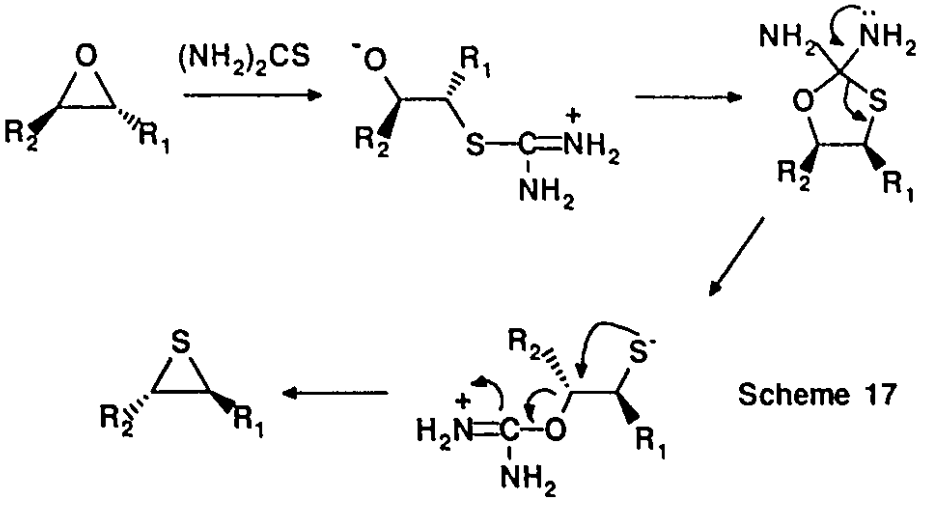
One of the most important and frequently used methods to prepare thiiranes is the reaction of oxirane with thiourea or alkali metal thiocyanates (Scheme 16).[146] The yields are high and the products are easily isolable. The accepted mechanism of reaction with thiocyanate involves a nucleophilic attack by the thiocyanate resulting in a C-O bond cleavage intermediate, followed by an intramolecular S to O cyano migration and ring closure (Scheme 16).[147]



Scheme 16

146 S. Searles, E. F. Lutz, H. R. Hays, and H. E. Mortensen, *Org. Synth.*, 42, 59 (1962).

147 a) M. G. Ettlinger, *J. Am. Chem. Soc.*, 72, 4792 (1950); b) E. E. van Tamelen, *J. Am. Chem. Soc.*, 73, 3444 (1951); c) C. C. Price and P. F. Kirk, *J. Am. Chem. Soc.*, 75, 2396 (1953).



Scheme 17

A similar mechanism can be envisaged using thiourea (Scheme 17). The stereochemistry is preserved and the optically active (R,R) oxirane gives optically active (S,S) thiirane. A number of new thiiranes with a variety of substituents have thus been obtained which were previously unavailable.[51a,94d,111,148] This reaction is slow if the oxirane ring is tri- or tetra-substituted or if the substituents are electron withdrawing. Most thiirane products are unstable due to the ease of sulfur elimination if substituents are electron withdrawing. However, thiiranes containing electron attracting substituents have been synthesized.[149]

Other sulfur reagents have been successfully employed in the preparation of thiiranes. Triphenylphosphine sulfide in the presence of acid has been used with success to convert the corresponding oxiranes to thiiranes with retention of configuration.[150] Silyl thiirane was formed by interaction of the corresponding oxirane with 3-methylbenzothiazole-2-thione (**43**) (Scheme 18).[151]

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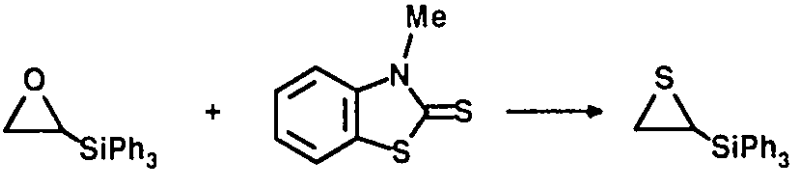
148 a) H. Bouda, M. E. Borredon, M. Delmas, and A. Gaset, *Synth. Comm.*, **17**, 943 (1987); b) R. L. Pederson, K. K. C. Liu, J. F. Rutan, L. Chen, and C. H. Wong, *J. Org. Chem.*, **55**, 4897 (1990).

149 R. Ketcham and V. P. Shah, *J. Org. Chem.*, **28**, 229 (1963).

150 a) T. H. Chan and J. R. Finkenbine, *J. Am. Chem. Soc.*, **94**, 2880 (1972); b) T. H. Chan and J. R. Finkenbine, *Int. J. Sulfur Chem.*, **8**, 45 (1973); c) W. E. Childers and C. H. Robinson, *J. Chem. Soc., Chem. Comm.*, 320 (1987). See also J. R. Finkenbine, Ph.D. thesis, McGill University, June 1974.

151 G. Barberi, *J. Organomet. Chem.*, **117**, 157 (1976).

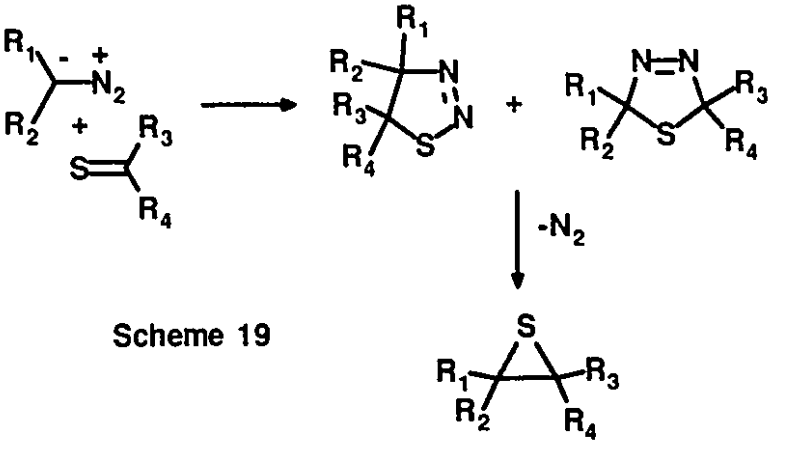


43 Scheme 18

The perhydrobenzothiazole-2-thione derivative has also been implemented.[152] One of the most effective new thiono compounds is dimethyl thioformamide which has been used to prepare thiiranes.[153] Also effective are 2-mercaptobenzothiazole[154] and 5-mercapto-1-phenyltetrazole.[155]

3.1.2 Condensation of Diazo Compounds

Coupling of diazo compounds with thiocarbonyls is one of the oldest methods to prepare thiiranes. Between 1916-1920, Staudinger reported the formation of thiirane from diazo compounds with thiocarbonyls.[49,156] An unstable 1,2,3 or 1,3,4 thiadiazoline was postulated as an intermediate which is converted to the thiirane with the concomitant evolution of nitrogen (Scheme 19).



Scheme 19

The reactions in these systems can easily be accounted for by initial formation of a carbene.[157] This method has been employed with a wide range of both diazo reagents and

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152 R.C. Cambie, G. D. Mayer, P. S. Rutledge, and P. D. Woodgate, *J. Chem. Soc., Perkin Trans. I*, 52 (1981).

153 T. Takido, Y. Kobayashi, and K. Itabashi, *Synthesis*, 779 (1986).

154 V. Calò, L. Lopez, and G. Pesce, *Gazz. Chim. Ital.*, **109**, 703 (1979).

155 E. Lippmann, D. Reifegerste, and E. Kleinpeter, *Z. Chem.*, **17**, 60 (1977).

156 a) H. Staudinger and F. Pfenninger, *Chem. Ber.*, **49**, 1941 (1916); b) H. Staudinger and J. Siegwart, *Helv. Chem. Acta*, **3**, 833 (1920).

157 N. Latif and I. Fathy, *J. Org. Chem.*, **27**, 1633 (1962).

thioketones resulting in many different thiiranes.[bl,158] Grignard reagents[159] and phenyl(trihalogenmethyl) mercury compounds[66] have also been used as sources of carbenes to prepare thiiranes.

3.1.3 Other Methods

Thiiranes have also been prepared by other methods which include the addition of sulfur to alkenes[160] although the yields are low, pyro- and photolytic methods[70b,161], as well as reactions involving ring cyclization *via* a thiolate anion.[162] A convenient synthesis of thiiranes is the addition of sulfenyl chlorides to alkenes followed by ring closure.[163] A new method was discovered by Zipplies[164] in which the reaction of dimethylaniline oxide with CS_2 in the presence of alkenes produced thiiranes. The reaction of thioaldehyde **44** with a Wittig reagent also gives thiirane (Scheme 20).[165] 2-Hydroxyalkanesulfenyl chlorides are converted stereospecifically to thiirane with triphenylphosphine;[166] diethoxy triphenylphosphorane was used to transform a 2-hydroxythiol to a thiirane.[167] An unusual class of thiiranes, vinylthio substituted thiiranes (**45**), has recently been synthesized using sulfenyl chlorides in the presence of

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158 a) M. Tashiro, S. Makata, and S. Ischi, *Heterocycles*, **12**, 184 (1979); b) M. S. Raasch, *J. Org. Chem.*, **44**, 632 (1979); c) G. L'abbe, J. P. Dekerk, C. Martens, and S. Toppet, *J. Org. Chem.*, **45**, 4366 (1980); d) E. Schaumann, H. Behr, G. Adwidjaja, A. Tangerman, B. H. M. Lammerink, and B. Zwanenberg, *Tetrahedron*, **37**, 219 (1981); e) T. Furuhata and W. Ando, *Tetrahedron Letts.*, **28**, 1179 (1987); f) K. Rall and W. Sundermeyer, *J. Fluorine Chem.*, **47**, 121 (1990).

159 a) R. C. Moreau, *Bull. Chim. Soc. Fr.*, 1044 (1955); b) P. Beak and J. W. Worley, *J. Am. Chem. Soc.*, **94**, 597 (1972).

160 a) S. Inoue, T. Tezuka, and S. Oae, *Phosphorus Sulfur*, **4**, 219 (1978); b) J. Emsley, D. W. Griffiths, G. J. J. Jayne, *J. Chem. Soc., Perkin Trans. I*, 228 (1979); c) C. Bertaïna, R. Fellous, F. Lemaire, and R Stringat, *Tetrahedron Letts.*, **26**, 5521 (1985); d) J. Joseph, R. K. Gosavi, A. Otter, G. Kotovych, E. M. Lown, and O. P. Strausz, *J. Am. Chem. Soc.*, **112**, 8670 (1990).

161 a) H. Quast and A. Fuss, *Angew. Chem. Int. Ed. Engl.*, **20**, 291 (1981); b) A. Krebs, W. Rüger, and W. H. Nickel, *Tetrahedron Letts.*, **22**, 4937 (1981).

162 a) R. C. Cambie, P. S. Rutledge, G. A. Strange, and P. D. Woodgate, *Heterocycles*, 1501 (1982); b) M. Michalska, E. Brzezińska, and P. Lipka, *J. Am. Chem. Soc.*, **113**, 7945 (1991); c) J. Uenishi, M. Motoyama, Y. Nishiyama, and S. Wakabayashi, *J. Chem. Soc., Chem. Comm.*, 1421 (1991).

163 a) F. K. Lautenschlaeger and N. V. Schwartz, *J. Org. Chem.*, **34**, 3991 (1969); b) F. K. Lautenschlaeger, *J. Org. Chem.*, **34**, 3998 (1969); c) T. Fujisawa and T. Kobori, *Chem. Lett.*, 935; 1065 (1972); d) M. U. Bombala and S. V. Ley, *J. Chem. Soc., Perkin Trans. I*, 3013 (1979); e) J. M. Majewski and J. Zakrzewski, *Tetrahedron Lett.*, **22**, 3659 (1981); f) W. A. Smit, N. S. Zefirov, and I. V. Bodrikov, *"Organic Sulfur Chemistry,"* R. K. Friedina and A. E. Skorova, Eds., Pergamon Press, 1981, p 159.

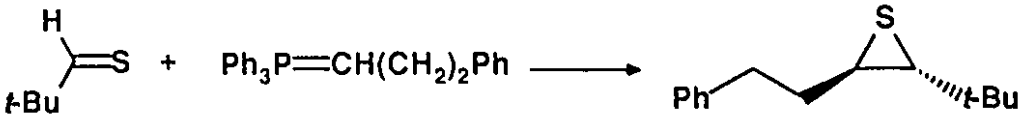
164 M. F. Zipplies, M.-J. De Vos, and T. C. Bruice, *J. Org. Chem.*, **50**, 3228 (1985).

165 E. Vedejs, D. A. Perry, and R. Wilde, *J. Am. Chem Soc.*, **108**, 2985 (1986).

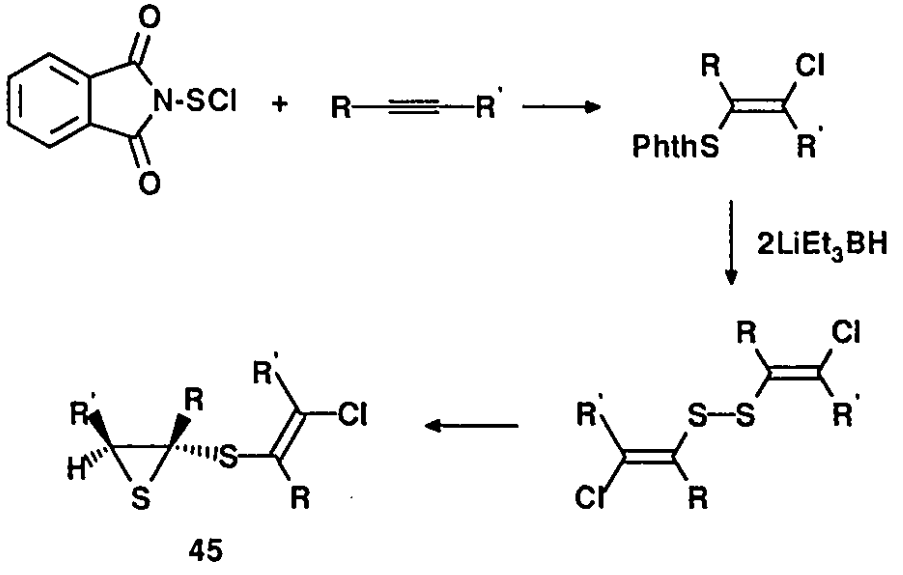
166 J. E. Baldwin and D. P. Hesson, *J. Chem. Soc., Chem. Comm.*, 667 (1976).

167 R. L. Robinson, J. W. Kelly, and S. A. Evans, *Phosphorus Sulfur Relat. Elem.*, **31**, 59 (1987).

alkynes and a boron superhydride.[168] More recently, thiiranes were prepared utilizing a reaction involving a dithioiminocarbonate and thiazoline with aldehydes promoted by fluoride ion.[169]



44 Scheme 20



45

3.2 Synthesis of 2,2-Dichloro-3-[9-fluorenyl] Episulfide (28)

As stated above, one of the more convenient methods of preparing fluorenyl substituted thiiranes is the coupling reaction of 9-diazofluorene with a thioketone. This was first reported by Staudinger and Siegwart[49] in which thiirane **28** was first prepared using their procedure. The diazo compound is obtained by oxidation of its corresponding hydrazone. A variety of hydrazones and their corresponding diazofluorenes are easily obtained by the method described by Baltzly and coworkers.[170] Following their procedure, readily available 9-fluorenone was easily converted to its hydrazone by treatment with hydrazine monohydrate in refluxing *n*-butanol followed by oxidation with

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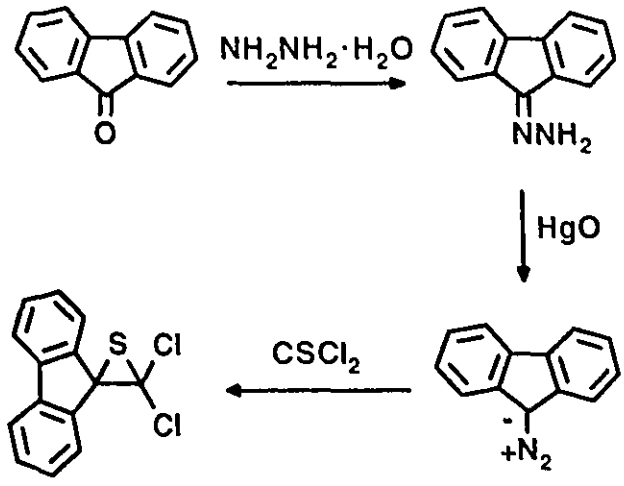
168 G. Capozzi, L. Gori, and S. Menichetti, *Tetrahedron*, 47, 7185 (1991).

169 Y. Tominaga, H. Ueda, K. Ogata, S Kohra, M. Hojo, M. Ohkuma, K. Tomita, and A. Hosomi, *Tetrahedron Lett.*, 33, 85 (1992).

170 R. Baltzly, N. B. Mehta, P. B. Russell, R. E. Brooks, E. M. Grivsky, and A. M. Steinberg, *J. Org. Chem.*, 26, 3669 (1961).

mercuric oxide to 9-diazofluorene (**46**). Thiirane **28** is obtained by reacting **46** with thiophosgene at 0°C following Staudinger's procedure (Scheme 21).

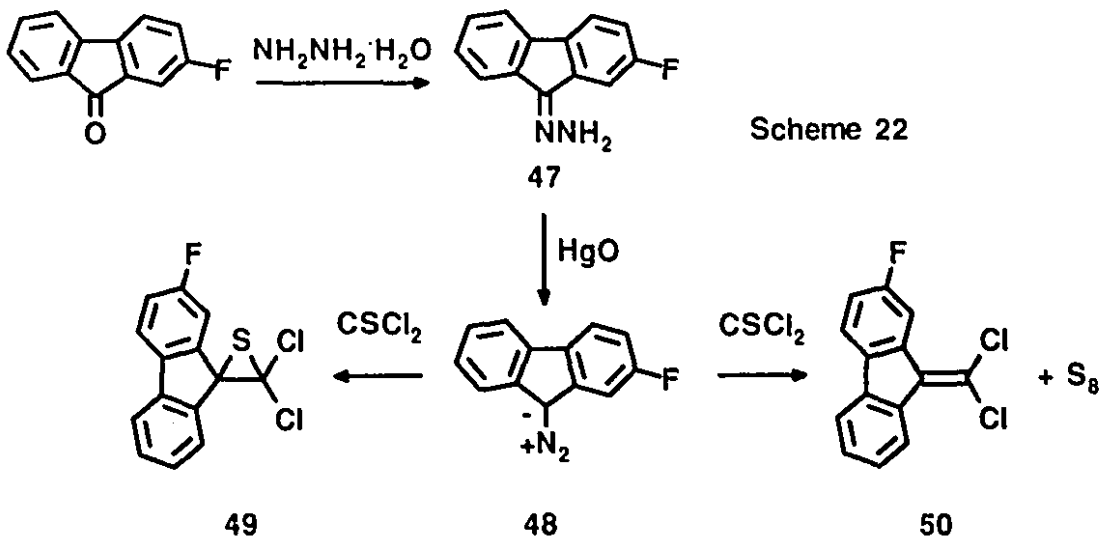


28 **46**

Scheme 21

3.3 Synthesis of 2,2-Dichloro-3-[2-fluoro-9-fluorenyl] Episulfide

In our quest to synthesize fluorene-substituted thiiranes in order to further examine the mechanism of sulfur extrusion, we extended Staudinger's synthetic methodology by attempting to synthesize the fluoro fluorenyl thiirane derivative **49**. Our initial strategy was to not alter the structure of the parent thiirane **28** at the 2 or 3 positions but rather putting a substituent on the fluorenyl ring system so that the reactivity of the compound will almost be similar to the parent thiirane. The simplicity of readily available monosubstituted fluorenones allowed us to attempt to prepare the thiiranes in three steps. We initiated work on 2-fluoro-9-fluorenone. The disadvantage is that the electronegative fluorine should decrease the stability of the thiirane. 2-Fluoro fluorenyl hydrazone (**47**) was prepared and consequently converted to its diazo compound **48** following Baltzly's approach.[170] Subsequent reaction of **48** with thiophosgene gave a ~3:1 ratio of olefin **50** to thiirane **49** (Scheme 22). Several attempts to prepare **49** were unsuccessful most likely due to the instability of the 3-membered heterocyclic ring with the additional fluorine atom (*cf.* Section 3.7).



Scheme 22

3.4 Methyl- and Methoxyfluorenyl substituted Episulfides

Our efforts turned to methyl- and methoxy-fluorenyl substituents. Unfortunately, alkyl or alkoxy substituted fluorenones are not readily available and thus had to be synthesized. The preparation of 3,6-dimethoxy-9-fluorenone was reported by Schuster and coworkers in 1985.[171] The advantage of this particular compound is the symmetrical aspect of the dimethoxy fluorenone which permitted us to easily characterize and identify the intermediates *via* ^{1}H and ^{13}C NMR. The synthesis involves a reaction between a Grignard reagent and an oxazoline followed by deprotection and intramolecular cyclization, giving the disubstituted fluorenone. The synthesis of the dimethoxyaryloxazoline **52** was accomplished by the procedure described by Meyers and coworkers[172] and is shown in Scheme 23. The first step requires protection of the carboxyl substituent. The 2-oxazoline group was suitable protection for the carboxyl function because of its resistance to Grignard reagents which would be used in a subsequent step in the synthesis.[173] Meyers has recently extended his methodology to the synthesis of 2-substituted napthalenes.[174] The acid chloride was prepared from 2,4-dimethoxy-benzoic acid by treatment with thionyl chloride and which, in turn, was transformed to the benzamide **51** by treatment with 2-amino-2-methylpropanol (Scheme

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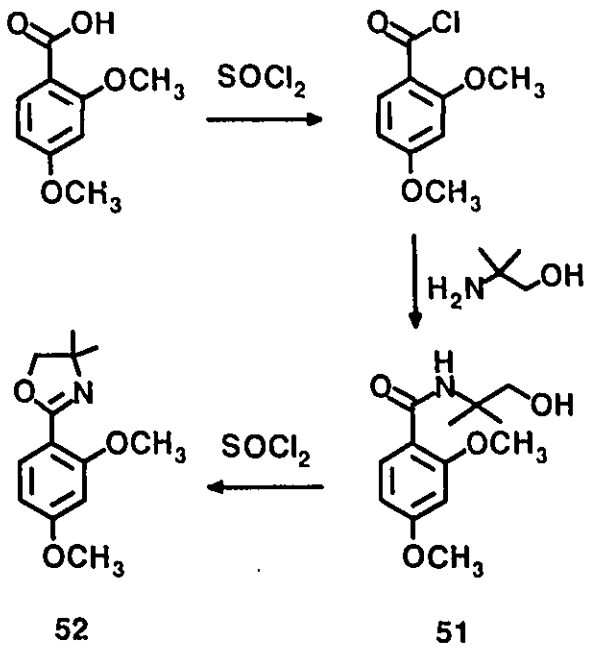
171 C. Chuang, S. C. Lapin, A. K. Schrock, and G. B. Shuster, *J. Am. Chem. Soc.*, **107**, 4238 (1985).

172 A. I. Meyers, R. Gabel, and E. D. Mihelich, *J. Org. Chem.*, **43**, 1372 (1978).

173 a) A. I. Meyers, D. L. Temple, D. Haidukewych, and E. D. Mihelich, *J. Org. Chem.*, **39**, 2787 (1974); b) A. I. Meyers, A. Meier, and D. J. Rawson, *Tetrahedron Lett.*, **33**, 853 (1992).

174 T. C. Gant and A. I. Meyers, *J. Am. Chem. Soc.*, **114**, 1010 (1992).

23). The 2-oxazoline **52** is then prepared by cyclization of **51** with thionyl chloride followed by chromatographic purification.



52 **51**

Scheme 23

With **52** in hand, a nucleophilic aromatic substitution reaction with 3-methoxyphenylmagnesium bromide was performed to yield the biphenyl **53** (Scheme 24). The Grignard reagent was easily prepared by heating 3-bromoanisole and magnesium metal in refluxing THF. It should be noted that the methoxy substituent ortho to the oxazoline is preferentially displaced over the para methoxy group, owing to the versatility of the oxazoline moiety acting also as an activating group. Substitution is facilitated at the ortho position apparently because of direct chelation of nitrogen (and/or possibly oxygen) and the methoxy oxygen with the magnesium.[173a] The biphenyl compound **53** was deprotected *via* the intermediate methiodide salt **54** and removal of the oxazolinium moiety was accomplished by alkaline hydrolysis to give the biphenyl carboxylic acid **55**. A milder method for converting oxazolines to carboxylic acids was recently described by Phillion and co-workers[175] in which trifluoromethanesulfonic anhydride was employed followed by alkali saponification. Poly(phosphoric) acid cyclization[176] of **55** gave 2 isomeric compounds, 3,6-dimethoxy-9-fluorenone (**56**) and 1,6-dimethoxy-9-fluorenone which were easily separated.

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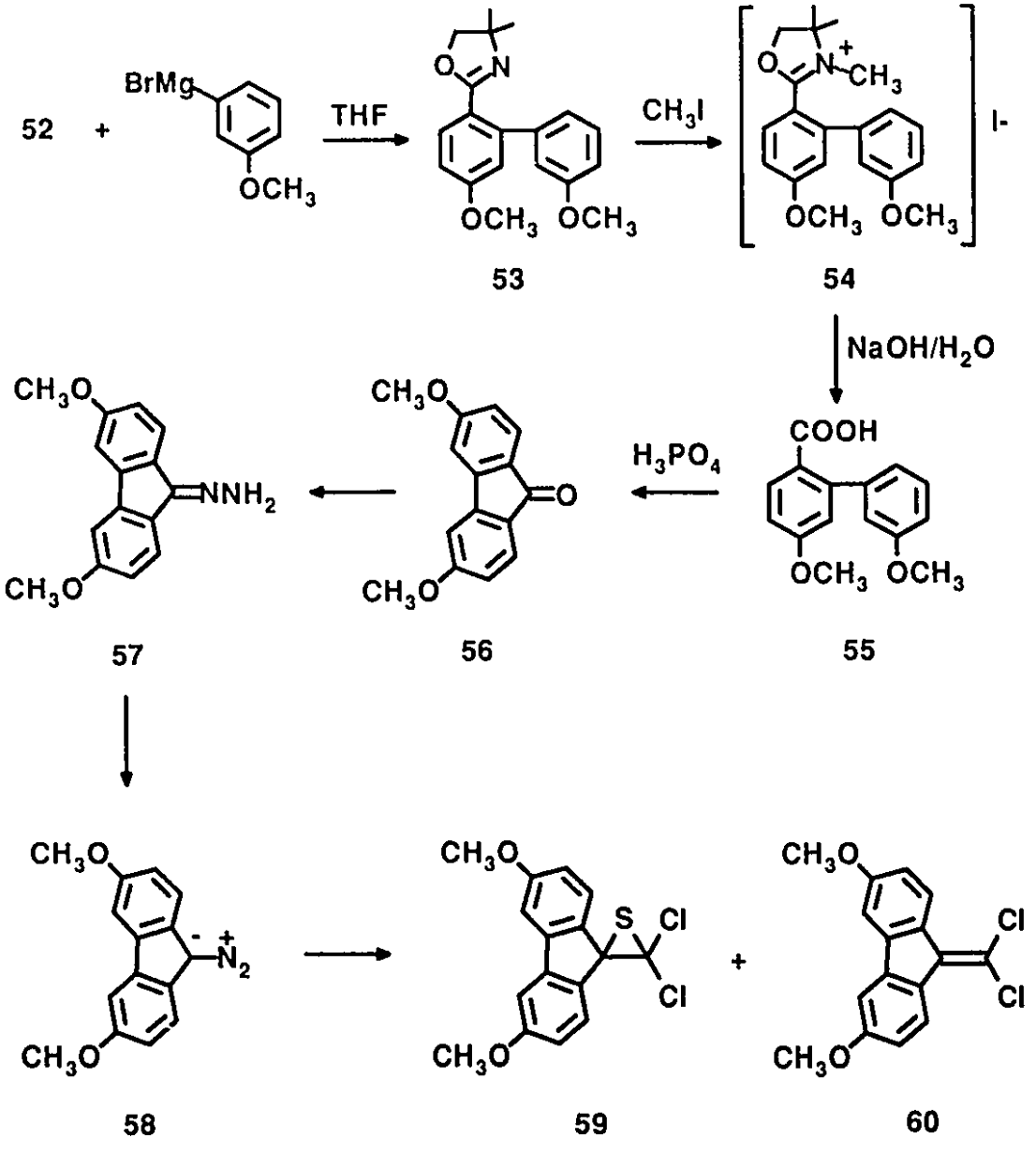
175 D. P. Phillion and J. K. Pratt, *Syn. Comm.*, 22, 13 (1992).

176 J. Koo, *J. Am. Chem. Soc.*, 75, 1891 (1953).



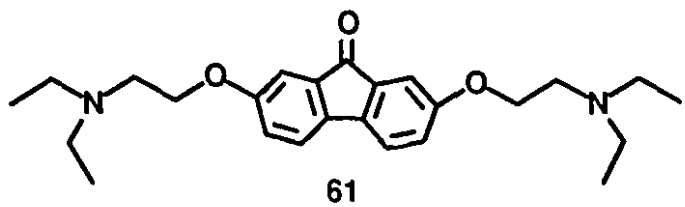
Scheme 24

Conversion of the symmetrical fluorenone **56** to the 9-diazofluorene compound **58** *via* hydrazone **57** is relatively straightforward following the procedure of Baltzly.[170] The synthesis of 2,2-dichloro-3-(3,6-dimethoxy-9-fluorenyl) thiirane (**59**), to our knowledge, has never been reported in the literature.

Treatment of the red diazo compound **58** with thiophosgene at 0°C gave only compound **60** as a red solid in 37% yield. In another attempt to prepare thiirane **59**,

hydrazone **57** was converted directly without isolation of the diazo compound. This route would minimize generation of azine side products which was observed if diazo compound **58** was isolated. Azines are known to form readily from diazo compounds[177] and hydrazones.[178] However, this method proved unsatisfactory as olefin **60** was the only product isolated. This was confirmed by ^{13}C NMR.

The methodology outlined above was extended allowing us to possibly prepare other substituted fluorenyl thiiranes. Following the general procedure in the preparation of **59**, it was decided this approach will be used with other arylsubstituted Grignard reagents in hopes of affording several new substituted fluorenones. Snieckus and co-workers described a convenient route to substituted fluorenones by a remote aromatic metalation strategy.[179] Substituted fluorenones are also known to be biologically and physiologically active compounds.[180] For example, 2,7-*bis*(*N*,*N*-diethylaminoethoxy) fluoren-9-one dihydrochloride (Tilorone) (**61**) is an interferon inducer and exhibits anti-viral activity.[181]



61

From the appropriate Grignard reagents, 2-oxazolines **65**, **66**, and **67** were obtained from treatment with 2-methylphenylmagnesium bromide (**62**), *p*-tolylmagnesium bromide (**63**), and phenylmagnesium bromide (**64**) respectively. The oxazolines were deprotected affording the biphenyl carboxylic acids **68**, **69**, and **70** which were converted to their disubstituted fluorenones **71**, **72**, and **73** *via* intramolecular poly(phosphoric) acid cyclization. These were then converted to their mixture of isomeric hydrazones **74**, **75**, and **76** by treatment of the ketone with hydrazine hydrate. Oxidation of the hydrazones afforded the red diazo compounds **77**, **78**, and **79** which

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177 a) H. H. Szmant and C. McGinnis, *J. Am. Chem. Soc.*, 72, 2890 (1950); b) S. G. Cohen, F. Cohen, and C. H. Wang, *J. Org. Chem.*, 28, 1479 (1963); c) C. J. Abelt and J. M. Pleier, *J. Am. Chem. Soc.*, **111**, 1795 (1989); d) M. H. Sugiyama, S. Celebi, and M. S. Platz, *J. Am. Chem. Soc.*, **114**, 966 (1992).

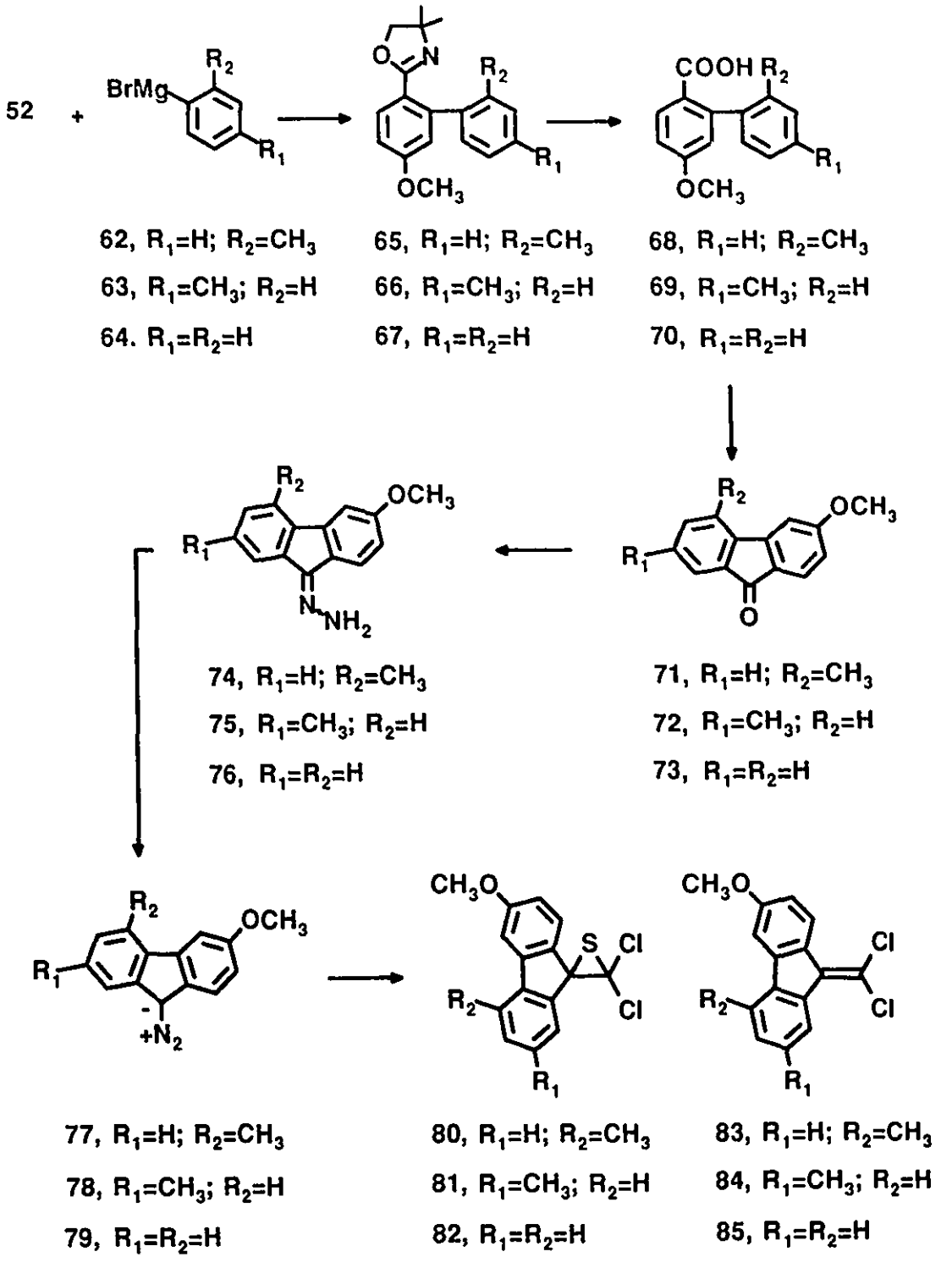
178 V. M. Kolb, A. C. Kuffel, H. O. Spiwek, and T. E. Janota, *J. Org. Chem.*, 54, 2771 (1989).

179 J.-M. Fu, B.-P. Zhao, M. J. Sharp, and V. Snieckus, *J. Org. Chem.*, **56**, 1683 (1991).

180 a) E. P. Kyba, S.-T. Liu, K. Chockalingam, and B. R. Reddy, *J. Org. Chem.*, 53, 3513 (1988); b) A. W. Nicholas, M. C. Mani, G. Manikumara, M. E. Wall, K. W. Kohn, and Y. Pommier, *J. Med. Chem.*, 33, 972 (1990).

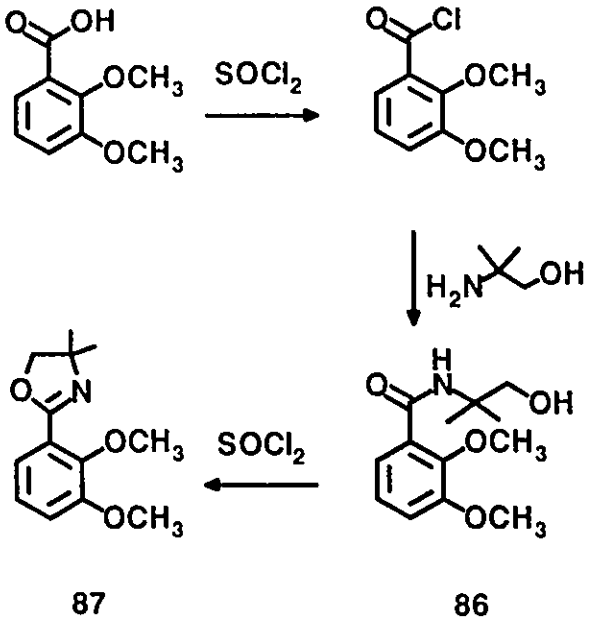
181 R. F. Krueger and G. D. Mayer, *Science*, **169**, 1213, 1214 (1970).

were not isolated but immediately treated with thiophosgene *in situ* in an attempt to prepare the fluorenyl substituted thiiranes (Scheme 25). In all three cases, the 3-methoxy substituted derivatives gave only the corresponding olefins, **83**, **84**, and **85**. These compounds were confirmed by ^{1}H and ^{13}C NMR and MS analyses. This is not surprising in view of the presence of the activating substituents (*cf.* Section 3.7).


52
+
BrMg
R2
R1
O
N
OCH3
COOH
62, R1=H; R2=CH3
63, R1=CH3; R2=H
64. R1=R2=H
65, R1=H; R2=CH3
66, R1=CH3; R2=H
67, R1=R2=H
68, R1=H; R2=CH3
69, R1=CH3; R2=H
70, R1=R2=H
71, R1=H; R2=CH3
72, R1=CH3; R2=H
73, R1=R2=H
74, R1=H; R2=CH3
75, R1=CH3; R2=H
76, R1=R2=H
77, R1=H; R2=CH3
78, R1=CH3; R2=H
79, R1=R2=H
80, R1=H; R2=CH3
81, R1=CH3; R2=H
82, R1=R2=H
83, R1=H; R2=CH3
84, R1=CH3; R2=H
85, R1=R2=H

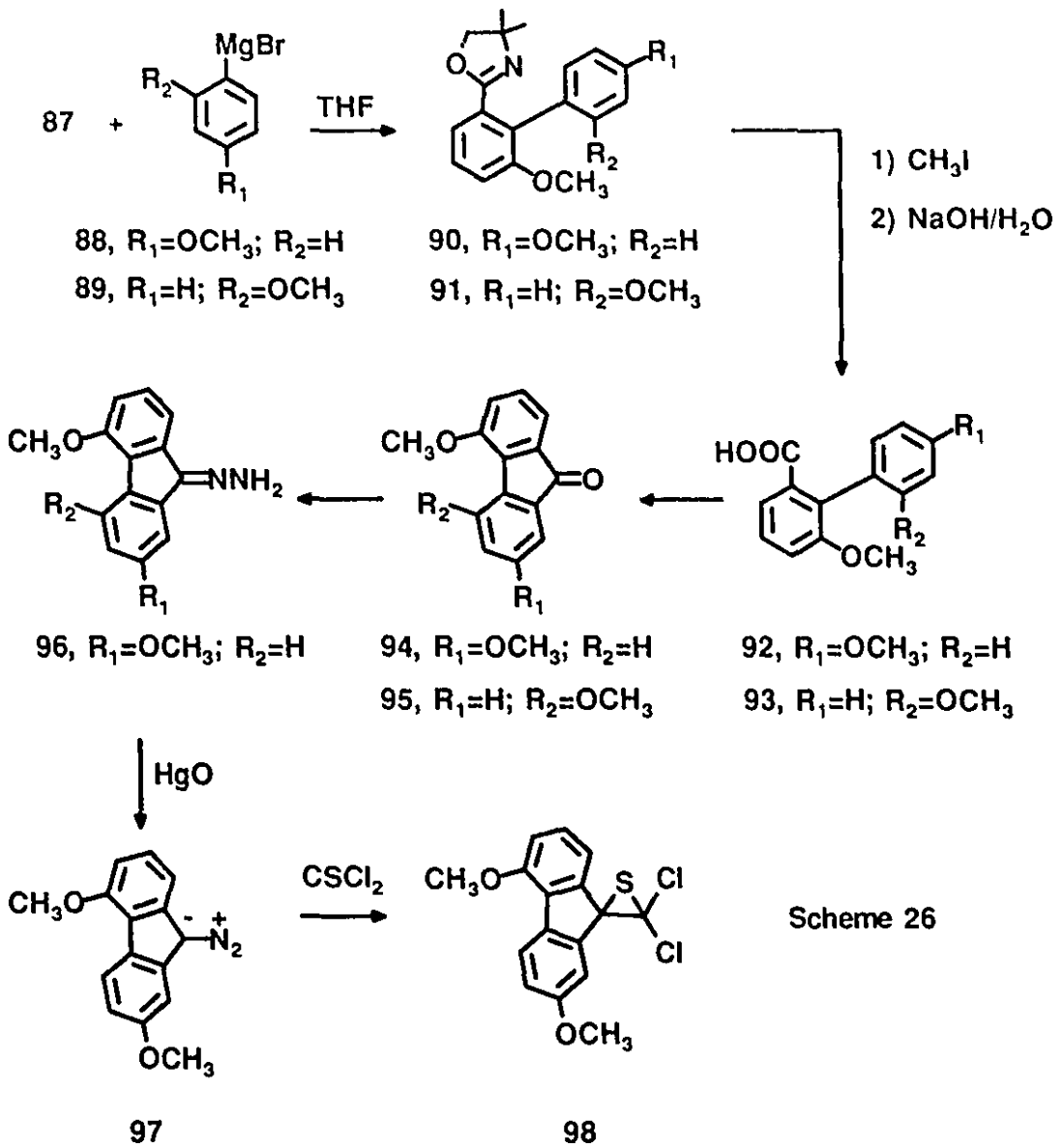
Scheme 25

We further expanded our efforts by applying the Meyers methodology[172] to prepare oxazoline **87**. Thus, the carboxyl group of 2,3-dimethoxybenzoic acid was converted to its acid chloride followed by conversion to its corresponding benzamide (**86**). Treatment with thionyl chloride afforded **87**.



87 **86**

Oxazoline **87** was treated with 4-methoxyphenylmagnesium bromide (**88**) to give biphenyl **90** (Scheme 26). Deprotection of the oxazoline moiety *via* the methiodide salt and aqueous sodium hydroxide gave the carboxylic acid **92**. 2,5-Dimethoxyfluorenone, **94**, was synthesized by poly(phosphoric) acid catalyzed cyclization of **92**. To our knowledge, this fluorenone derivative has not been prepared previously. Transformation of the ketone to hydrazone **96** was performed by reacting with hydrazine monohydrate in refluxing ethanol. The hydrazone was oxidized to the diazo compound **97** with mercuric oxide which was then treated with thiophosgene to yield, after chromatography, thiirane **98**. Satisfactory ^{1}H and ^{13}C NMR spectra were obtained.

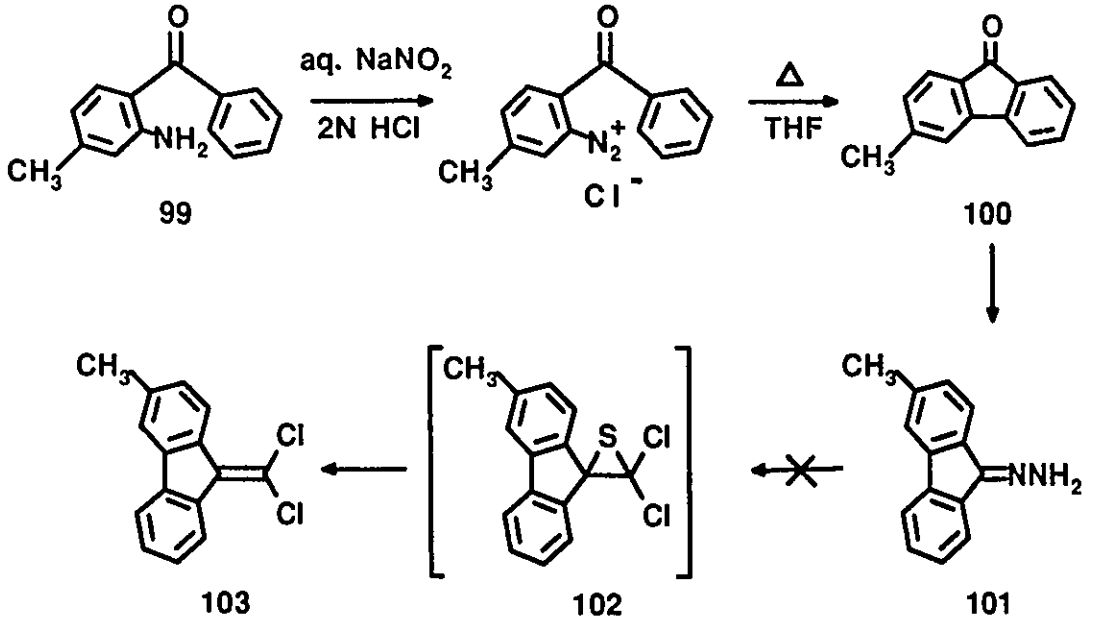


Scheme 26

Following a similar procedure, the Grignard reaction between oxazoline **87** and 2-methoxyphenylmagnesium bromide (**89**) gave the dimethoxybiphenyl **91**. Deprotection produced the carboxylic acid **93**. 4,5-Dimethoxyfluorenone (**95**) was then prepared from **93** *via* intramolecular cyclization initiated by poly(phosphoric) acid. To our knowledge, fluorenone **95** has been synthesized for the first time. Derivatization to its hydrazone, however, proved very difficult. In refluxing ethanol or ethylene glycol containing hydrazine monohydrate, only the starting ketone was recovered. No further attempt to convert the ketone to its hydrazone was performed.

The synthesis of the 3-methyl fluorenyl derivative involved another approach. In the preparation of the previously described methoxy substituted derivatives, it required an ortho methoxy substituted benzoic acid as starting material which was readily available. However, 2-methoxy-4-methyl benzoic acid required to make the 3-methyl fluorenyl compound was not readily available. The preparation of the fluorenones entailed a Grignard coupling reaction followed by an internal cyclization under acidic conditions. However, with suitable 2-aminobenzophenone compounds, the carbonyl functionality is already in place. Under standard Pschorr-type cyclization conditions, the ortho amino group is converted to the diazonium group and ring closure is easily effected by uncatalyzed intramolecular C-C bond formation to the other ortho position in the other ring. The Pschorr-type reaction has been used to synthesize a variety of substituted fluorenone and azafluorenones.[180a]

Thus, 2-amino-4-methylbenzophenone (**99**) in 2N HCl was treated with aqueous sodium nitrite to obtain the diazonium intermediate. After heating in refluxing THF, 3-methylfluorenone (**100**) was obtained (Scheme 27). Conversion to the hydrazone **101** was straightforward but then an attempt to prepare thiirane **102** failed and the corresponding olefin product **103** was obtained exclusively. The presence of olefin was confirmed by ^{13}C NMR, MS and elemental analysis.

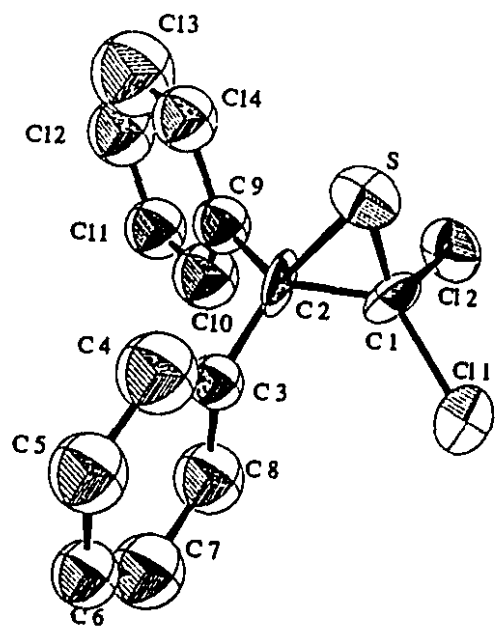


Scheme 27

3.5 Diaryl Episulfides

A related molecule, 2,2-dichloro-3,3-diphenylthiirane (**110**), was successfully synthesized following the procedure described by Staudinger and Siegwart.[49] This compound has the advantage in that the 3-membered ring heterocycle is predicted to be more stable than the fluorenyl substituted compound because of it being less strained. The degree of aromaticity is less than that of the fluorenyl group. Starting with benzophenone (**104**), the hydrazone **106** and the diazo derivative **108** were easily prepared by known methods[170] and readily converted to **110** as white crystals (Scheme 28). Confirmation of the structure was obtained from the X-ray crystal structure of the compound.[182] Figure 19 shows the ORTEP representation and Table 18 shows selected bond lengths and bond angles. As predicted, the phenyl groups are not co-planar and are arranged in such a fashion as to minimize their interaction. The thiirane ring structure is unsymmetrical as seen from the slightly shorter C(1)-S bond compared to the C(2)-S bond. The C(1)-C(2) bond length, however, was found to be characteristically shorter than those found in the literature[11,12] but the length is comparable to others.[13b,183] Similarly, the 4,4'-dimethoxybenzophenone thiirane derivative (**111**) was also prepared using the same procedure but was found to decompose readily at room temperature as predicted with the presence of the moderately activating methoxy groups.

Figure 19. ORTEP representation of 2,2-dichloro-3,3-diphenyl episulfide (**110**).

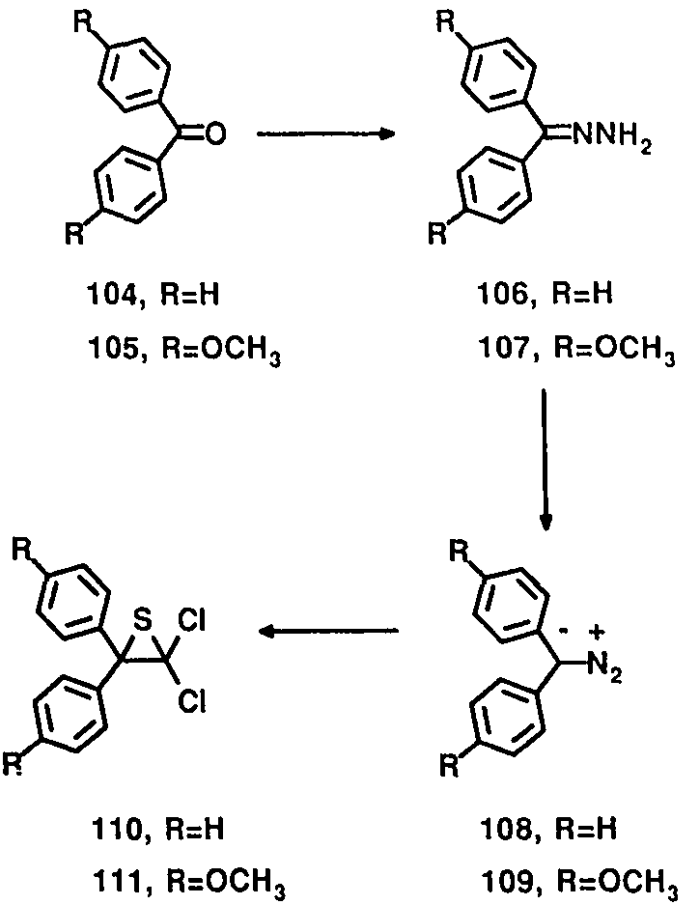


182 We gratefully acknowledge Dr. Rosie Hynes, McGill University for obtaining the X-ray crystallographic data.

183 N. V. Riggs, U. Zoller, M. T. Nguyen, and L. Radom, *J. Am. Chem. Soc.*, **114**, 4354 (1992).

Table 18. Selected bond lengths and bond angles for 2,2-dichloro-3,3-diphenyl episulfide (**110**). Estimated σs refer to the last digit.

Bond lengths (Å)	
Cl (1) - C(1)	1.781(23)
Cl (2) - C(1)	1.80(23)
S -C (1)	1.773(24)
S - C (2)	1.830(22)
C (1) - C (2)	1.43(3)
Bond Angles (°)	
C (1) - S - C (2)	46.6(11)
Cl (1) - C (1) - Cl (2)	106.2(13)
Cl (1) - C (1) - S	116.3(13)
Cl (1) - C (1) - C (2)	124.1(19)
Cl (2) - C (1) - S	116.1(13)
Cl (2) - C (1) - C (2)	121.1(15)
S - C (1) - C (2)	68.8(14)
S - C (2) - C (1)	64.6(12)



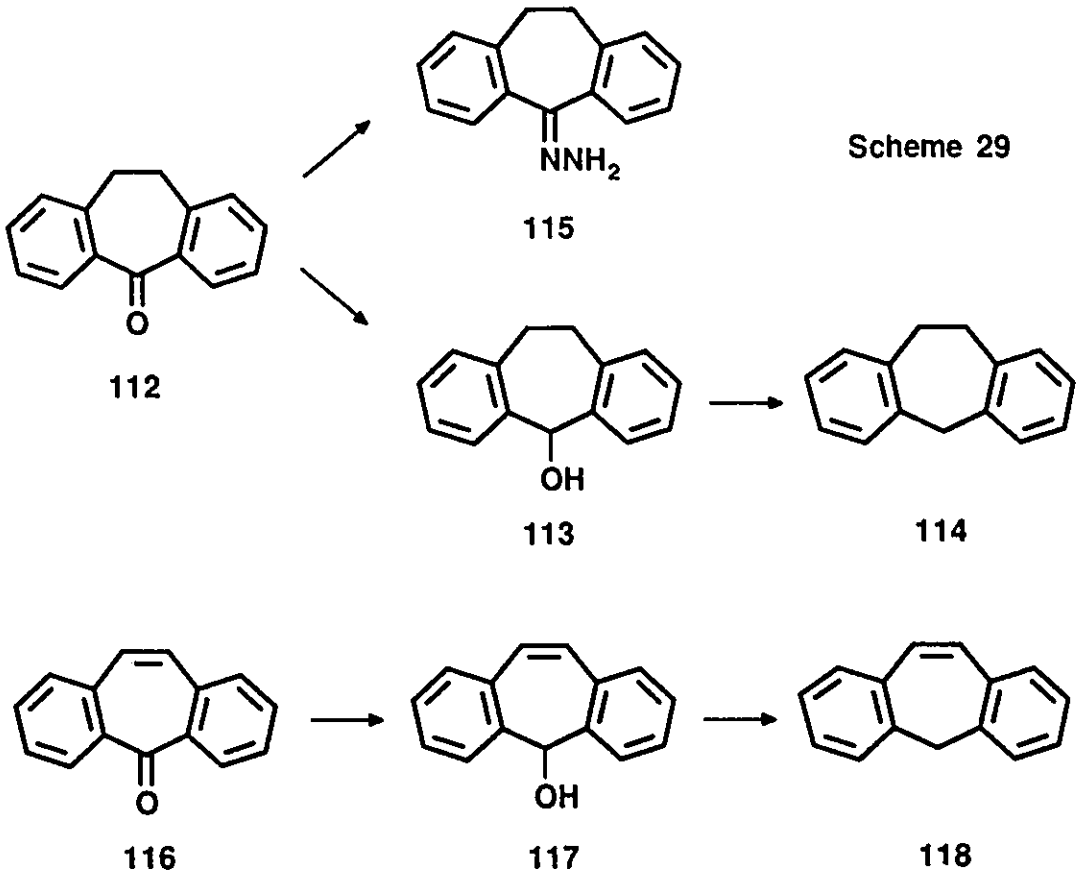
Scheme 28

3.6 Synthesis of 2,2-Dichloro-3-dibenzosuberonyl Episulfide

The synthesis of dibenzosuberone episulfide has never been accomplished previously. As such, we attempted to synthesize it following a similar procedure described previously in the preparation of thiirane **28**.

Initial attempts to prepare the hydrazone from readily available dibenzosuberone (**112**) in refluxing *n*-butanol were unsuccessful. In these reactions, only the alcohol **113** was obtained (Scheme 29). Under identical reaction conditions, the analogous alcohol **117** from dibenzosuberenone (**116**) was obtained (Scheme 30). Furthermore, only Wolff-Kishner reduction products **114** and **118** were isolated when 98% hydrazine was used as the reagent under refluxing ethylene glycol. However, dibenzosuberone was easily derivatized to its hydrazone **115** using hydrazine monohydrate in refluxing

ethylene glycol for 2 hr.[184] Further refluxing gave **114**. Similarly, dibenzosuberenone (**116**) gave **118** after 24 hr reflux in ethylene glycol. We can conclude that temperature, time of reaction, and strength of the hydrazine reagent are all vital in the preparation of dibenzosuberone hydrazone (**115**). This is rather surprising in view of the similarities between **112** and 9-fluorenone.



112 **115** **113** **114** **116** **117** **118**

Scheme 29

Scheme 30

We also attempted to extend the above methodology to synthesize hydrazones of anthrone (**119**) and anthraquinone (**120**). However, after several attempts, we were unable to isolate any desired products. In some experiments, anthracene (**121**) was the only isolated product (Scheme 31). Anthracene most likely arose from prolonged heating. The starting ketones were reduced to their corresponding alkanes which would rapidly aromatize.

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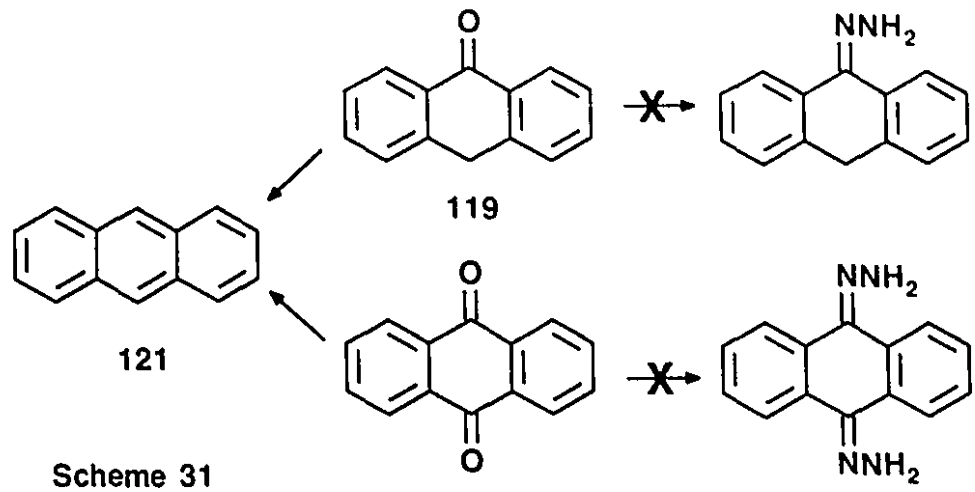
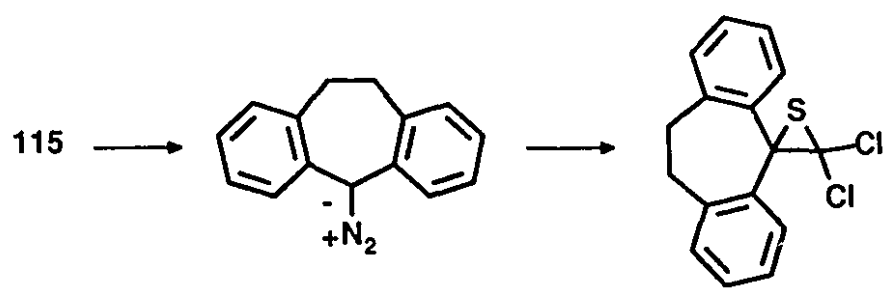
184 H. H. Szmant and C. E. Alciaturi, *J. Org. Chem.*, 42, 1081 (1977).



Scheme 31

With dibenzosuberone hydrazone (**115**) in hand, it was conveniently oxidized to its analogous diazo compound **122** as violet crystals. Conversion to its 2,2-dichloro thiirane **123** was straightforward by treatment with thiophosgene to afford straw yellow crystals (Scheme 32).



Scheme 32

122 123

The structure was confirmed by obtaining the X-ray crystallographic data[182] of **123** which shows some interesting features (Figure 20). As with compound **110**, the thiirane ring is slightly unsymmetrical and the C(1)-C(2) bond length of 1.507(8)Å is in agreement with other thiirane ring systems. The dihedral angle between the planes of both aryl groups was determined to be 60.1(3)^{o} indicating the non planarity of the rings. Table 19 shows the selected bond lengths and bond angles for **123**.

Figure 20. ORTEP representation of 2,2-dichloro-3-dibenzosuberonyl episulfide (**123**).

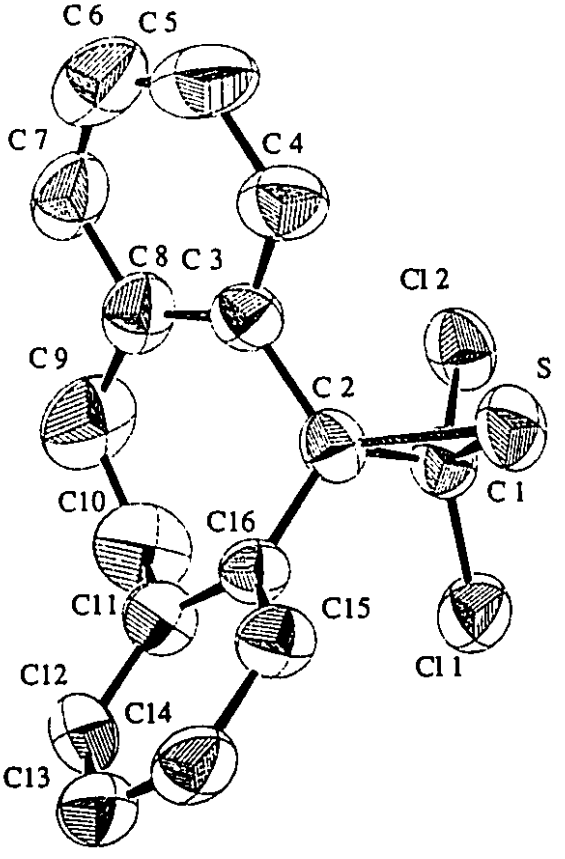
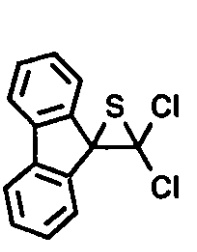


Table 19. Selected bond lengths and bond angles for 2,2-dichloro-3-dibenzosuberonyl episulfide (**123**). Estimated σs refer to the last digit.

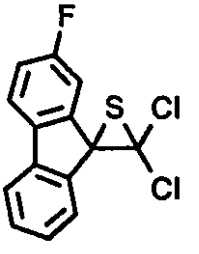
Bond lengths (Å)	
Cl (1) - C(1)	1.763(6)
Cl (2) - C(1)	1.761(6)
S -C (1)	1.769(6)
S - C (2)	1.844(6)
C (1) - C (2)	1.507(8)
Bond Angles ( )	
C (1) - S - C (2)	49.2(3)
Cl (1) - C (1) - Cl (2)	109.5(3)
Cl (1) - C (1) - S	117.3(3)
Cl (1) - C (1) - C (2)	119.6(4)
Cl (2) - C (1) - S	118.2(3)
Cl (2) - C (1) - C (2)	119.1(4)
S - C (1) - C (2)	68.0(3)
S - C (2) - C (1)	62.8(3)

3.7 Reactivity of Fluorenyl Substituted Episulfides

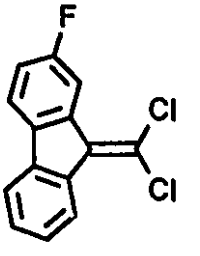
The study of the reactivity of substituted derivatives of **28** entailed measuring the possible loss of sulfur when heated in toluene at 80°C for 45 min. The unsubstituted thiirane **28**, as expected, converted entirely to its corresponding olefin. If our proposed mechanism has as the slow step (unimolecular path) the ionization of the C-S bond (Scheme 14), the reaction would be predicted to lose sulfur much faster in the presence of activating groups on the fluorenyl ring system since these substituents would stabilize the developing cation. In the presence of deactivating groups, the dipolar intermediate would be unfavourable and we would not expect the compound to lose sulfur as easily.



28



49



50

The inability to cleanly isolate the fluoro substituted derivative **49** is consistent with our argument. The fluorine atom could stabilize the dipolar intermediate *via* resonance[185] and therefore, it could facilitate desulfurization. On the other hand, its deactivating properties or its inductive effect should destabilize the intermediate and thus **49** should not desulfurize. Our experiments show that a mixture of **49** and **50** was obtained which is in agreement with our qualitative argument. The appearance of both **49** and olefin **50** dictates that the inductive effects of fluorine and the resonance contributing factors of fluorine plus the resonance effects of the fluorenyl ring system are equally capable of governing the stability of **49**.

A similar explanation can be envisioned for the failure to synthesize thiiranes **59**, **80**, **81**, and **82**. The presence of methoxy activating substituents would stablize the proposed cationic intermediate and enhance its decomposition. The presence of additional activating methyl groups in **80** and **81** further increases desulfurization. The synthesis of 2,5 dimethoxy substituted fluorenyl thiirane **98** was successful, although in very poor yield. Initial studies show that when **98** was heated at 80°C for 2 hr, no desulfurization occurred. Although the two methoxy substituents present in **98** would enhance desulfurization by its resonance effect, a closer examination of the resonance

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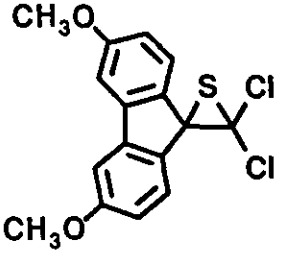
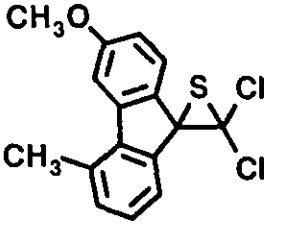
185 R. G. Pews, *J. Am. Chem. Soc.*, 89, 5605 (1967).

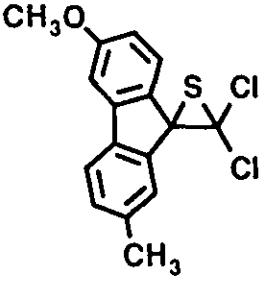
contributors could explain why we do not observe any desulfurization (Figure 21). In order for **98** to desulfurize, resonance structures I or II should be fairly stable. However, these resonance structures destroy the overall aromaticity of the ring system and therefore, both I and II should make relatively unimportant contributions to the resonance description of the cation. Conversely, resonance contributor III (Figure 21) in compounds **59**, **80**, **81** or **82** does not disrupt the aromaticity of the entire ring system and hence, should be a major resonance contributor. Desulfurization should, therefore, occur. Furthermore, it was discovered that introduction of only a methyl substituent at the 3-position of the fluorenyl group in **28** (compound **102**) causes desulfurization as expected. The methyl activating group would stabilize the carbonium ion in the fluorenyl ring skeleton thereby increasing the rate of desulfurization.



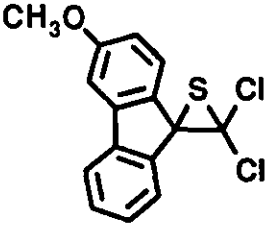
59



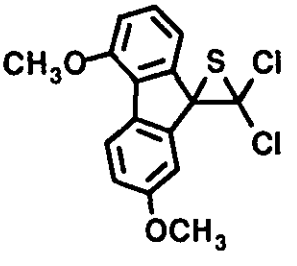
80



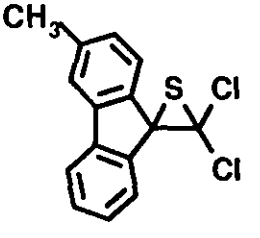
81



82

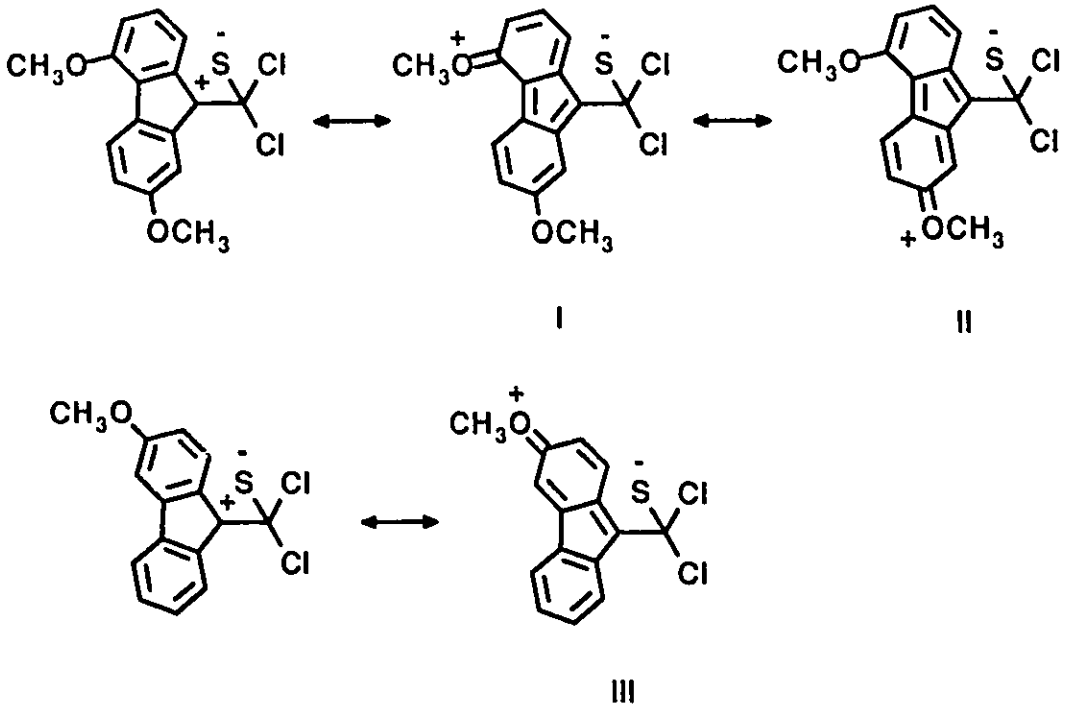


98



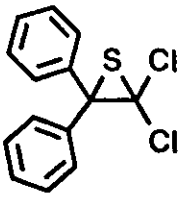
102

Figure 21. Resonance structures for compounds 98 and 82 in a unimolecular desulfurization pathway.

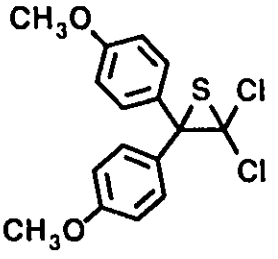


A very interesting characteristic was observed when we studied the reactivity of the diphenyl substituted thiiranes **110** and **111**. The advantages of having thiirane **110** or **111** is that synthesis consists of three relatively easy steps in which the thiirane can be obtained pure and in high yield and the precursors as well as the thiirane are stable for months in the refrigerator without noticeable decomposition. We can predict the relative stability of **110** and **111** *vs.* **28** on the basis of their structures. We find that, unlike **28**, **110** does not desulfurize when heated at 80°C for 45 min. This observation can be explained by the differences in the aromatic systems which influence their ability to promote the cation generated in the unimolecular rate determining step. The planar fluorenyl group in **28** can delocalize the cation more efficiently than the non-coplanar phenyl groups of **110** (Figure 19). It is known from solvolysis reactions of alkyl chlorides containing either the fluorenyl or biphenyl aromatic systems that the fluorenyl substituent is a better transmitter of π electrons in stabilizing carbonium ions. The phenyl groups, meanwhile, are less effective in stabilizing the incipient carbonium ion

since the π system is twisted out of the plane.[186] The phenyl groups in **111** are also non-coplanar which will inhibit their effectiveness at stabilzing the incipient carbocation. However, the 4,4'-dimethoxyphenyl-substituted derivative **111** was found to decompose spontaneously in solution. The para activating methoxy groups would be more effective at stabilizing the carbonium ion and, therefore, facilitate desulfurization.

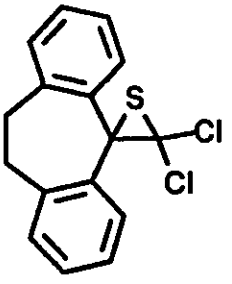


110



111

2,2-Dichloro-3-dibenzosuberonyl episulfide (**123**) did not desulfurize under the reaction conditions (2 hr, 80°C) but was found to desulfurize, although to a 50% extent, when heated at 100°C for eight days. After seventeen days, approximately 75% had decomposed. This is not surprising as we would predict from the structure (Figure 20) that with two methylene groups bridging the phenyl groups, the π system becomes more planar than the diphenyl or the dimethoxydiphenyl systems but less than that of the fluorenyl system. The aryl groups in **123** are ~60° out of the plane and the phenyl groups in **110** are > 60° out of the plane whereas the fluorenyl group in **28** is planar. Since the fluorenyl system decomposes readily while the diphenyl system does not desulfurize, we would expect some decomposition to occur with **123** but at a very slow rate.



123

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186 a) R. Bolton, M. E. Jones, and S. W. Tucker, *J. Chem. Soc.*, 1464 (1964); b) R. Bolton, *J. Chem. Soc.*, 1542 (1965); c) R. Bolton and R. E. M. Burley, *J. Chem. Soc., Perkin Trans. II*, 426 (1977); d) Y. Tsuno, Y. Tairaka, M. Sawada, and T. Fujii, *Bull. Chem. Soc. Jpn.*, **51**, 601 (1978).

Consequently, we can summarize the aromatic systems in increasing order of reactivity :

diphenyl < dibenzosuberonyl < fluorenyl

and

diphenyl << 4,4'-dimethoxydiphenyl.

4,4'-Dimethoxydiphenyl would be predicted to be more reactive than fluorenyl since the activating methoxy groups would override the resonance effect of the planar fluorenyl ring system.

Qualitatively, we can state that amongst the substituted fluorenyl derivatives the increasing order of reactivity would be as follows :

fluorenyl < 2,5-dimethoxyfluorenyl < 2-fluorofluorenyl < 3-methylfluorenyl < 3-methoxyfluorenyl < 3-methoxy-5-methyl-fluorenyl = 3-methoxy-7-methylfluorenyl < 3,6-dimethoxyfluorenyl.

CHAPTER 4

DIATOMIC SULFUR EXTRUSION

4.1 INTRODUCTION

It has been proposed that in some instances sulfur extrusion in organic reactions proceeds in a manner which involves a chelotropic loss of a sulfur atom.[187] Such a process, however, seems unfavorable due to the high energy of formation (66.3 kcal/mol) of a sulfur atom.[188] Sulfur extrusion must, therefore, proceed through other transient species of much lower energy. Such a species could be in the form of diatomic sulfur which would combine to form stable elemental sulfur.[189]

4.2 BRANCH-BONDED SULFUR ATOMS

One of the more attractive mechanisms in sulfur extrusion reactions was first conceived by Foss in 1950.[190] The initial step involves the combination of two sulfur species followed by a transfer of a sulfur atom forming a thiosulfoxide-type intermediate **124**. This intermediate could acquire more sulfur atoms, thereby lengthening the sulfur chain. At any intermediate step, the chain could cyclize to form stable species of sulfur. The thiosulfoxide moiety and the concatenation of sulfur atoms mechanism is well discussed in the literature.[98,187e,191]

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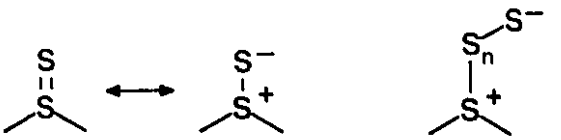
187 a) W. E. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **77**, 68 (1955); b) A. Padwa, D. Crumrine, and A. Shubber, *J. Am. Chem. Soc.*, **88**, 3064 (1966); c) R. Grigg, R. Hayes, and J. L. Jackson, *J. Chem. Soc.*, 1167 (1969); d) W. H. Mueller, *J. Org. Chem.*, **34**, 2955 (1969); e) K. J. Miller, K. F. Moschner, and K. T. Potts, *J. Am. Chem. Soc.*, **105**, 1705 (1983).

188 "JANAF Thermochemical tables," Dow Chemical Co., Midland, Mich., 1966, plus later supplements to 1976.

189 D. N. Harpp, *Perspectives in the Organic Chemistry of Sulfur*, B. Zwanenburg, A. J. H. Klunder, Eds., Elsevier: Amsterdam, 1987, pp 1-22.

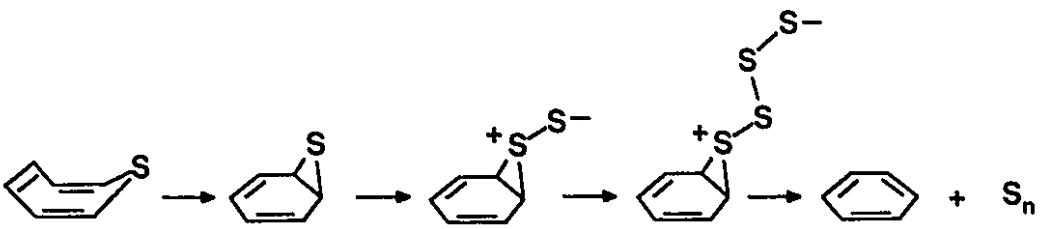
190 O. Foss, *Acta. Chem., Scan.*, 4, (1950).

191 a) F. Seel and D. Gölitz, *Z. Anorg. Chem.*, 32 (1964); b) G. Höfle and J. E. Baldwin, *J. Am. Chem. Soc.*, **93**, 6307 (1971); c) R. D. Baechler and S. K. Daley, *Tetrahedron Lett.*, 101 (1978); d) R. D. Baechler, S. K. Daley, B. Daly, and K. McGlynn, *Tetrahedron Lett.*, 105 (1978); e) D. N. Harpp, K. Steliou, and C. J. Cheer, *J. Chem. Soc., Chem. Comm.*, 825 (1980); f) G. W. Kutney and K. Turnbull, *Chem. Rev.*, **82**, 333 (1982); g) M. Green, E. M. Cown, and O. P. Strausz, *J. Am. Chem. Soc.*, **106**, 6938 (1984); h) W. Ando, H. Sonobe, and T. Akasaka, *Tetrahedron Lett.*, **31**, 5093 (1990).



124

Gleiter[192] studied the loss of sulfur from thiepins and concluded that the extrusion of sulfur proceeds *via* rearrangement to a thiirane intermediate **125** followed by the linking of sulfur atoms to give intermediate **126** which would eventually lose elemental sulfur. The extrusion of S_2 or S_8 would be an energetically more favorable pathway than explusion of other forms of sulfur.



125 126

In the addition adduct of dimethylthiophene and singlet oxygen **127**, Matturro[193] described that the decomposition of **127** involved the elimination of elemental sulfur by a concatenation of sulfur atoms. Similarly, Huisgen[194] suggested that in the thermal decomposition of trithiolane **128** a thiobenzophenone-*S*-sulfide (**129**) is formed which undergoes abstraction of sulfur atoms leading to the formation of S_8 and thiobenzophenone.

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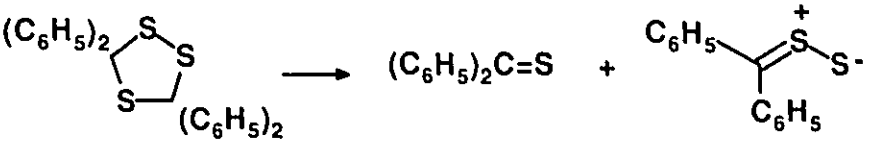
192 R. Gleiter, G. Krennrich, D. Cremer, K. Yamamoto, and I. Murata, *J. Am. Chem. Soc.*, **107**, 6874 (1985).

193 M. J. Matturro, R. P. Reynolds, R. V. Kastrup , and C. F. Pictroski, *J. Am. Chem. Soc.*, **108**, 2775 (1986).

194 R. Huisgen and J. Rapp, *J. Am. Chem. Soc.*, **109**, 902 (1987).

127



128 129

In a more recent article, Kamata and coworkers isolated a tetrathiane in the reaction of *cis*- or *trans*-2,3-diphenylthiirane with a catalytic amount of tris(p-bromophenyl)aminiumhexachloroantimonate in dichloromethane.[195] The proposed mechanism of formation involved a thiirane cation radical abstracting a sulfur atom from another thiirane cation radical resulting in a two sulfur species cation radical **130** with a concomitant release of stilbene. Further linkage of two more sulfur atoms gave intermediate **131** which cyclized affording the tetrathiane **132**.

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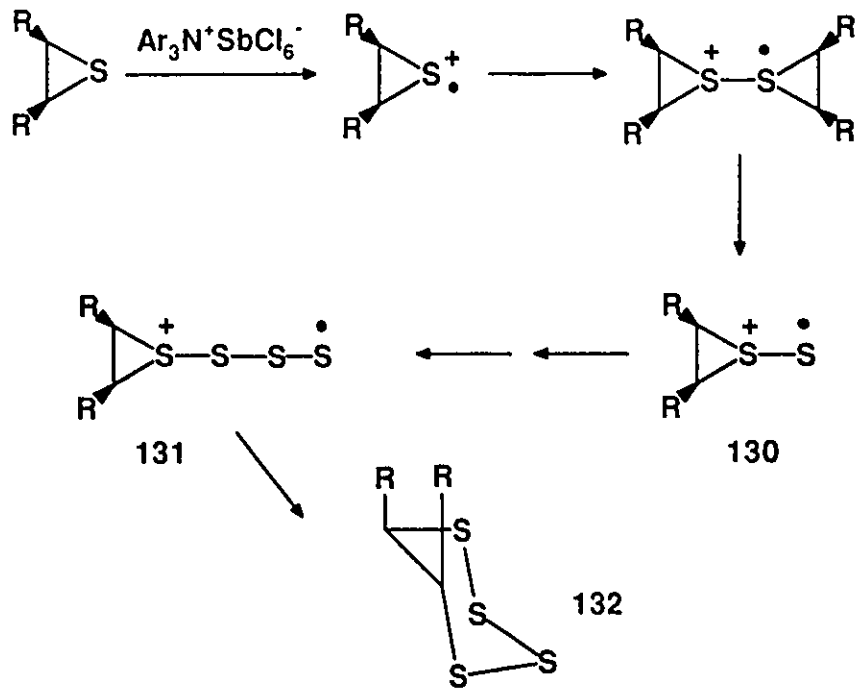
195 M. Kamata, K. Murayama, T. Suzuki and T. Miyashi, *J. Chem. Soc., Chem. Comm.*, 827 (1990). The tetrathiane was confirmed by X-ray crystallography.



4.3 Diatomic Sulfur Precursors

The rapid development in singlet oxygen chemistry has initiated considerable interest in its analogous sulfur species, $^1S_2$. Singlet oxygen is known to play an important role in many biological processes and the possibility of emulating singlet oxygen chemistry with singlet sulfur is being actively developed. Singlet diatomic sulfur, $^1S_2$, has so far been found to be a valuable synthetic tool for organic chemists. Its important in organic synthetic chemistry and drug synthesis has been reviewed by Steliou.[196]

A wide variety of methods for the generation of $^1S_2$ has been employed in recent years and is discussed in a recent account.[197] Several unsuccessful approaches have been tried where $^1S_2$ is implicated but in these cases, no trapped products were identified.[145b,198] A seemingly simply route to $^1S_2$ would be to imitate the phosphine

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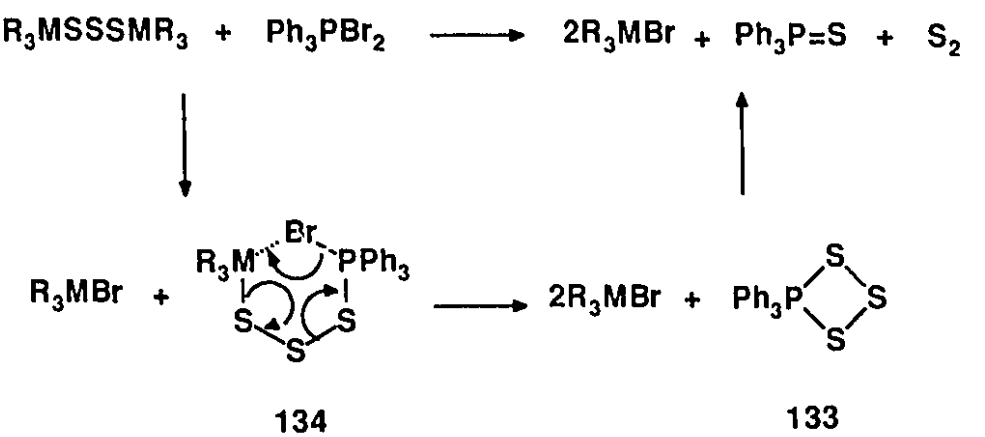
196 K. Steliou, Y. Gareau, G. Milot, and P. Salama, *Phosphorus, Sulfur, and Silicon*, C. T. Pedersen and J. Becher, Eds., Gordon and Breach, Science Publishers Inc.: England, 1989, pp 209-241.

197 K. Steliou, *Acc. Chem. Res.*, 341 (1991).

198 a) D. L. Smith, University Microfilms, Ann Arbor, Mich., 77-11451; b) A Orahovatz, M. J. Levinson, P. J. Carroll, M. V. Lakshmikanthan, and M. P. Cava, *J. Org. Chem.*, **50**, 1550 (1985); c) W. Ando, Y. Kumamoto, N. Tokitoh, *Tetrahedron Lett.*, **28**, 4833 (1987); d) J. E. Bishop, S. A. Dagam, and H. Rapoport, *J. Org. Chem.*, **54**, 1876 (1989).

ozonide method in the generation of $^1O_2$.[199] However, thiozone is not a readily accessible form of sulfur.[200]

The first synthetically useful $^1S_2$ precursor was reported by Steliou.[201] The reaction of an organometallic trisulfide with triphenylphosphine dibromide gave $^1S_2$ which was captured as a Diels-Alder adduct (Scheme 34). Two intermediates were postulated in the reaction. A thiozone intermediate **133** analogous to a thiozonide[202] as well as the six-membered species depicted in **134**. Later, the same authors discovered another precursor to $^1S_2$. This method was based on a novel head-to-head dimerization of 2,2'-bis(thiobenzoyl)biphenyl (**135**) generated from 2,2'-bis(benzoyl)biphenyl in the presence of generated B_2S_3. A dithietane intermediate which has been postulated could spontaneously release $^1S_2$ and 9,10-diphenylphenanthrene (Scheme 35).[203] To date, this route remains the most efficient means for generating diatomic sulfur.



134 **133**

Scheme 34

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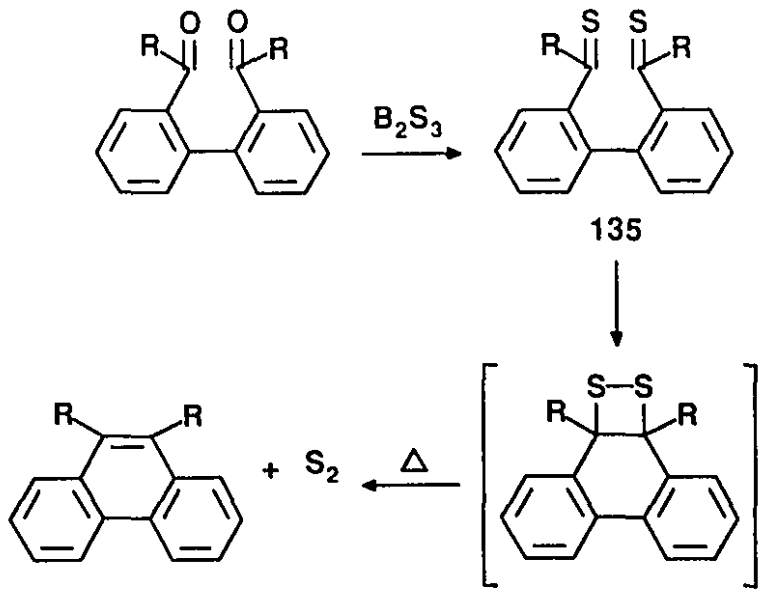
199 a) *"Singlet Oxygen"*, H. H. Wasserman and R. W. Murray, Eds., Academic Press: New York, 1979; b) W. Herz and R.-R. Juo, *J. Org. Chem.*, **50**, 618 (1985).

200 a) T. Ghosh and P. D. Bartlett, *J. Am. Chem. Soc.*, **110**, 7499 (1988); b) R. Sato, S. Satoh, and M. Saito, *Chem. Lett.*, 139 (1990).

201 K. Steliou, Y. Gareau, and D. N. Harpp, *J. Am. Chem. Soc.*, **106**, 799 (1984).

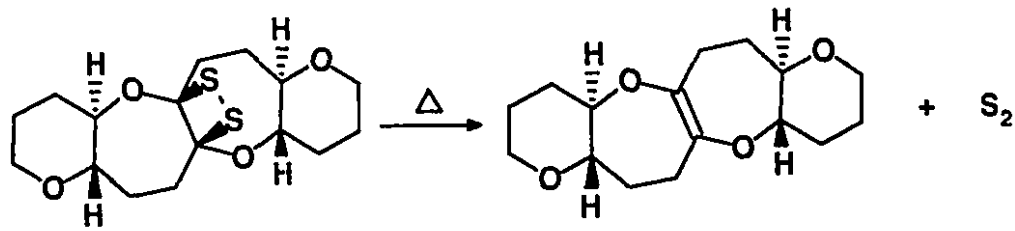
202 P. D. Bartlett and C. M. Lonzetta, *J. Am. Chem. Soc.*, **105**, 1984 (1983).

203 K. Steliou, P. Salama, D. Brodeur, and Y. Gareau, *J. Am. Chem. Soc.*, **109**, 926 (1987).



Scheme 35

Although the 1,2-dithietane was inferred as an intermediate, no stable isolated 1,2-dithietane was known until Nicolaou and coworkers synthesized and isolated dithiatopazine (**136**), the first example of a 1,2-dithietane.[60a] When **136** was heated to 100°C, it smoothly delivered diatomic sulfur which was trapped with 2,3-diphenyl-1,3-butadiene to give the cyclic disulfide and the corresponding olefin **137**.[204]



136 **137**

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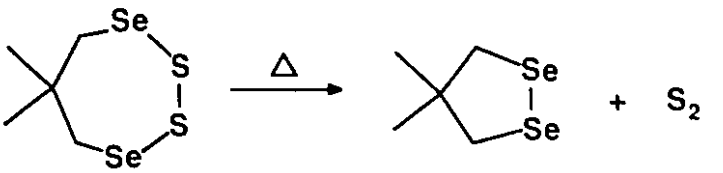
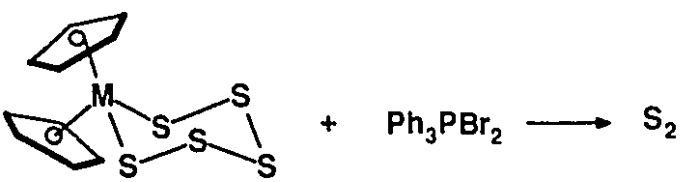
[204] K. C. Nicolaou, C.-K. Hwang, S. DeFrees, and N. A. Stylianides, *J. Am. Chem. Soc.*, **110**, 4868 (1988).

Schmidt and Görl showed unequivocally that a tetrachalcogen **138** undergoes thermal decomposition with ring contraction to transfer S_2 which was trapped by 2,3-dimethyl-1,3-butadiene.[205]



138

The most recent generation of $^1S_2$ was reported by Harpp and MacDonald in which a variety of organometallic pentasulfides (Scheme 36) fragmented in the presence of triphenylphosphine dibromide. Ejected $^1S_2$ species were trapped by dienes to afford the cyclic disulfides.[206]



Scheme 36

Another pathway towards the production of $^1S_2$ has been reported involving an anthracene endodisulfide.[145c,191h] However, it is unclear whether the trapped products were actually isolated as the yields were based on the amount of recovered product.

4.4 Attempts Towards Trapping $^1S_2$ in 2,2-Dichloro-3-(9-fluorenyl) Episulfide (28)

As previously mentioned (*cf.* Chapter 1.8.2), thiiranes undergo sulfur extrusion under a variety of conditions to form elemental sulfur and their corresponding olefin. In conjunction with our studies on the mechanism of sulfur extrusion of thiiranes, we studied the possibility that diatomic sulfur could be lost in the thermal decomposition of

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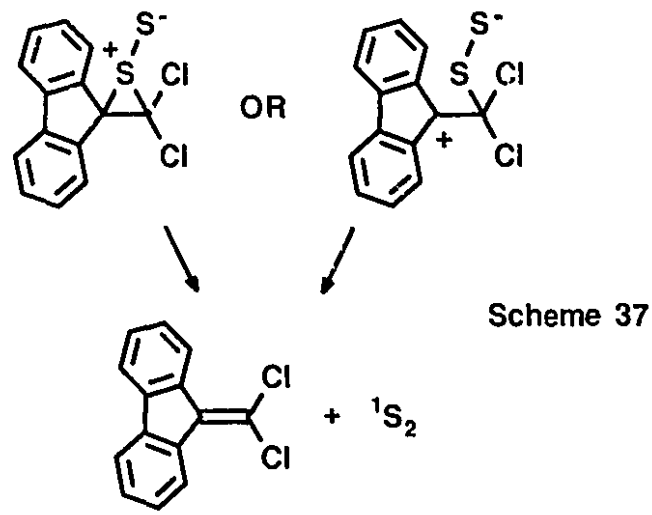
205 M. Schmidt and U. Görl, *Angew. Chem. Ind. Ed.*, 9, 887 (1987).

206 D. N. Harpp and J. G. MacDonald, *J. Org. Chem.*, 53, 3812 (1988).

thiirane **28**. We have proposed that the mechanism of sulfur extrusion in **28** and possibly in other thiiranes follows a pathway that involves branch-bonded sulfur atoms (Scheme 14). It is quite conceivable that during the thermal decomposition $^1S_2$ can be extruded as shown in Scheme 37.



Scheme 37

Rapid oligomerization of these transient species would form the more stable S_6 or S_8. Therefore, our attention focussed on heating a sample of thiirane **28** in the presence of a diene trap. A number of reactions were performed under a variety of conditions including solvent, temperature, time of reaction, and diene trap. Table 20 summarizes the different reaction conditions employed. In all cases, no trapped cyclic disulfide was isolated. Only elemental sulfur and the corresponding alkene **29** was isolated. The addition of *cis*-1,2-dichloroethylene (entry 11) also gave the alkene **29**, elemental sulfur and recovered trapping agent. The thermal decomposition of 2,2-dichloro-3,3-(4,4'-dimethoxydiphenyl) episulfide (**111**) in $CDCl_3$ in the presence of Danishefsky's diene[207,208] (1-methoxy-3-trimethylsilyloxy-1,3-butadiene) also gave elemental sulfur and its corresponding olefin with no indication of any trapped product. The unsuccessful trapping of a $^1S_2$ species suggests the more favorable pathway preferred is the continuous abstraction of sulfur atoms until a 6 or 8 sulfur atom chain is achieved which cyclizes to release S_6 or S_8 (Scheme 14). If $^1S_2$ is indeed released, then the failure to trap it can be

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207 S. Danishefsky and T. Kitahara, *J. Am. Chem. Soc.*, **96**, 7807 (1974).

208 S. Danishefsky, C.-F. Yan, R. K. Singh, R. B. Gammill, P. M. McCurry, Jr., N. Fritsch, and J. Clardy, *J. Am. Chem. Soc.*, **101**, 7001 (1979).

attributed to the fact that the combination of 3 $^1S_2$ species to form S_6 or 4 $^1S_2$ species to form S_8 is much faster than the Diels-Alder trapping.

Table 20. Reaction conditions in the thermal decomposition of **28**.

Entry	Solvent	Temperature (°C)	Time (hr)	Trapping Reagent
1	Decalin	100	2	2,3-diphenyl-1,3-butadiene
2	Decalin	60	3.5	2,3-dimethyl-1,3-butadiene
3	Decalin	190	3	2,3-diphenyl-1,3-butadiene
4	Benzene	80	2	2,3-diphenyl-1,3-butadiene
5	Benzene	80	2	Danishefsky's diene[a]
6	Toluene	111	6	2,3-diphenyl-1,3-butadiene
7	1,4 Dioxane	100	3	2,3-dimethyl-1,3-butadiene
8	DME	85	3	2,3-dimethyl-1,3-butadiene
9	DME	25	24	Danishefsky's diene
10	CH_2Cl_2	25	3	2,3-dimethyl-1,3-butadiene
11	CH_2Cl_2	25	24	*cis*-1,2-dichloroethylene
12	THF	67	2	Danishefsky's diene
13	THF	25	2	b

[a] 1-methoxy-3-trimethylsilyloxy-1,3-butadiene

[b] 1-methoxy-2,4-dimethyl-3-trimethylsilyloxy-1,3-butadiene

HPLC analysis[209] of a sample of thiirane **28** heated in refluxing toluene for 2.5 hr showed that S_6 and S_8 were, in fact, produced. The retention times indicate that the S_6 peak is not due to residual amounts of undecomposed **28**. Peak areas do not represent relative concentrations of the various products but also on the extinction coefficients at 254 nm. Figure 22a is chromatogram of thiirane **28** in chloroform solution and Figure 22b is a

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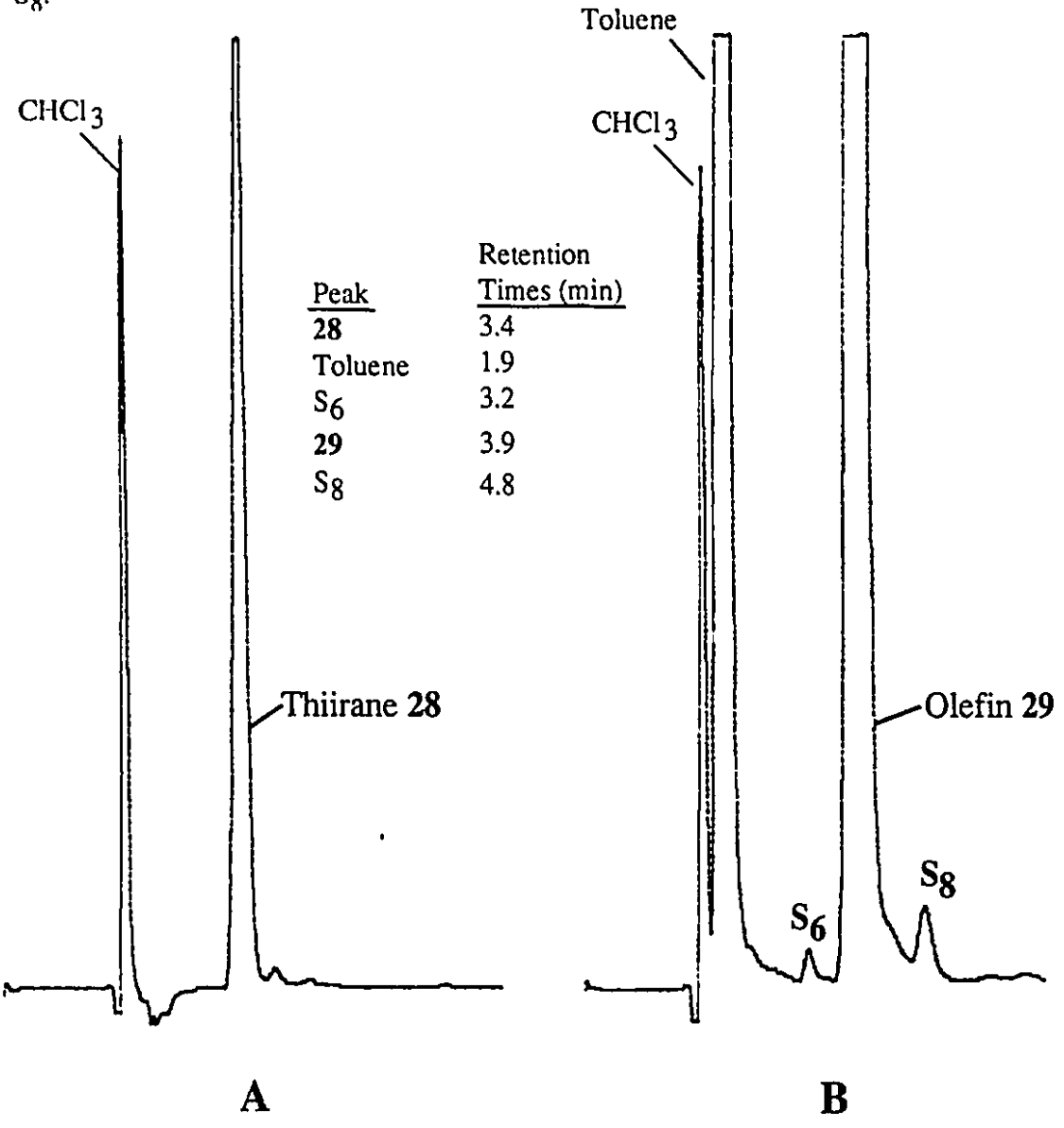
209 We gratefully acknowledge Prof. Ralf Steudel and Stefan Förster, Technische Universität Berlin, Institut für Anorganische und Analytische Chemie, Sekr. C2, D-1000 Berlin 12 for performing the analysis. A UV absorbance detector at $\lambda = 254$ nm was used.

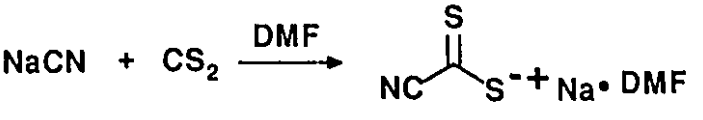
chromatogram after the reaction. The thiirane is totally converted to its corresponding olefin and the presence of S_6 and S_8 in the reaction mixture is clearly seen. Any S_7 produced would be hidden under the olefin peaks. The sulfur rings suggest they originated from chain-like polysulfanes and for energetic reasons, seem not to be derived from S_2 species.

Figure 22. a) HPLC chromatogram showing pure thiirane **28**; b) HPLC chromatogram after 2.5 hr in refluxing toluene showing olefin **29** and peaks due to presence of S_6 and S_8.



4.5 Dimerization of Sodium Cyanodithioformate

In 1955, Bähr and Schleitzer reported the synthesis of sodium cyanodithioformate salts (**139**) by reaction of sodium cyanide with carbon disulfide in dimethylformamide solution (Scheme 38).[210] These sodium salts were found to spontaneously dimerize to give disodium dimercaptomaleonitrile (**140**) and elemental sulfur.[211] A likely mechanism for this unique reaction is the head-to-head dimerization of the thiocarbonyl functionalites (Scheme 39) resulting in a 1,2 dithietane intermediate which would eliminate $^1S_2$. Thiocarbonyls usually undergo dimerizations or trimerizations in a head-to-tail manner.[212] It was demonstrated by Steliou[156] that a head-to-head dimerization of two thiones can be effected which eliminates $^1S_2$. However, careful attempts to trap $^1S_2$ with dienes failed and only elemental sulfur was obtained in 49% yield.



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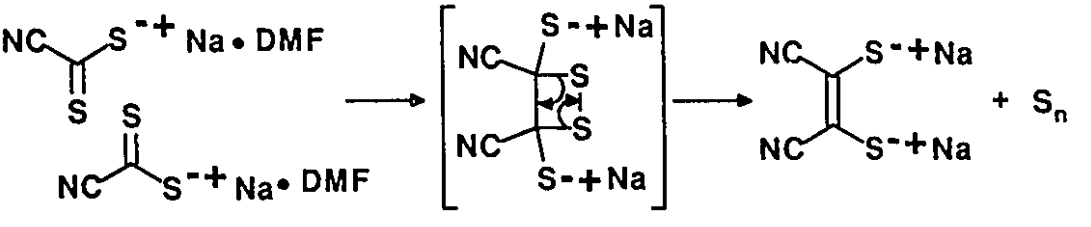
Scheme 38



140

Scheme 39

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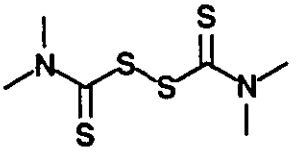
210 G. Bähr and G. Schleitzer, *Chem. Ber.*, 88, 1771 (1955).

211 a) G. Bähr, *Angew. Chem.*, 68, 525 (1956); b) G. Bähr and G. Schleitzer, *Chem. Ber.*, 90, 438 (1957).

212 a) P. S. Fraser, L. V. Robbins, and W. S. Chilton, J. Org. Chem., 39, 2509 (1974); b) L. Field, *Synthesis*, 713 (1978); c) K. Oka, A. Dobashi, and S. Hara, *Tetrahedron Lett.*, 21, 3579 (1980).

4.6 Chlorination of Tetramethyl Thiuram Disulfide

The chlorination of tetramethylthiuram disulfide (**141**) gives *N,N*-dimethyl thiocarbamyl chloride with concomitant extrusion of two sulfur atoms. This reaction was observed by Cava in 1983.[213] A conceivable mechanism for this reaction is depicted in Scheme 40. The initial step would be electrophilic attack of sulfuryl chloride giving 1 mole of thiocarbamyl chloride. Rearrangement of electrons would then give the second mole of thiocarbamyl chloride with evolution of sulfur dioxide and extrusion of $^1S_2$. If sulfur is released as $^1S_2$ then in the presence of diene, this species could be trapped. Table 21 summarizes the various reaction conditions that were attempted to see if $^1S_2$ could be obtained from **141**. It was found that in the ^1H NMR spectrum of the reaction carried out at room temperature using SO_2Cl_2 or Cl_2 (entries 3, 4, 5, 8) showed minor peaks that is consistent with those of the cyclic disulfide adducts as well as the tetrasulfide products.[172,214] However, careful chromatographic procedures gave only the tetrasulfide product in low yield. The main problem encountered in reactions using chlorine gas as the chlorinating reagent is the direct chlorination of the diene which may inhibit possible $^1S_2$ addition. Chlorine gas is known to react with 1,3-dienes.[215] In cases with SO_2Cl_2, SO_2 may also be trapped to give 3,4 dimethyl sulfolene. This would also hinder any formation of Diels-Alder adducts. The possibility that SO_2 or Cl_2 can react with $^1S_2$ is also likely although this reaction is not precedented in the literature. No reaction took place when only diene was added to the thiuram disulfide.

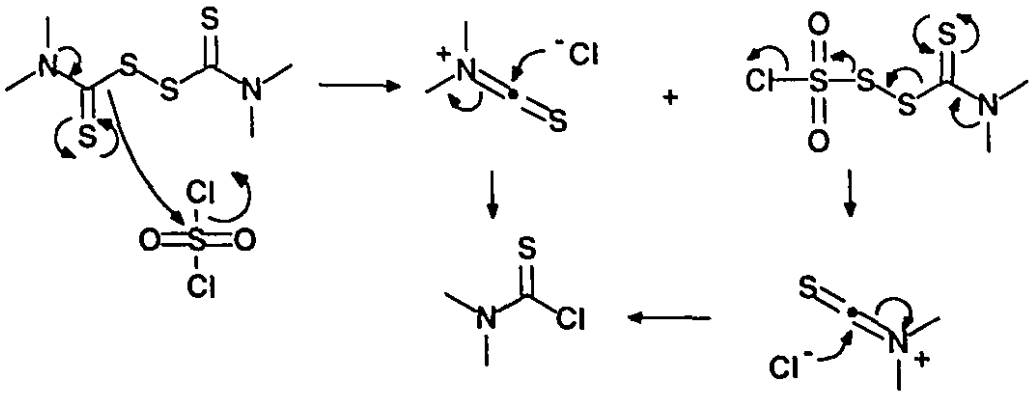


141

213 K.-Y. Jen and M. P. Cava, *J. Org. Chem.*, **48**, 1449 (1983).

214 C. R. Williams, Ph.D. thesis, McGill University, June 1991.

215 a) M. L. Poutsma, *J. Org. Chem.*, **88**, 4167 (1966); b) E. Z. Said and A. E. Tipping, *J. Chem. Soc., Perkin Trans. I*, 1986 (1972); c) M.-C. Lasne and A. Thuillier, *Bull. Chem. Soc. Fr.*, 1142 (1974).



Scheme 40

Table 21. Reaction conditions for the chlorination of tetramethylthiuram disulfide.

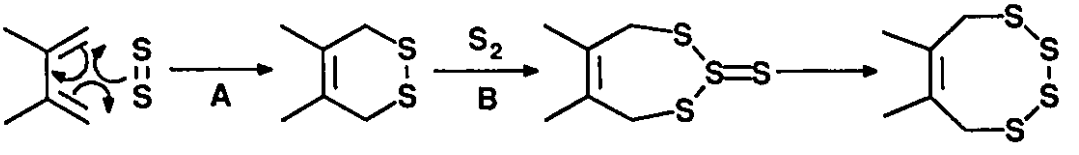
Entry	Solvent	Temp. (°C)	Reaction Time (hr)	Chlorinating Reagent	Trapping Reagent
1	Toluene	111	24	SO_2Cl_2	a
2	$CDCl_3$	61	24	SO_2Cl_2	b
3	CCl_4	25	24	SO_2Cl_2	a
4	CCl_4	25	24	Cl_2	a
5	CCl_4	25	2.5	SO_2Cl_2	a
6	CCl_4	-20	2	Cl_2	a
7	CCl_4	60	24	none	a
8	CCl_4	60	24	Cl_2	a
9	CCl_4	77	15.5	SO_2Cl_2	a
10	CCl_4	77	2.5	SO_2Cl_2	none

[a] 2,3-dimethyl-1,3-butadiene; [b] 1,4-dichloro-1,3-butadiene

It is also possible that the observation of disulfide and tetrasulfide adducts could arise from sulfuration of the diene. Sulfur is known to react with alkenes to afford

products containing cyclic thianes.[145,200b] We discount this pathway because in a separate reaction of *N,N*-dimethylthiocarbamyl chloride in the presence of diene and elemental sulfur, no reaction occurred after 3 days. Hence, we feel that the presence of cyclic disulfide and tetrasulfide products in our reaction mixtures came from Diels-Alder trapping of diatomic sulfur.

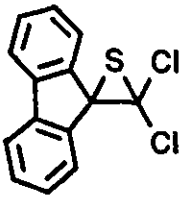
A proposed mechanism of formation of the di- and tetrasulfide adducts would be as follows (Scheme 41). The S_2 species that is generated (Scheme 40) is trapped in a Diels-Alder type reaction (path A) or a combination of two S_2 species would form the cyclic tetrasulfide adduct (path B).



Scheme 41

CONCLUSIONS AND CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

A detailed kinetic study on the thermal decomposition of 2,2-dichloro-3-[9-fluorenyl] episulfide (**28**) was undertaken. Strong evidence towards the nature of the desulfurization process is given which could pertain to the overall desulfurization mode of thiiranes in general. The kinetic analysis enables us to derive a two-term rate equation consisting of a first and second order term with respect to concentration that governs the decomposition reaction. A plausible mechanism is proposed to account for the observed rate behaviour. At low concentrations, the dominant pathway is unimolecular involving C-S bond fission in the rate determining step. At high concentrations, the bimolecular portion of the rate equation becomes more important and it is this pathway that becomes the rate determining step.



28

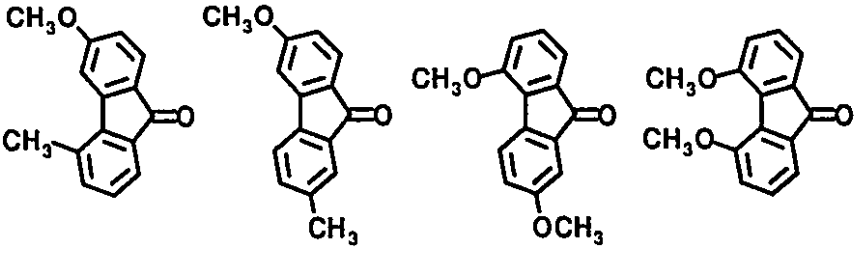
An extended solvent study in 15 different media at different temperatures supports our proposed ionic mechanism. Activation energies, enthalpies, entropies, and free energies were determined and evaluated with respect to differences in solvation of the ground and transition states. The integrity of calculated rate constants and Arrhenius parameters were also assessed. A true isokinetic relationship which showed good linearity was found. This observation allows us to deduce that the desulfurization of thiiranes proceeds by the same mechanism in all solvents. Stereochemical aspects were also addressed to an extent where we can possibly predict the stereochemical outcome of thiirane decomposition reactions. Rates of reaction were found to be directly proportional to the dielectric constant of the bulk solvent as well as the π^* scale of Kamlet and Taft. While clean linearity was not observed, the plot as a function of dielectric constant was comparable with similar published work.

A solvent isotope effect showed a decrease in the overall rate when deuterium is substituted for hydrogen in ethanol. The rate of desulfurization is also observed to decrease in the presence of acetic acid. Both studies are consistent with a dipolar ionic mechanism. A radical mechanism is ruled out from a rate study in the presence of radical inhibitors.

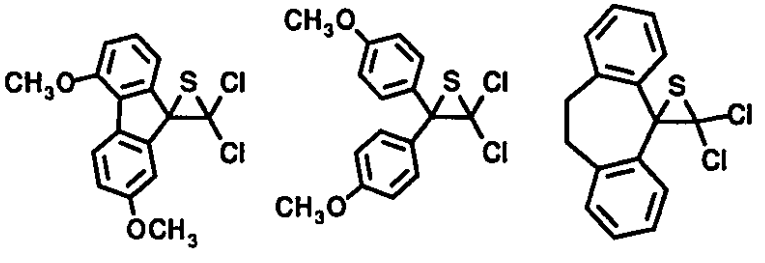
Several novel 9-fluorenones were synthesized including 3-methoxy-5-methyl-9-fluorenone (**71**), 3-methoxy-7-methyl-9-fluorenone (**72**), 2,5-dimethoxy-9-fluorenone (**94**), and 4,5-dimethoxy-9-fluorenone (**95**). These fluorenones and other mono and disubstituted fluorenones were used in an attempt to prepare unique 2,2-dichloro-3-[substituted fluorenyl] thiiranes. Only 2,2-dichloro-3-(2,5-dimethoxy-9-fluorenyl) thiirane (**98**) was synthesized in ten steps. Syntheses of 2,2-dichloro-3,3-(4,4'-dimethoxy)diphenyl episulfide (**111**) and 2,2-dichloro-3-dibenzosuberonyl episulfide (**123**) were achieved for the first time.

The X-ray crystal structures of 2,2-dichloro-3,3-diphenyl episulfide (**110**) and 2,2-dichloro-3-dibenzosuberonyl episulfide (**123**) were also obtained for the first time.

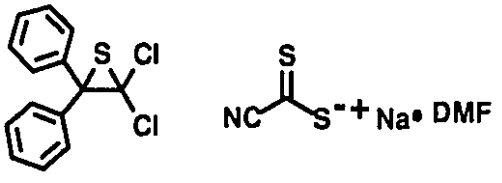
The thermally induced reactions of thiirane **28** and sodium cyanodithioformate (**139**) were also investigated as possible precursors to diatomic sulfur. In either case, no indication of diatomic sulfur was found under various conditions. When tetramethylthiuram disulfide, in the presence of 1,3-dienes, was treated with SO_2Cl_2 or Cl_2, it afforded products that were consistent with the trapping of diatomic sulfur, albeit in low yield.



71 **72** **94** **95**



98 **111** **123**



110 **139**

CHAPTER 5

EXPERIMENTAL

5.1 GENERAL METHODS

Melting points (Mp.) were determined using a Gallenkamp melting point apparatus using open end capillaries and are uncorrected. UV spectra were recorded on a Phillips Pye Unicam PU8800 UV-Vis spectrophotometer equipped with an Accuron PSX 876 Series 2 temperature programme controller. Low resolution electron impact (EI) mass spectra were obtained on a Dupont Instruments 21-492B or Kratos MS25RFA mass spectrometer equipped with a 70eV ionizing energy source and used in direct-inlet mode. Elemental analyses were performed by Guelph Chemical Laboratories Ltd. (Guelph, Ontario).

^{1}H NMR spectra were recorded on either the Varian XL200 or XL300 spectrometers using deuteriochloroform as the reference solvent unless otherwise indicated. The assignments were compared with literature values or based on homonuclear decoupling experiments. Multiplicity assignments are recorded using the following abbreviations : s, singlet; d, doublet; t, triplet, q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were obtained at 75.4 MHz using the Varian XL300, 67.9 MHz using the JEOL CPF-270, or at 50.3 MHz using the Varian Gemini-200 spectrometers. The $^{13}CDCl_3$ (δ 77.00), $^{13}C_6D_6CD_3$ (δ 20.4), $^{13}CD_3OD$ (δ 49.00), CD_3COCD_3 (δ 29.8) and $^{13}CD_2Cl_2$ (δ 53.80) signals were used as references in these solvents. In some cases, APT experiments were used to determine peak assignments. ^{19}F NMR spectra are reported relative to external dichlorodifluoromethane and were not proton decoupled.

Infrared spectra were recorded on an Analect Instruments ASQ-18 FTIR spectrometer equipped with an Analect Instruments MAP-67 Data System and displayed on a RAM-56 color monitor. Spectra are reported in wavenumbers (cm^{-1}). Raman spectra were recorded on a S. A. Ramonor spectrometer equipped with a U-1000 double monochromator and a Spectra-Physics Argon ion laser at 514.5 nm or a Bruker IFS-88 FT Raman spectrometer equipped with a ND:YAG laser operating at 300 mW with a 4 cm^{-1} resolution and are also reported in wavenumbers.

High performance liquid chromatography (HPLC) was performed courtesy of Prof. Ralf Steudel and Stefan Förster, Technische Universität Berlin, Institut für Anorganische und Analytische Chemie, Sekr. C2, D-1000 Berlin 12, Germany.

Hexanes was distilled over 7% by volume sulfuric acid and passed through an alumina column before use. Methylene chloride was distilled from P_2O_5. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Isobutanol, 2-chloroethanol, toluene, and *o*-dichlorobenzene were purified by distillation from calcium hydride and stored over 4Å molecular sieves prior to use. All other solvents were used as purchased from Aldrich Chemical Company without further treatment. DMSO was stored over 4Å molecular sieves. *o*-Xylene, *m*-xylene, and *p*-xylene were HPLC grade quality. Thin layer chromatography (tlc) was performed using Kieselgel 60 F_{254} plates with polyester backing and visualized by UV and/or dipping in a solution of ammonium molybdate (2.5 g) and ceric sulfate (1.0 g) in 10% v/v aqueous sulfuric acid (100 ml), followed by heating. Flash column chromatography was performed using Kieselgel 60 (Merck 70-230-mesh) silica gel. Chromatographic solvent mixtures are volume/volume percentages. Experiments requiring inert atmospheric conditions were done using pre-purified nitrogen.

5.2 UV Rate Measurements

The rates of decomposition were measured by following the increase in UV absorption of **29** on a Phillips Pye Unicam PU8800 UV/Vis spectrophotometer equipped with an Accuron PSX 876 Series 2 temperature programme controller. Quartz UV cells (Hellma Canada Ltd.) containing the solvent were allowed to equilibrate for 10-15 mins. at the desired temperatures prior to injection of the samples. The samples were injected *via* Hamilton syringes and the cells were capped, shaken and placed in the cell compartments. The absorbances were measured at various time intervals at λ = 325 nm and at a bandwidth of 2 nm. The method of initial rates was used in calculating observed rate constants.

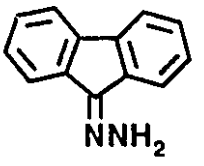
5.3 ^{1}H NMR Rate Measurements (Radical Inhibitor Study)

Rates were measured on a Varian XL300 spectrometer using toluene-d_8 as the reference solvent. A 5mm (diameter) NMR tube was containing the inhibitor dissolved in toluene-d_8 was allowed to equilibrate at 80°C for 5-10 mins. in the sample probe prior to adding the episulfide. The episulfide was injected and immediately placed in the sample probe. ^{1}H NMR spectra were acquired at various intervals over a period between 12 - 16 hr. All spectra were obtained by acquiring 64 transients. The rates were calculated first by calculating the ratio of the peak heights measured at 8.3 ppm (in cm) and the peak height of toluene. Assuming the episulfide was completely converted to the olefin, the ratio of peak heights of the final spectrum would equal the initial

concentration of episulfide. Thus, the concentration of olefin at any time was easily obtained. By plotting the concentration *vs.* time, the second order rate constant, k_2, can be calculated using the initial rate method. The first order rate constant was assumed to be negligible since the initial concentration of the episulfide ranged from *ca.* 6 - 16 mM.

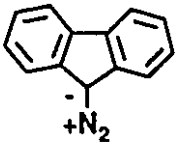
5.4 Preparation of 2,2-Dichloro-3-[9-fluorenyl] episulfide

9-Fluorenone hydrazone



To a solution of 7 g (39 mmol) of 9-fluorenone in 40 ml of *n*-butanol, 5 ml of 85% aqueous hydrazine monohydrate was added. After 4 hrs of reflux, the hot solution was poured into 100 ml of methanol. The resulting yellow mixture was allowed to cool yielding 7.2 g of hydrazone as yellow needles which was purified by recrystallization with methanol (95%). Mp. 152 - 155°C (lit.[170] Mp. 152°C). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 6.40 (s, 2H, NNH_2), 7.3 - 7.91 (m, 8H, aromatic). ^{13}C NMR (50.3 MHz, $CDCl_3$) : δ 119.6, 120.6, 120.8, 125.6, 127.8, 128.0, 128.6, 129.8, 130.3, 137.8, 138.7, 141.4, 145.7. MS m/z (rel. intensity) 194 ($M^{+\cdot}$, 100), 177 (11), 151 (12), 139 (9), 165 (85).

9-Diazofluorene (46)



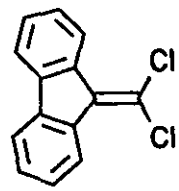
To 2.0 g (64 mmol) of **45** in 125 ml anhydrous ether, 0.5 g KOH was added and the mixture was stirred vigorously. Yellow mercuric oxide (18.4 g, 85 mmol) was added in 4 portions with each of the orange mixtures stirred until a brown sludge became visible. The solution was decanted after each addition. The clear purple solution was then dried over $MgSO_4$ and evaporated under reduced pressure furnishing deep orange crystals. After recrystallization with pentane, the yield of **46** was 1.42 g (71%). Mp. 94 - 96.5°C (lit.[170] Mp. 99°C). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 7.27 - 7.43 (m, 4H), 7.51 (d, 2H), 7.94 (d, 2H). ^{13}C NMR (50.3 MHz, $CDCl_3$) : δ 119.4, 121.1, 124.7, 126.5, 131.6, 133.1. The carbene carbon resonance could not be observed. MS m/z (rel. intensity) 192 ($M^{+\cdot}$, 30), 164 ($M^{+\cdot}$ - N_2, 100).

2,2 Dichloro-3-[9-fluorenyl] episulfide (28)

To 2.5 g (13 mmol) of **46** suspended in 50 ml petroleum ether, 1 ml (13 mmol) of thiophosgene in 5 ml petroleum ether was added dropwise with the reaction being kept at 0°C. The red suspension turned orange upon slow addition of the thiophosgene and the evolution of nitrogen was apparent. After a few minutes, straw yellow needles began to appear. After allowing the solution to warm to room temperature for 1 hr, the mixture was filtered off yielding 2.2 g (61%) of the episulfide. The ^{13}C NMR showed that **28** was pure and no minor peaks were

observed. Mp. 89 - 91°C (lit.[49] Mp. 97°C). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 7.29 (dt, 2H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.45 (dt, 2H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.54 (dd, 2H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.75 (dd, 2H, J_1 = 7.6 Hz, J_2 = 1.2 Hz). ^{13}C NMR (75.4 MHz, CD_2Cl_2) : δ 60.3, 77.3, 120.6, 126.6, 127.3, 130.2, 140.7, 142.3. MS m/z (rel. intensity) 278 ($M^{+\cdot}$, 2), 246 ($M^{+\cdot}$ - S, 100), 208 (95). Raman : 652 cm^{-1}.

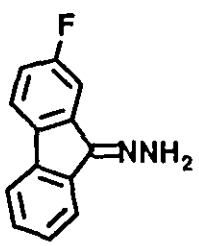
1,1 Dichloro-2-[9-fluorenyl] ethylene (29)



A solution of **28** (0.15 g, 0.53 mmol) in 8 ml toluene was heated at reflux for 2.5 hr. The reaction was monitored by analytical thin layer chromatographic plates measuring 6.5 cm x 2.0 cm (hexanes eluent) for the presence of sulfur (R_f = .58) and the corresponding olefin (R_f = .45). After evaporating the solvent, the sulfur and olefin are then isolated by silica gel chromatography (hexanes eluent). The first fraction was collected and identified to be sulfur. It was obtained after evaporating the hexanes under reduced pressure. Isolated yield of sulfur = 16.6 mg (97%). Mp. 111 - 111.5°C. The second fraction was identified to be **29**. Isolated yield of olefin **29** = 92.8 mg (70%). Mp. 128 - 130°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 7.31 (dt, 2H, J_1 = 7.5 Hz, J_2 = 1.4 Hz), 7.39 (dt, 2H, J_1 = 7.5 Hz, J_2 = 1.4 Hz), 7.70 (dd, 2H, J_1 = 7.5 Hz, J_2 = 1.4 Hz), 8.32 (dd, 2H, J_1 = 7.5 Hz, J_2 = 1.4 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 119.6, 122.3, 125.8, 127.5, 129.1, 134.2, 136.5, 140.2. MS m/z (rel. intensity) 250 (11), 248 (64), 246 ($M^{+\cdot}$, 100), 176 ($M^{+\cdot}$ - 2xCl, 70.9), 123 (16), 105 (15), 88 (33). UV : λ_{max} (decalin) 308, 320 (ε = 4918, 5450).

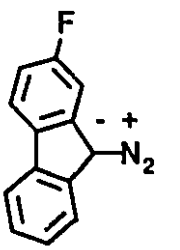
5.5 Attempted preparation of 2,2-Dichloro-3-[2-fluoro-9-fluorenyl] episulfide

2-Fluoro-9-fluorenone hydrazone (47)



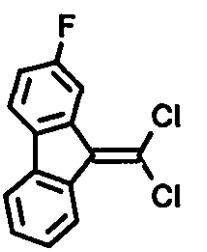
2-Fluoro-9-fluorenone (1.5 g, 7.5 mmol) was dissolved in 35 ml ethanol. Hydrazine monohydrate (1.33 g, 0.026 mol) was added and the yellow solution was heated at reflux for 24 hr. After allowing the mixture to cool, the hydrazone precipitated. Following filtration, hydrazone **47** was recrystallized with ethanol yielding 0.73 g of yellow needles (45%). Mp. 157 - 160°C (mixture of both isomers). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 6.48 (s, 2H, NNH_2), 6.96 - 7.91 (m, 7H, aromatic). ^{19}F NMR (282.2 MHz, $CDCl_3$) : δ 63.34, 63.58. MS m/z (rel. intensity) 212 ($M^{+\cdot}$, 100), 183 (87).

9-Diazo-(2-fluoro)-fluorenone (48)



2-Fluoro-9-fluorenyl hydrazone **47** (0.45 g, 2.1 mmol) was dissolved in 40 ml anhydrous THF. Sodium sulfate (0.75 g) was added followed by yellow mercuric oxide (1.27 g, 5.9 mmol) and 10 drops of ethanolic KOH. The mixture was stirred until a sludge appears which was then decanted and a fresh portion of HgO was added. The red solution was then filtered, the solvent evaporated under vacuo to afford 0.27 g (61%) of the diazo compound **48**. Mp. 83 - 84°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 7.06 - 8.14 (m, 7H, aromatic). ^{19}F NMR (282.2 MHz, $CDCl_3$) : δ 62.13. MS (FAB, glycerol) m/z (rel. intensity) 365 ((M$^{+\cdot}$ - $N_2)_2$ + H$^+$, 3), 183 (MH$^{+\cdot}$ - N_2, 100).

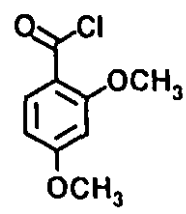
1,1-Dichloro-2-[2-fluoro-9-fluorenyl] ethylene (50)



Diazo compound **48** (0.27 g, 1.27 mmol) was suspended in 12 ml anhydrous THF. Thiophosgene (0.63 g, 5.5 mmol) in 2 ml anhydrous THF was added dropwise to the cooled (-15°C) suspension. The mixture was stirred for 20 mins and then allowed to warm to room temperature. The mixture was filtered and the filtrate concentrated, chromatographed (4:1 hexanes:CH_2Cl_2 eluent) to yield 0.27 g (71%) of a ~1:3 mixture of **49** and **50** as determined by ^{13}C NMR analysis. The mixture could not be separated as both compounds have identical R_f values. Mp. 114 - 120°C. ^{1}H NMR of **50** only (200 MHz, $CDCl_3$) : δ 7.06 - 7.68 (m, 5H, aromatic), 8.02 (dd, 1H, J_1 = 10.8 Hz, J_2 = 2.5 Hz), 8.30 (d, 1H, J = 7.9 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 113.4 (d, J = 26.3 Hz), 116 (d, J = 23.3 Hz), 119.4, 120.4 (d, J = 9.0 Hz), 123.6, 125.8, 127.2, 129.4, 133.6, (d, J = 2.8 Hz), 136.2, 136.5, 138.1 (d, J = 9.2 Hz), 139.4, 162.5 (d, J = 243.9). ^{19}F NMR (282.2 MHz, $CDCl_3$) : δ 63.68. MS m/z (rel. intensity) 268 (11), 266 (64), 264 (M$^{+\cdot}$, 100), 229 (M$^{+\cdot}$ - Cl, 7), 194 (M$^{+\cdot}$ - 2xCl, 53), 183 (11), 168 (6), 132 (10), 114 (8), 97 (21).

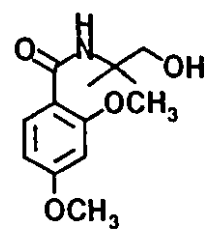
5.6 Attempted preparation of 2,2-Dichloro-3-[3,6-dimethoxy-9-fluorenyl] episulfide

2,4-Dimethoxybenzoyl chloride



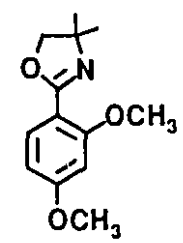
A solution of 2,4-dimethoxybenzoic acid (11.0 g, 60 mmol) in thionyl chloride (19.4 g, 163 mmol) was stirred at room temperature for 24 hr. After evaporating the excess $SOCl_2$, the white solid was treated a second time with $SOCl_2$ for 4 hr. Excess thionyl chloride was evaporated giving 11 g (91%) of the acid chloride as a white solid. Mp. 55 - 55.5°C. ^1H NMR (200 MHz, $CDCl_3$) : δ 3.89 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.45 (d, 1H, J = 2.3 Hz), 6.54 (dd, 1H, J_1 = 9.0 Hz, J_2 = 2.3 Hz), 8.15 (d, 1H, J = 9.0 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.7, 55.9, 98.2, 105.4, 113.8, 137.9, 162.0, 162.2, 166.5.

N-(Dimethyl-2-hydroxyethyl)-2,4-dimethoxy benzamide (51)



A solution of the acid chloride (11 g, 55 mmol) in 20 ml CH_2Cl_2 was added dropwise to a solution of 2-methyl-2-amino-1-propanol (11.7 g, 131 mmol) in 35 ml CH_2Cl_2 kept at 0°C. After stirring at room temperature for 2.5 hr, the mixture was filtered and the filtrate was concentrated under reduced pressure to yield 12.8 g (92%) of amide **51** as a viscous oil. ^1H NMR (200 MHz, $CDCl_3$) : δ 1.37 (s, 6H), 3.65 (s, 2H), 3.84 (s, 3H), 3.93 (s, 3H), 6.47 (s, 1H), 6.58 (d, 1H, J = 8.9 Hz), 8.12 (d, 1H, J = 8.7 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 25.0, 55.5, 55.9, 70.2, 71.3, 98.7, 105.3, 114.3, 133.8, 158.6, 163.5, 165.7.

2-(2,4-Dimethoxyphenyl)-4,4-dimethyl-2-oxazoline (52)



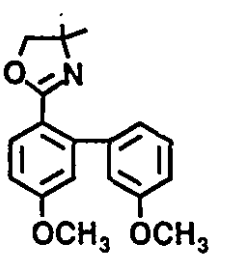
Thionyl chloride (18 g, 151 mmol) was added dropwise to **51** (12.8 g, 51 mmol) and the mixture magnetically stirred until no further gases have evolved. The solution was then transferred to 100 ml ether and allowed to stand until the oxazoline hydrochloride salt precipitated which was then filtered off. The salt was neutralized with 100 ml of 20% NaOH and the alkaline solution was extracted with ether. The combined ethereal extracts were dried with $MgSO_4$ and evaporated to give the crude oxazoline. After silica gel chromatography (EtOAc eluent), 3.63 g (31%) of pure oxazoline **52** was obtained as a yellow syrup. ^1H NMR (200 MHz, $CDCl_3$) : δ 1.36 (s, 6H, $C(CH_3)_2$), 3.81 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.03 (s, 2H,

CH_2), 6.45 - 6.48 (m, 2H), 7.72 (d, 1H, J = 9.0 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 28.4, 55.3, 56.1, 67.1, 78.6, 98.,9, 104.4, 110.4, 132.6, 159.7, 161.0, 162.9. MS m/z (rel. intensity) 235 ($M^{+\cdot}$, 82), 220 ($M^{+\cdot}$ - CH_3, 100), 206 (12), 192 (48), 163 (36), 149 (52), 135 (27), 121 (21).

3-Methoxyphenylmagnesium bromide

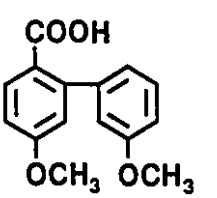
Magnesium (0.49 g, 20 mmol) was covered with 3 ml dry THF and the flask was flushed with nitrogen for 30 mins. A solution of 3-bromoanisole (3.74g, 20 mmol) in 11 ml dry THF was added dropwise under nitrogen to the magnesium. The resulting dark mixture was heated at reflux for 2 hr. The Grignard reagent was then used directly in the next step.

2-[2-(3-Methoxyphenyl)-2-(4-methoxyphenyl)]-4,4-dimethyl-2-oxazoline (53)



A solution of the oxazoline **52** (3.63 g, 15.4 mmol) in 15 ml dry THF was flushed with nitrogen for 0.5 hr. The Grignard reagent was transferred slowly under nitrogen and the mixture allowed to stir for 2-3 days. The reaction was then quenched with 30 ml saturated aqueous NH_4Cl. The organic layer was separated and the aqueous layer extracted 3 times with 40 ml portions of ether. The combined extracts were washed with 40 ml water, dried with $MgSO_4$, and evaporated under reduced pressure to obtain a dark yellow oil which was purified by silica gel chromatography (1:1 EtOAc : hexanes eluent) to give 2.43 g (51%) of **53** as a viscous oil. ^1H NMR (200 MHz, $CDCl_3$) : δ 1.27 (s, 6H, $C(CH_3)_2$), 3.77 (s, 2H, CH_2), 3.81 (s, 3H), 3.84 (s, 3H), 6.85 - 7.68 (m, 7H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 27.8, 55.1, 55.3, 67.1, 79.3, 112.6, 113.0, 113.8, 115.5, 120.4, 120.9, 129.0, 131.9, 142.8, 142.9, 159.5, 161.1, 163.8. MS m/z (rel. intensity) 311 ($M^{+\cdot}$, 30), 310 ($M^{+\cdot}$ - 1, 100) 296 ($M^{+\cdot}$ - CH_3, 9), 255 (10), 225 (16).

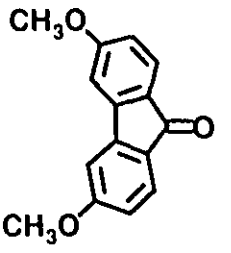
2-(3-Methoxyphenyl)-4-methoxybenzoic acid (55)



Methyl iodide (2.22 g, 15.6 mmol) was added to **53** (2.43 g, 7.81 mmol) and the mixture stirred for 3 hr. Excess methyl iodide was then evaporated under reduced pressure. The methiodide salt **54** was dissolved in 20 ml methanol and 20 ml of 20% aqueous NaOH was added. The mixture was allowed to stir at reflux for 24 hr. The cooled mixture was then acidified to pH = 2 at which point **55** began to precipitate. After filtration and recrystallization with ethanol the yield was

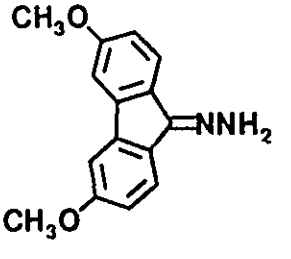
2.01 g (99%) of **55**. Mp. 128 - 129°C (lit.[171] Mp. 130 - 131°C). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.77 (s, 3H), 3.84 (s, 3H), 6.79 - 7.84 (m, 7H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.1, 55.4, 112.6, 112.8, 114.2, 116.4, 121.1, 123.2, 129.0, 132.9, 143.2, 145.3, 159.3, 162.0, 172.8. MS m/z (rel. intensity) 258 ($M^{+\cdot}$, 83), 241 ($M^{+\cdot}$ - OH, 42), 86 (34), 72 (100).

3,6-Dimethoxy-9-fluorenone (56)



Acid **55** (2.01 g, 7.78 mmol) was placed in a 250 ml flask equipped with a mechanical stirrer. Poly(phosphoric acid) (30 ml) was added and the mixture stirred for 3 hr at room temperature until a dark brown slurry was obtained. To the slurry was added 150 ml iced water and swirled until the brown slurry dissipates. The precipitate that formed was extracted 3 times with 80 ml portions of $CHCl_3$. The organic extracts were washed with 50 ml water and then twice with 50 ml aqueous NH_4Cl. After drying with $MgSO_4$, the solvent was evaporated to afford after recrystallizing with ethanol bright yellow needles of **56** : 243 mg (24 %). Mp. 141 - 143°C (lit.[171] Mp. 142 - 144°C). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.89 (s, 6H, OCH_3), 6.73 (dd, 2H, J_1 = 8.0 Hz, J_2 = 2.0 Hz), 6.98 (s, 2H), 7.57 (d, 2H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.7, 107.0, 112.9, 125.7, 128.3, 145.9, 164.9, 191.4. MS m/z (rel. intensity) 240 ($M^{+\cdot}$, 100), 211 (9), 197 (17), 169 (17), 126 (9). The mother liquor contained the **1,6-dimethoxy-9-fluorenone** isomer : 0.56 g (57%). Mp. 114-116°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.81 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.81 - 6.92 (m, 4H), 7.28 (t, 1H, J_1 = 8.5 Hz, J_2 = 6.7 Hz), 7.97 (d, 1H, J = 8.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.2, 55.5, 107.1, 112.7, 112.9, 114.1, 116.5, 120.9, 125.8, 128.9, 133.3, 142.7, 145.9, 159.0, 162.3. MS m/z (rel. intensity) 240 ($M^{+\cdot}$, 59), 129 (19). The sample was contaminated with the 3,6-dimethoxy isomer.

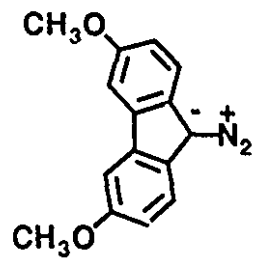
3,6-Dimethoxy-9-fluorenone hydrazone (57)



A solution of the fluorenone derivative **56** (243 mg, 1.01 mmol) in 8 ml ethanol was prepared to which hydrazine monohydrate (2.5 ml) was added and the mixture was heated at reflux for 24 hr during which a yellow precipitate formed. The precipitate was filtered to give 224 mg (92%) of pure hydrazone **57**. Mp. = 204 - 204.5°C (lit.[171] Mp. 202 - 203°C). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.89 (s, 3H, OCH_3), 3.93 (s,

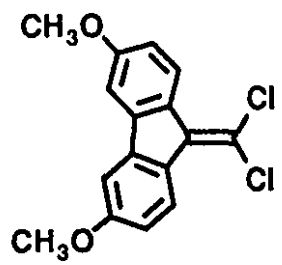
3H, OCH_3), 6.10 (s, 2H, NNH_2), 6.85 (dd, 2H, J_1 = 8.5 Hz, J_2 = 2.5 Hz), 7.13 (s, 1H), 7.23, (s, 1H), 7.62 (d, 1H, J = 8.4 Hz), 7.87 (d, 1H, J = 8.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.9 (2xCH_3), 106.5, 106.8, 113.9, 114.7, 124.0, 126.3, 131.3, 131.8, 143.4, 144.8, 154.7, 163.2, 163.3. MS m/z (rel. intensity) 254 ($M^{+\cdot}$, 100), 239 ($M^{+\cdot}$ - NH, 21), 225 (17), 210 (17), 139 (11), 129 (27.1), 112 (11).

3,6-Dimethoxy-9-diazofluorene (58)



Hydrazone **57** (224 mg, 0.88 mmol) was dissolved in 40 ml anhydrous THF. Pulverized yellow mercuric oxide (0.75 g, 3.46 mmol) was added followed by 0.35 g Na_2SO_4 and 10 drops of a solution of 10% KOH in ethanol. The mixture was stirred at room temperature for 24 hr. The mixture was filtered and the filtrate was evaporated under reduced pressure. The crude solid was dissolved in 150 ml ether, washed with 30 ml water, dried with $MgSO_4$ and concentrated to give 92.6 mg (42%) of diazo product **58**. Mp. 232°C (dec.) (lit.[171] Mp. 240°C (dec.)). ^1H NMR (200 MHz, $CDCl_3$) : δ 3.92 (s, 6H, OCH_3), 6.98 (dd, 2H, J_1 = 8.5 Hz, J_2 = 2.4 Hz), 7.35 (s, 1H), 7.40 (s, 1H), 7.43 (d, 2H, J = 2.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.6, 104.7, 113.0, 127.5, 132.3, 136.1, 142.2, 160.2. MS m/z (rel. intensity) 224 ($M^{+\cdot}$ - N_2, 99).

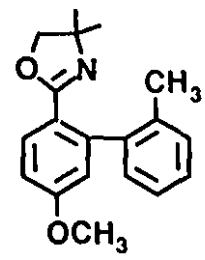
1,1-Dichloro-2-[3,6-dimethoxy-9-fluorenyl] ethylene (60)



Diazo compound **58** (92.6 mg, 0.36 mmol) was dissolved in 10 ml anhydrous ether. A solution of thiophosgene (0.30 g, 2.62 mmol) in 2 ml ether was added dropwise to the cooled (0°C) diazo solution. After the evolution of nitrogen has ceased the ethereal solution was cooled to -27°C and a precipitate was obtained after filtering and washing with cold ether which was determined to be **60**. Yield = 46.5 mg (37.3 %). Mp. 122 - 123°C. ^1H NMR (200 MHz, $CDCl_3$) : δ 3.90 (s, 6H, OCH_3), 6.84 (dd, 2H, J_1 = 8.5 Hz, J_2 = 2.5 Hz), 7.17 (d, 2H, J = 2.3 Hz), 8.20 (d, 2H, J = 8.9 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.5, 105.1, 113.1, 118.1, 126.8, 130.2, 133.2, 141.6, 160.6. MS m/z (rel. intensity) 310 (11), 308 (65), 306 ($M^{+\cdot}$, 100), 263 (29), 220 (11), 153 (15), 129 (27), 112 (10).

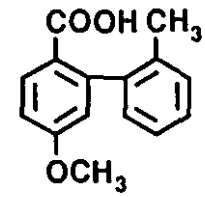
5.7 Attempted Preparation of 2,2-Dichloro-3-[5-methyl-9-fluorenyl] episulfide

2-[2-(2-Methylphenyl)-2-(4-methoxyphenyl)]-4,4-dimethyl-2-oxazoline (65)



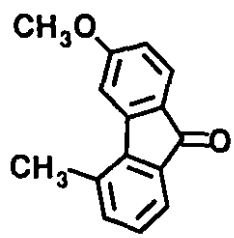
Following the general procedure in the preparation of compound **53**, the oxazoline **52** was treated with 2-methylphenylmagnesium bromide (**62**) yielding 57% of **65**. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 1.17, 1.19 (2xs, 6H, $C(CH_3)_2$), 2.11 (s, 3H, CH_3), 3.64 (s, 2H, CH_2), 3.82 (s, 3H, OCH_3), 6.73 (d, 1H, J = 2.5 Hz), 6.89 (dd, 1H, J_1 = 8.6 Hz, J_2 = 2.6 Hz), 7.14 - 7.20 (m, 4H), 7.77 (d, 1H, J = 8.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 20.0, 28.0, 55.3, 66.9, 79.2, 112.6, 115.5, 121.0, 125.0, 127.2, 128.8, 129.3, 131.3, 135.6, 141.2, 143.3, 160.8, 163.3. MS m/z (rel. intensity) 295 ($M^{+\cdot}$, 5), 280 ($M^{+\cdot}$ - CH_3, 100), 209 (9).

2-(2-Methylphenyl)-4-methoxybenzoic acid (68)



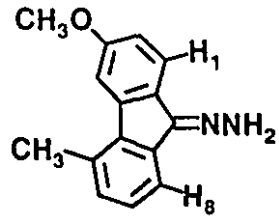
Following the general procedure in the preparation of compound **55**, oxazoline **65** gave acid **68** in 16% yield. Mp. 141 - 142°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 2.06 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 6.70 (d, 1H, J = 2.5 Hz), 6.92 (dd, 1H, J_1 = 8.5 Hz, J_2 = 2.5 Hz), 7.09 - 7.25 (m, 4H), 8.05 (d, 1H, J = 8.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 19.9, 55.5, 112.8, 116.3, 120.8, 125.3, 127.3, 128.2, 129.5, 133.4, 135.3, 141.4, 146.1, 162.6, 170.1. MS m/z (rel. intensity) 242 ($M^{+\cdot}$, 97), 227 ($M^{+\cdot}$ - CH_3, 51), 225 ($M^{+\cdot}$ - OH, 100), 197 (19), 181 (22), 165 (35), 152 (28), 120 (23).

3-Methoxy-5-methyl-9-fluorenone (71)



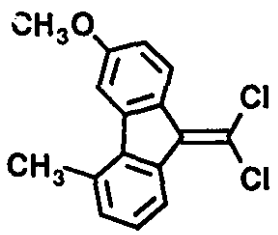
Following the general procedure in the preparation of compound **56**, acid **68** gave ketone **71** in 53% yield. Mp. 138 - 140°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 2.56 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 6.72 (dd, 1H, J_1 = 8.3 Hz, J_2 = 2.2 Hz), 7.14 - 7.22 (m, 3H), 7.50 (d, 1H, J = 8.0 Hz), 7.64 (d, 1H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 20.1, 55.7, 111.0, 111.4, 121.6, 126.2, 127.6, 128.9, 133.5, 135.7, 136.9, 140.9, 147.6, 165.1, 192.8. MS m/z (rel. intensity) 224 ($M^{+\cdot}$, 100), 181 (15), 170 (6), 165 (17), 152 (20).

3-Methoxy-5-methyl-9-fluorenone hydrazone (74)



Following the general procedure in the preparation of compound **57**, the yellow hydrazone **74** was obtained after evaporating the solvent. Ketone **71** gave hydrazone in 91% yield as a mixture of two isomers. In some cases, ketone **71** was contaminated by the Wolff-Kishner reduction product (3-methoxy-5-methyl fluorene) which was removed by column chromatography (1:1 CH_2Cl_2 : hexanes eluent). Mp. 128 - 134°C (mixture of both isomers). ^1H NMR (200 MHz, $CDCl_3$) : major isomer (NNH_2 syn to H_1) δ 2.65 (s, 3H, CH_3), 3.91 (s, 3H, OCH_3), 6.19 (s, 2H, NNH_2), 6.83 (m, 2H, both isomers), 7.12 - 7.23 (m, 4H, both isomers), 7.43, (d, 1H, J = 2.4 Hz), 7.60 (d, 1H, J = 7.8 Hz), 7.89 (d, 1H, J = 8.5 Hz). minor isomer (NNH_2 syn to H_8) δ 2.69 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 6.24 (s, 2H, NNH_2), 7.32, (d, 1H, J = 2.2 Hz), 7.68 (d, 1H, J = 7.8 Hz), 7.81 (d, 1H, J = 8.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : major isomer δ 20.8, 55.6, 110.6, 110.9, 118.3, 124.0, 126.5, 127.7, 131.3, 131.4, 132.8, 139.1, 140.9, 146.0, 160.4, minor isomer δ 21.2, 55.6, 109.7, 111.9, 121.4, 123.3, 127.6, 131.1, 132.4, 133.8, 136.2, 138.8, 144.5, 145.9, 160.8. MS m/z (rel. intensity) 238 ($M^{+\cdot}$, 100), 223 ($M^{+\cdot}$ - CH_3, 19), 209 (32), 195 (17), 165 (27), 152 (19).

1,1-Dichloro-2-[3-methoxy-5-methyl-9-fluorenyl] ethylene (83)

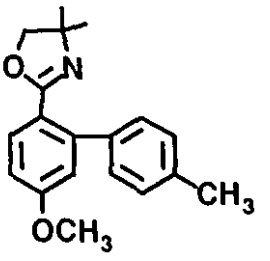


Hydrazone **74** (35.1 mg, 0.14 mmol) was dissolved in 10 ml anhydrous ether and 0.25 g sodium sulfate was added to the solution. Yellow mercuric oxide (100 mg, 0.46 mmol) was then added followed by 3 drops of ethanolic potassium hydroxide (1 g KOH in 10 ml ethanol). The mixture was stirred at room temperature for 45 mins, decanted from the sludge and cooled to 0°C. Thiophosgene (24 mg, .21 mmol) in 2 ml anhydrous ether was added dropwise to the red-orange diazotized solution. Evolution of nitrogen was apparent. The solution was then stirred for another 20 mins at 0°C and after allowing to warm to room temperature, the solution was filtered and flash chromatographed (3:2 hexanes : CH_2Cl_2 eluent) yielding 13.3 mg of corresponding olefin **83**. Mp. 96 - 96.5°C. R_f = 0.75. ^1H NMR (200 MHz, $CDCl_3$) : δ 2.43 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 6.79 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.6 Hz), 7.15 (d, 1H, J = 2.5 Hz), 7.19 (d, 1H, J = 7.8 Hz), 7.53 (d, 1H, J = 7.7 Hz), 8.10 (s, 1H), 8.18 (d, 1H, J = 8.8 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$) : δ 22.0, 55.5, 104.8, 112.4, 119.3, 119.7, 119.8,

126.5, 126.9, 129.4, 129.7, 133.8, 137.3, 137.6, 142.2, 160.7. MS m/z (rel. intensity) 294 (11), 292 (65), 290($M^{+\cdot}$, 100), 247 (44), 212 (21), 176 (36), 88 (17).

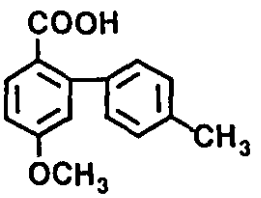
5.8 Attempted Preparation of 2,2-Dichloro-3-[7-methyl-9-fluorenyl] episulfide

2-[2-(4-Methylphenyl)-2-(4-methoxyphenyl)]-4,4-dimethyl-2-oxazoline (66)



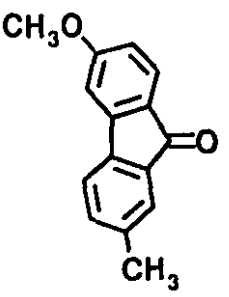
Following the general procedure in the preparation of compound **53**, the oxazoline **52** was treated with 4-methylphenylmagnesium bromide (**63**) yielding 27.5% of **66**. ^1H NMR (200 MHz, $CDCl_3$) : δ 1.28 (s, 6H, $C(CH_3)_2$), 2.38 (s, 3H, CH_3), 3.76 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 6.84 - 6.87 (m, 2H), 7.23 (dd, 4H, J_1 = 13.0 Hz, J_2 = 7.9 Hz), 9.10 (d, 1H, J = 9.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 21.2, 28.0, 55.4, 67.1, 79.3, 112.3, 115.5, 120.4, 128.1, 128.7, 131.9, 137.0, 138.3, 143.3, 161.0, 163.8. MS m/z (rel. intensity) 295 ($M^{+\cdot}$, 25), 294 ($M^{+\cdot}$ - 1, 100), 280 ($M^{+\cdot}$ - CH_3, 3), 239 (7), 209 (12), 108 (15), 43 (44).

2-(4-Methylphenyl)-4-methoxybenzoic acid (69)



Following the general procedure in the preparation of compound **55**, oxazoline **66** gave acid **69** in 21% Mp. 167 - 169°C. ^1H NMR (200 MHz, $CDCl_3$) : δ 2.39 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 6.81 (d, 1H, J = 2.5 Hz), 6.90 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.6 Hz), 7.21 (s, 4H), 7.97 (d, 1H, J = 8.7 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 21.2, 55.5, 112.5, 116.6, 121.0, 128.3, 128.7, 133.4, 137.1, 138.3, 146.2, 162.3, 171.4. MS m/z (rel. intensity) 242 ($M^{+\cdot}$, 100), 225 ($M^{+\cdot}$ - OH, 67), 182 (10), 165 (9), 152 (11), 120 (14).

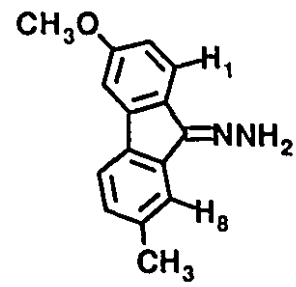
3-Methoxy-7-methyl-9-fluorenone (72)



Following the general procedure in the preparation of compound **56**, acid **69** gave ketone **72** in 28% yield. Mp. 118 - 120°C. ^1H NMR (200 MHz, $CDCl_3$) : δ 2.36 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 6.69 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2.2 Hz), 6.96 (d, 1H, J = 2.2 Hz), 7.30 (m, 2H), 7.42 (s, 1H), 7.57 (d, 1H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 21.5, 55.8, 106.8, 112.4, 119.9, 124.6, 126.1, 127.2, 134.4, 135.5, 139.4, 140.6, 147.1,

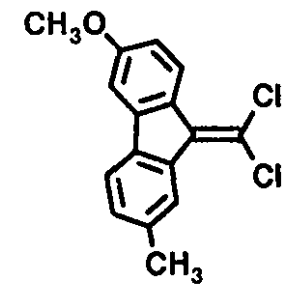
165.2, 170.0. MS m/z (rel. intensity) 224 ($M^{+\cdot}$, 100), 181 (15), 165 (11), 153 (13).

3-Methoxy-7-methyl-9-fluorenone hydrazone (75)



Following the general procedure in the preparation of compound **74**, ketone **72** gave hydrazone **75** in 85% yield as a mixture of two isomers. Mp. 121 - 131°C (mixture of both isomers). ^{1}H NMR (200 MHz, $CDCl_3$) : major isomer (NNH_2 syn to H_1) δ 2.40 (s, 3H, CH_3), 3.91 (s, 3H, OCH_3), 6.17 (s, 2H, NNH_2), 6.80 (dd, 2H, J_1 = 8.6 Hz, J_2 = 2.2 Hz, both isomers), 7.14 (d, 2H, J = 7.6 Hz, both isomers), 7.22, (d, 2H, J = 2.2 Hz, both isomers), 7.60 (dd, 2H, J_1 = 8.4 Hz, J_2 = 2.3 Hz, both isomers), 7.75 (s, 1H), 7.82 (d, 1H, J = 8.3 Hz). minor isomer (NNH_2 syn to H_8) δ 2.44 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 6.24 (s, 2H, NNH_2), 7.49 (d, 1H, J = 7.6 Hz), 7.53 (s, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) : major isomer δ 21.7, 55.6, 106.1, 112.0, 119.2, 121.2, 123.6, 126.7, 129.2, 131.3, 138.0, 138.7, 140.2, 146.0, 161.0, minor isomer δ 21.9, 55.6, 104.6, 106.1, 113.3, 120.0, 121.7, 126.5, 130.2, 130.3, 135.8, 137.7, 138.3, 143.6, 160.6. MS m/z (rel. intensity) 238 ($M^{+\cdot}$, 100), 223 ($M^{+\cdot}$ - CH_3, 18), 209 (29), 195 (16), 165 (26), 152 (25).

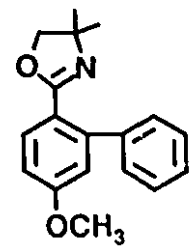
1,1-Dichloro-2-[3-methoxy-7-methyl-9-fluorenyl] ethylene (84)



Following the procedure in the preparation of compound **59**, only its corresponding ethylene compound **84** was isolated in 20% yield. Mp. 82 - 85°C. R_f = 0.64. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 2.67 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 6.82 (dd, 1H, J_1 = 8.9 Hz, J_2 = 2.5 Hz), 7.17 - 7.22 (m, 2H), 7.40 (d, 1H, J = 2.5 Hz), 8.23 (d, 1H, J = 8.6 Hz), 8.31 (d, 1H, J = 7.6 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$) : δ 21.3, 55.5, 110.0, 110.8, 119.3, 123.4, 126.6, 127.1, 129.8, 131.9, 132.9, 133.6, 137.6, 137.8, 142.9, 160.3. MS m/z (rel. intensity) 294 (11), 292 (65), 290 ($M^{+\cdot}$, 100), 247 (36), 212 (25), 176 (40).

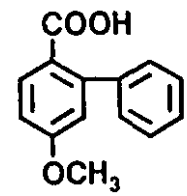
5.9 ATTEMPTED PREPARATION OF 2,2-DICHLORO-3-[3-METHOXY-9-FLUORENYL] EPISULFIDE

2-[2-Phenyl-2-(4-methoxyphenyl)]-4,4-dimethyl-2-oxazoline (67)



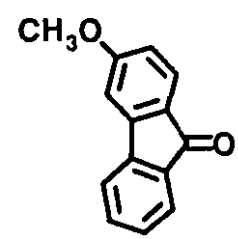
Following the general procedure in the preparation of compound **53**, the oxazoline **52** was treated with phenylmagnesium bromide (**64**) yielding 5% of **67**. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 1.27 (s, 6H, $C(CH_3)_2$), 3.75 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 6.87 - 6.90 (m, 2H), 7.36 - 7.39 (m, 5H), 7.70 (d, 1H, J = 8.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 28.0, 55.4, 67.2, 79.2, 112.5, 115.5, 120.3, 127.2, 127.9, 128.2, 131.8, 141.2, 143.4, 160.9, 163.7. MS m/z (rel. intensity) 281 ($M^{+\cdot}$, 25), 280 ($M^{+\cdot}$ - 1, 100), 195 (28), 152 (11), 94 (11).

2-Phenyl-4-methoxybenzoic acid (70)



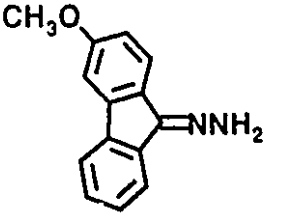
Following the general procedure in the preparation of compound **55**, oxazoline **67** gave acid **70** in 25% yield. Mp. 163 - 165°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.86 (s, 3H, OCH_3), 6.82 (d, 1H, J = 2.5 Hz), 6.90 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.6 Hz), 7.31 - 7.35 (m, 5H), 7.98 (d, 1H, J = 8.8 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.5, 112.6, 116.7, 121.0, 127.3, 127.9, 128.4, 133.4, 141.3, 146.3, 162.4, 172.0. MS m/z (rel. intensity) 228 ($M^{+\cdot}$, 100), 211 ($M^{+\cdot}$ - OH, 96), 168 (27), 152 (15), 139 (31).

3-Methoxy-9-fluorenone (73)



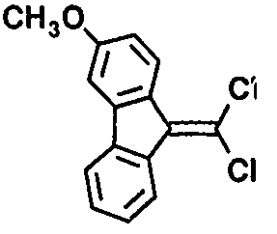
Following the general procedure in the preparation of compound **56**, acid **70** gave ketone **73** in 61% yield. Mp. 95 - 96°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.85 (s, 3H, OCH_3), 6.67 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2.2 Hz), 6.94 (d, 1H, J = 2.2 Hz), 7.20 - 7.30 (m, 2H), 7.42 (s, 1H), 7.57 (d, 1H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.8, 107.0, 112.9, 120.0, 123.8, 126.2, 127.1, 129.2, 134.1, 135.3, 143.3, 146.9, 165.3, 192.5. MS m/z (rel. intensity) 210 ($M^{+\cdot}$, 100), 180 (13), 167 (15), 152 (9), 139 (28).

3-Methoxy-9-fluorenone hydrazone (76)



Following the general procedure in the preparation of compound **57**, ketone **73** gave hydrazone **76** in 9% yield. Mp. 118 - 125°C (mixture of both isomers). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.89, 3.91 (2xs, 6H, OCH_3, both isomers), 6.81 - 7.94 (m, 14H, both isomers). ^{13}C NMR (75.4 MHz, $CDCl_3$) : major isomer δ 55.6, 106.4, 112.6, 119.5, 120.7, 123.6, 126.8, 128.1, 128.4, 138.3, 140.2, 141.0, 143.5, 161.1, minor isomer δ 74.7, 104.9, 113.9, 120.4, 121.8, 125.6, 127.9, 129.6, 131.0, 138.6, 139.8, 141.6, 145.9, 160.7. MS m/z (rel. intensity) 224 ($M^{+\cdot}$, 100), 209 ($M^{+\cdot}$ - NH, 23), 195 (30), 180 (19), 165 (11), 152 (43).

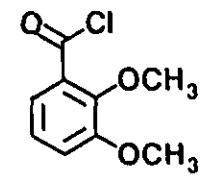
1,1-Dichloro-2-[3-methoxy-9-fluorenyl] ethylene (85)



Hydrazone **76** (16.4 mg, 0.073 mmol) was dissolved in 10 ml anhydrous THF and 0.25 g sodium sulfate was added to the solution. Yellow mercuric oxide (39 mg, 0.18 mmol) was then added followed by 3 drops of ethanolic KOH (1 g KOH in 10 ml ethanol). The mixture was stirred at room temperature for 45 mins, decanted from the sludge and cooled to 0°C. Thiophosgene (24 mg, 0.21 mmol) in 2 ml anhydrous ether was added dropwise to the red solution of the diazotized solution. Evolution of nitrogen was apparent. The solution was then stirred for another 20 mins at 0°C and after allowing to warm to room temperature, the solution was filtered and flash chromatographed (1:1 CH_2Cl_2 : hexanes eluent) yielding 78 mg of a yellow-brown solid which was determined to be **85** (47%). Mp. 86-89°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.91 (s, 3H, OCH_3), 6.74 (dd, 1H, J_1 = 8.20 Hz, J_2 = 2.2 Hz), 7.03 (d, 1H, J = 2.4 Hz), 7.15 - 7.50 (m, 4H), 7.62 (d, 1H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.8, 107.1, 112.9, 120.1, 123.9, 126.3, 127.2, 128.3, 129.3, 134.1, 135.4, 137.8, 143.4, 147.0, 165.4. MS m/z (rel. intensity) 280 (11), 278 (64), 276 ($M^{+\cdot}$, 100), 233 (41), 198 (12), 163 (29).

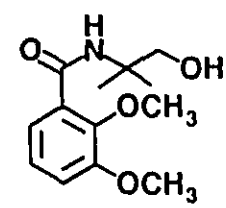
5.10 Preparation of 2,2-Dichloro-3-[2,5-dimethoxy-9-fluorenyl] episulfide

2,3-Dimethoxybenzoyl chloride



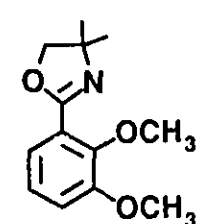
Following the general procedure in the preparation of 2,4-dimethoxybenzoyl chloride, 2,3-dimethoxybenzoic acid (10.2 g, 55 mmol) when treated with excess thionyl chloride (18.0 g, 151 mmol) yielded 10.5 g (92 %) of the acid chloride as a white solid. Mp. 56-57°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.89 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 7.13 (d, 1H, J = 1.2 Hz), 7.15 (d, 1H, J = 1.2 Hz), 7.52 (dd, 1H, J_1 = 2.2 Hz, J_2 = 1.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 56.2, 61.6, 117.9, 123.7, 123.8, 128.9, 149.0, 153.5, 164.8.

N-(Dimethyl-2-hydroxy ethyl)-2,3-dimethoxy benzamide (86)



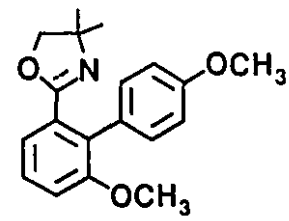
Following the general procedure in the preparation of **51**, the acid chloride (10.5 g, 52 mmol) when treated with 2-methyl-2-amino-1-propanol (11.7 g, 131 mmol) yielded 12.1 g (92 %) of the benzamide **86** as a beige solid. Mp. 83-86°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 1.40 (s, 6H, $C(CH_3)_2$), 3.68 (s, 2H, CH_2), 3.89 (s, 3H. OCH_3), 3.90 (s, 3H, OCH_3), 7.05 (d, 1H, J = 1.2 Hz), 7.15 (t, 1H, J = 1.2 Hz), 7.72 (d, 1H, J = 1.2 Hz), 8.26 (s, 1H, NH). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 24.9, 56.1, 61.2, 70.8, 115.5, 122.5, 124.5, 126.9, 147.2, 152.5, 165.5.

2-(2,3-Dimethoxyphenyl)-4,4-dimethyl-2-oxazoline (87)



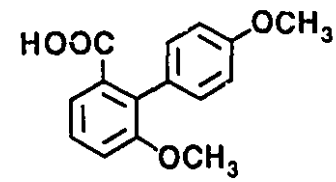
Following the general procedure in the preparation of **52**, benzamide **86** (12.1 g, 48 mmol) was treated with thionyl chloride. After workup, 5.2 g (46 %) of oxazoline **87** was obtained as a gold-colored solid. Mp. 46 - 47.5°C (lit.[172] Mp. 49 - 50°C). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 1.57 (s, 6H, $C(CH_3)_2$), 3.84 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 4.34 (s, 2H, CH_2), 7.07 (d, 1H, J = 2.2 Hz), 7.09 (d, 1H, J = 2.2 Hz), 7.48 (dd, 1H, J_1 = 5.4 Hz, J_2 = 3.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 28.3, 56.1, 61.3, 67.3, 79.1, 115.0, 122.5, 123.3, 123.7, 148.6, 153.2, 161.2. MS m/z (rel. intensity) 235 ($M^{+\cdot}$, 94), 220 (36), 206 (31), 192 (28), 178 (21), 163 (100), 151 (29), 149 (73), 135 (36), 121 (31).

2-[2-(4-Methoxyphenyl)-2-(3-methoxyphenyl)]-4,4-dimethyl-2-oxazoline (90)



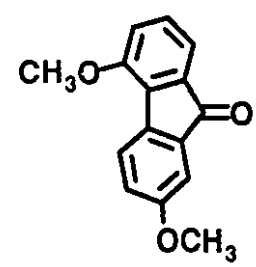
Following the general procedure in the preparation of compound **53**, the oxazoline **87** (5.2 g, 22 mmol) was treated with 4-methoxyphenylmagnesium bromide (**88**) (1.3 eq.) yielding 3.45 g (61%) of **90** as a viscous oil which could not totally purified. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 1.20 (s, 6H, $C(CH_3)_2$), 3.69 (s, 2H, CH_2), 3.73 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 6.89 - 7.27 (m, 7H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 27.9, 55.1, 55.8, 60.3, 79.9, 112.8, 113.0, 121.8, 128.0, 128.7, 130.1, 130.7, 130.9, 156.7, 158.6, 163.5. MS m/z (rel. intensity) 310 ($M^{+\cdot}$ - 1, 7), 163 (100).

2-(4-Methoxyphenyl)-3-methoxybenzoic acid (92)



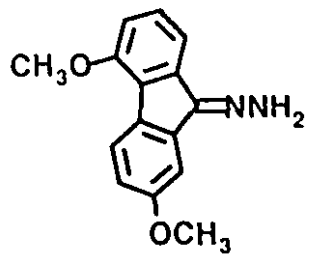
Following the general procedure in the preparation of compound **55**, oxazoline **90** (3.45 g, 11 mmol) gave 0.16g (6%) of pure white acid **92** after recrystallizing with 1:1 H_2O:EtOH. Mp. 170 - 172°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.77 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.90 - 7.55 (m, 7H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.1, 56.0, 113.3, 114.5, 122.1, 128.1, 128.2, 130.7, 131.2, 131.8, 157.2, 158.8, 172.3. MS m/z (rel. intensity) 258 ($M^{+\cdot}$, 100), 225 (9), 197 (12), 184 (7), 122 (11).

2,5-Dimethoxy-9-fluorenone (94)



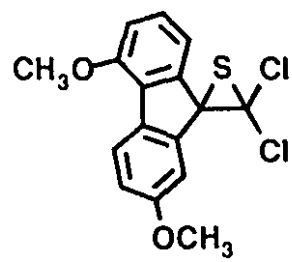
Following the general procedure in the preparation of compound **56**, acid **92** (0.16g, 0.6 mmol) gave 0.12 g of ketone **94** in 81% yield as a bright orange solid. Mp. 160 - 163°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.82 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 6.90 - 7.55 (m, 5H), 7.66 (d, 1H, J = 8.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.5, 55.6, 109.4, 116.5, 117.9, 119.9, 125.1, 127.2, 128.1, 129.2, 135.2, 135.8, 136.3, 154.7, 160.0. MS m/z (rel. intensity) 240 ($M^{+\cdot}$, 100), 225 (63), 197 (20), 126 (11).

2,5-Dimethoxy-9-fluorenone hydrazone (96)



Following the general procedure in the preparation of compound **57**, the hydrazone **96** was obtained after evaporating the solvent and flash chromatography (CH_2Cl_2 then 1:1 EtOAc : hexanes eluent). Ketone **94** (0.12g, 0.5 mmol) gave 5 mg (4%) of hydrazone **96** as a mixture of two isomers. In some cases, ketone **94** was contaminated by the Wolff-Kishner reduction product (2,5-dimethoxy fluorene) which was removed by column chromatography (CH_2Cl_2 eluent). ^1H NMR (200 MHz, $CDCl_3$) : δ 3.88 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 6.88 (d, 1H, J = 8.2 Hz), 6.97 (d, 1H, J = 8.2 Hz), 7.24 (d, 1H, J = 8.0 Hz), 7.28 (s, 1H), 7.48 (d, 1H, J = 8.0 Hz), 7.87 (d, 1H, J = 8.0 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : major isomer δ 55.4, 55.5, 104.8, 112.7, 115.3, 117.9, 124.5, 127.7, 129.0, 131.7, 138.9, 145.7, 155.2, 159.4, 169.8, minor isomer δ 55.3, 55.7, 110.9, 112.6, 113.2, 113.7, 122.3, 124.9, 128.2, 131.0, 133.5, 139.3, 154.8, 158.9, 169.8.

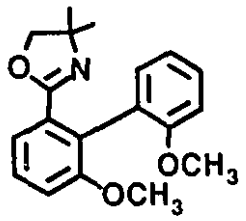
2,2 Dichloro-3-[2,5 dimethoxy-9-fluorenyl] episulfide (98)



Hydrazone **96** (5.0mg, 0.019 mmol) was dissolved in 10 ml anhydrous ether and to the solution was added 0.25 g sodium sulfate. Yellow mercuric oxide (100 mg, 0.46 mmol) was then added followed by 10 drops of ethanolic potassium hydroxide (1 g KOH in 10 ml ethanol). The mixture was stirred at room temperature for 2 hr, decanted from the sludge and then a second portion of mercuric oxide was added. The mixture was then stirred for 24 hr, filtered, concentrated to about 2 ml, and cooled to 0°C. Thiophosgene (5 drops) in 2 ml anhydrous ether was added dropwise to the diazotized solution. Evolution of nitrogen was apparent. The solution was then stirred for 20 mins at 0°C and after allowing to warm to room temperature, the solution was flash chromatographed (1:1 CH_2Cl_2 : hexanes eluent) yielding 7 mg of a orange-yellow residue which was determined *via* ^{13}C NMR to be the episulfide **98**. ^1H NMR (200 MHz, $CDCl_3$) : δ 3.87 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 6.91 (d, 1H, J = 8.5 Hz), 6.92 (d, 1H, J = 8.5 Hz), 7.20 (t, 1H, J = 8.1 Hz), 7.91 (s, 1H), 7.92 (d, 1H, J = 8.0 Hz), 8.17 (d, 1H, J = 8.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.4, 55.6, 65.5, 91.6, 111.7, 112.2, 114.0, 118.3, 124.5, 127.1, 132.7, 134.7, 137.3, 138.2, 154.7, 158.7. MS m/z (rel. intensity) 310 (2), 309 (12), 308 (12), 307 (65), 306 ($M^{+\cdot}$ - S, 65.2), 305 ($M^{+\cdot}$ - SH, 100), 290 (59), 262 (12), 247 (10), 150 (13), 76 (15).

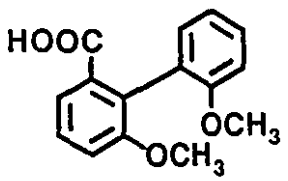
5.11 Preparation of 4,5-dimethoxy-9-fluorenone

2-[2-(2-Methoxyphenyl)-2-(3-methoxyphenyl)]-4,4-dimethyl-2-oxazoline (91)



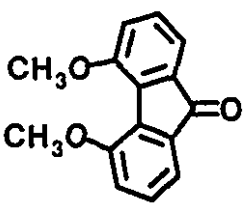
Following the general procedure in the preparation of compound **53**, the oxazoline **87** (10.2 g, 43 mmol) was treated with 2-methoxyphenylmagnesium bromide (**89**) (1.3 eq.) yielding 1.95 g (14%) of **91** as a viscous oil which did not solidify. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 1.38 (s, 6H, $C(CH_3)_2$), 3.88 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 4.08 (s, 2H, CH_2), 6.76 - 6.98 (m, 4H, aromatic), 7.24 (dd, 2H, J_1 = 7.9 Hz, J_2 = 1.6 Hz), 7.52 (dd, 1H, J_1 = 7.8 Hz, J_2 = 1.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 28.4, 56.1, 56.2, 67.0, 78.4, 111.1, 111.7, 112.1, 115.1, 118.0, 119.5, 121.8, 128.4, 133.3, 148.3, 150.3, 155.9, 163.7. MS m/z (rel. intensity) 280 ($M^{+\cdot}$ - OCH_3, 23), 149 (100).

2-(2-Methoxyphenyl)-3-methoxybenzoic acid (93)



Following the general procedure in the preparation of compound **55**, oxazoline **91** (0.36 g, 1.16 mmol) gave 0.30g (99%) of a pure white acid **93** after recrystallizing with 1:1 H_2O:EtOH. Mp. 194 - 196°C (lit.[172] 196 - 197°C). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.70 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 6.92 (d, 1H, J = 8.2 Hz), 7.01 (d, 1H, J = 7.4 Hz), 7.15 (dd, 2H, J_1 = 7.6 Hz, J_2 = 2.1 Hz), 7.33 (t, 1H, J = 8.3 Hz), 7.38 (t, 1H, J = 8.1 Hz), 7.52 (d, 1H, J = 7.8 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.6, 56.2, 110.9, 115.1, 120.3, 122.2, 125.2, 128.2, 128.3, 128.9, 131.0, 131.8, 156.7, 157.3, 169.8. MS m/z (rel. intensity) 258 ($M^{+\cdot}$, 100), 227 ($M^{+\cdot}$- OCH_3, 48), 211 (12), 197 (7), 184 (9), 168 (21), 165 (58), 139 (12).

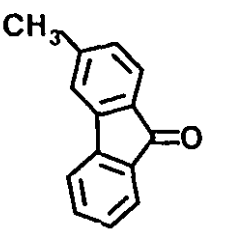
4,5-Dimethoxy-9-fluorenone (95)



Following the general procedure in the preparation of compound **56**, acid **93** (0.30 g, 1.16 mmol) gave 0.12 g of ketone **95** in 44% yield as a beige solid. Mp. 134 - 137.5°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 4.06 (s, 6H, 2xOCH_3), 7.51 (t, 2H, J = 8.0 Hz), 8.06 (dd, 2H, J_1 = 7.9 Hz, J_2 = 1.2 Hz), 8.93 (dd, 2H, J_1 = 8.3 Hz, J_2 = 1.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 56.0, 116.8, 117.2, 122.6, 124.3, 128.5, 129.2, 129.6. MS m/z (rel. intensity) 240 ($M^{+\cdot}$, 6), 226 (100), 211 (49), 155 (19), 139 (8), 127 (13). IR (cm^{-1}) : 1724 (C=O).

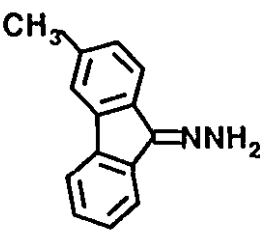
5.12 Attempted Preparation of 2,2-Dichloro-3-[3-methyl-9-fluorenyl] episulfide

3-Methyl-9-fluorenone (100)



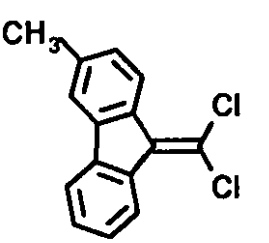
2-Amino-4-methyl benzophenone (**99**) (3.1 g, 14.5 mmol) was suspended in 2 N HCl and stirred at 0°C for 15 mins. Sodium nitrite (1.0g, 14.5 mmol) dissolved in 5 ml water was then added dropwise to the arylamine. After 1 hr, the red precipitate was filtered, dissolved in 25 ml anhydrous THF, dried with Na_2SO_4, and then heated at reflux for 2.5 hr. The solvent was removed under vacuo leaving a dark red residue which was chromatographed ($CHCl_3$ eluent) yielding 282 mg of **100** as a red solid (10%). Mp. 166 - 169°C. ^1H NMR (200 MHz, $CDCl_3$) : δ 2.33 (s, 3H, CH_3), 6.98 (d, 1H, J = 7.0 Hz), 7.17 - 7.23 (m, 2H), 7.35 - 7.39 (m, 2H), 7.44 (d, 1H, J = 7.6 Hz), 7.56 (d, 1H, J = 7.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 22.0, 119.9, 121.0, 123.8, 124.0, 128.7, 129.3, 131.6, 134.2, 134.4, 14.0, 144.5, 145.6, 193.3. MS m/z (rel. intensity) 194 ($M^{+\cdot}$, 100), 165 (80).

3-Methyl-9-fluorenone hydrazone (101)



3-Methyl-9-fluorenone (**100**) (112 mg, 0.57 mmol) was dissolved in 20 ml ethanol and hydrazine monohydrate (0.35 ml, 7.2 mmol) was added. The mixture was refluxed until a clear yellow solution was obtained. The solvent was removed yielding 0.12 g of **101** as a yellow solid (100%). Mp. 95 - 102°C (mixture of both isomers). ^1H NMR (200 MHz, $CDCl_3$) : δ 2.43, 2.46 (2xs, 6H, CH_3, both isomers), 6.31 (s, 2H, NNH_2, both isomers), 7.13 - 7.92 (m, 14H, aromatic, both isomers). MS m/z (rel. intensity) 208 ($M^{+\cdot}$, 100), 193 ($M^{+\cdot}$ - NH, 6), 179 (60), 165 (23), 152 (14).

1,1-Dichloro-2-[3-methyl-9-fluorenyl] ethylene (103)

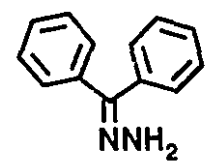


3-Methyl-9-fluorenyl hydrazone (**101**) was dissolved in 30 ml anhydrous ether and yellow mercuric oxide (1.0 g, 4.6 mmol) was added followed by 10 drops of ethanolic KOH. The mixture was stirred until the sludge appears which was decanted and a second portion of HgO was added. Fresh portions of HgO were added until the ethereal solution became faint red in color.

The solution was then concentrated to about 5 ml and then cooled to 0°C. Thiophosgene (1.5 g, 13 mmol) in 4 ml anhydrous ether was added dropwise and the solution allowed to stand at 0°C for 1 hr. After filtering the mixture, the filtrate was concentrated and chromatographed (hexanes eluent) yielding 54 mg (89%) of a yellow solid which was identified to be ethylene compound **103**. Mp. 67 - 70°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 2.43 (s, 3H, CH_3), 7.11 (d, 1H, J = 7.2 Hz), 7.29 - 7.38 (m, 2H), 7.48 (s, 1H), 7.65 (d, 1H, J = 6.9 Hz), 8.16 (d, 1H, J = 7.9 Hz), 8.29 (d, 1H, J = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 21.6, 119.4, 120.2, 121.2, 125.5, 125.7, 127.3, 128.3, 128.6, 133.9, 134.1, 136.8, 139.2, 140.2, 140.3. MS m/z (rel. intensity) 264 (11), 262 (64), 260 ($M^{+\cdot}$, 100), 225 ($M^{+\cdot}$ - Cl, 37), 190 (34), 189 (71), 163 (10), 94 (36). Anal. Calc'd for $C_{15}H_{10}Cl_2$: C, 68.99; H, 3.86. Found: C, 68.90; H, 3.73.

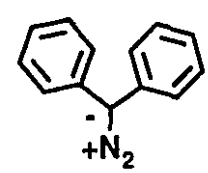
5.13 Preparation of 2,2-Dichloro-3,3-diphenyl episulfide

Benzophenone hydrazone (106)



Benzophenone (**104**) (14 g, 77 mmol) was dissolved in 80 ml *n*-butanol and hydrazine monohydrate (5 ml) was added. The mixture was heated to reflux for 24 hr. After cooling the mixture, the precipitated hydrazone **106** was filtered and recrystallized with methanol yielding 12.6 g (83%). Mp. 88 - 91°C (lit.[170] Mp. 98°C). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 5.43 (s, 2H, NNH_2), 7.26 - 7.59 (m, 10H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 126.3, 127.9, 128.0, 128.7, 128.8, 129.3, 132.8, 138.3, 149.0. MS m/z (rel. intensity) 196 ($M^{+\cdot}$, 70), 180 (17), 165 (28), 119 (11), 85 (67), 83 (100), 77 (38).

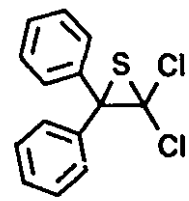
Diphenyldiazomethane (108)



To a rapidly stirred solution of benzophenone hydrazone (**106**) (5.0 g, 25 mmol) in 200 ml anhydrous ether, 0.4 g KOH was added followed by 0.2 ml H_2O. The solution was stirred until dissolution of the KOH. Yellow mercuric oxide (6.0 g, 28 mmol) was added and the mixture was decanted from the heavy sludge after stirring for 5 min. A fresh portion of HgO was added to the rose color solution and the mixture allowed to stir for 48 hr. The ethereal solution was dried with $MgSO_4$, filtered, and concentrated down furnishing 3.2 g (66%) of **108** as a deep purple solid. Mp. 29 - 31°C (lit.[170] Mp. 30°C). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 7.14 - 7.44 (m, 10H, aromatic).

^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 125.1, 125.6, 128.3, 129.1, 129.5. MS (FAB, glycerol) m/z (rel. intensity) 166 ($M^{+\cdot}$ - N_2, 57), 165 (100), 152 (13).

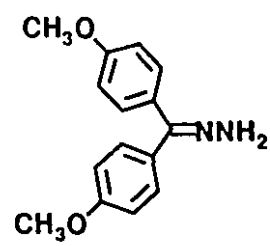
2,2-Dichloro-3,3-diphenyl episulfide (110)



Diphenyldiazomethane (**108**) (325 mg, 1.7 mmol) was dissolved in 1.67 ml anhydrous THF and cooled to 0°C. Thiophosgene (192 mg, 1.7 mmol) in 1.67 ml anhydrous THF was added dropwise to the diazo solution. The mixture was stirred for 10 min and then warmed to room temperature. The clear yellow solution was concentrated under vacuo and chromatographed (hexanes eluent) furnishing 271 mg (57%) of **110** as a white powder. Mp. 86 - 87°C (lit.[49] Mp. 89 - 90°C). ^1H NMR (200 MHz, $CDCl_3$) : δ 7.28 - 7.39 (m, 6H, aromatic), 7.58 - 7.64 (dd, 4H, J_1 = 7.3 Hz, J_2 = 1.4 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 66.8, 80.7, 128.1 (C-5), 128.1 (C-7), 129.4, 138.9. MS m/z (rel. intensity) 280 (M^+, 2), 248 ($M^{+\cdot}$ - S, 19), 245 ($M^{+\cdot}$ - Cl, 32), 210 (100), 178 (66), 165 (81). Raman : 691 cm^{-1}. Anal. Calc'd for $C_{14}H_{10}SCl_2$: C, 59.79; H, 3.59. Found: C, 59.85; H, 3.07.

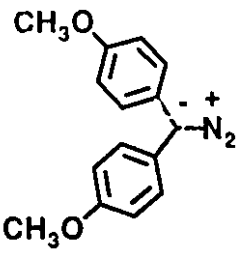
5.14 Preparation of 2,2-Dichloro-3,3-(4,4'-dimethoxy)diphenyl episulfide

4,4'-Dimethoxybenzophenone hydrazone (107)



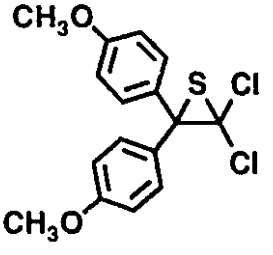
4,4'-Dimethoxybenzophenone (**105**) (3.0 g, 12.4 mmol) was dissolved in 60 ml warm *n*-butanol and hydrazine monohydrate (5 ml) was added. The mixture was heated to reflux for 2.5 hr and then cooled whereupon the yellow hydrazone precipitated. Following filtration, 1.11 g (35%) of hydrazone **107** was obtained which was purified by chromatography (1:1 $CHCl_3$:ethyl acetate eluent). Mp. 72 - 75°C (lit.[170] Mp. 85°C). ^1H NMR (200 MHz, $CDCl_3$) : δ 3.79 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 5.32 (s, 2H, NNH_2), 6.81 (d, 2H, J = 8.7 Hz), 7.03 (d, 2H, J = 8.7 Hz), 7.22 (d, 2H, J = 8.4 Hz), 7.40 (d, 2H, J = 9.0 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.3, 113.4, 114.6, 125.0, 127.9, 130.1, 131.6, 149.2, 159.6. MS m/z (rel. intensity) 256 ($M^{+\cdot}$, 100), 240 (22), 225 ($M^{+\cdot}$ - OCH_3, 35), 199 (10), 148 (29), 133 (40), 77 (17).

Diazo-4,4'-dimethoxybenzophenone (109)



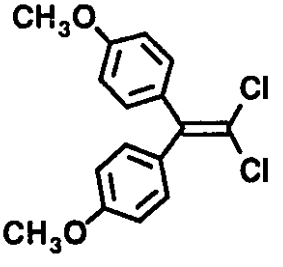
Following the general procedure in the preparation of diphenyldiazomethane (**108**), 4,4'-dimethoxybenzophenone hydrazone **107** gave 1.74 g (81%) of **109** as a purple amorphous solid. Mp. 106 - 108°C (lit.[170] Mp. 112°C). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.81 (s, 6H, OCH_3) 6.93 (d, 4H, J = 9.0 Hz), 7.17 (d, 4H, J = 9.0 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 55.4, 114.8, 121.5, 126.5, 132.2, 157.7. MS m/z (rel. intensity) 452 (($M^{+\cdot}$ - N_2)$_2$, 91), 226 ($M^{+\cdot}$- N_2, 100), 211 (90), 183 (19), 168 (18), 152 (17), 135 (34), 113 (27).

2,2-Dichloro-3,3-(4,4'-dimethoxy)diphenyl episulfide (111)



Diazo compound **109** (0.2 g, 0.79 mmol) was dissolved in 10 ml anhydrous ether and cooled to 0°C. Thiophosgene (0.11 g, 0.94 mmol) in 2 ml anhydrous ether was added dropwise. Spontaneous evolution of nitrogen was apparent as the purple solution faded to a yellow color. The mixture was allowed to stir for 0.5 hr at room temperature. The ether was evaporated under vacuo and the residue chromatographed (1:1 CH_2Cl_2:hexanes eluent) furnishing 0.20 g (74%) of episulfide **111** as an orange-brown solid. Mp. 86 - 87°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.79 (s, 6H, OCH_3), 6.87 (d, 4H, J = 8.9 Hz), 7.51 (d, 4H, J = 8.9 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$) : δ 55.6, 66.4, 82.0, 113.7, 131.1, 131.6, 159.6. MS m/z (rel. intensity) 311 (2), 309 (13), 308 ($M^{+\cdot}$ - S, 4), 307 ($M^{+\cdot}$ - SH, 20), 238 ($M^{+\cdot}$ - $CSCl_2$), 223 (7), 69 (18), 66 (100), 57 (88), 41 (30). Raman : 665 cm^{-1}. Anal. Calc'd for $C_{16}H_{14}O_2SCl_2$: S, 9.39. Found: S, 9.37.

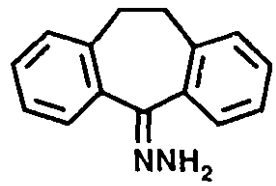
1,1-Dichloro-2,2-bis(4-methoxyphenyl) ethene



The second fraction yielded 14.2 mg of a caramel colored solid which was identified as the ethylene compound. Mp. 128 - 132°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.88 (s, 6H, OCH_3), 6.95 (d, 4H, J = 8.9 Hz), 7.78 (d, 4H, J = 8.9 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$) : δ 55.4, 113.4, 113.7, 128.4, 130.7, 132.2, 162.8. MS m/z (rel. intensity) 308 ($M^{+\cdot}$, 0.2), 242 (23), 227 (24), 211 (10), 135 (100), 107 (12), 92 (17), 77 (20).

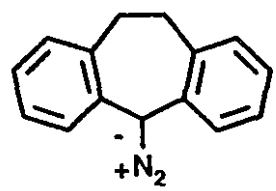
5.15 Preparation of 2,2-Dichloro-3,3-dibenzosuberonyl episulfide

Dibenzosuberone hydrazone (115)



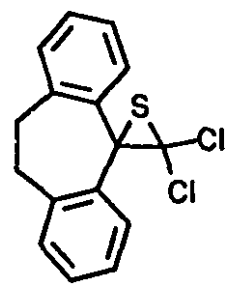
Dibenzosuberone (**112**) (1.0g, 4.8 mmol) was dissolved in 20 ml ethylene glycol and hydrazine monohydrate (2.5ml, 51 mmol) was added. The mixture was allowed to reflux for 2 hr upon which a yellow solution was observed. The mixture was cooled, diluted with water and extracted twice with 40 ml benzene. The extracts were combined, dried with $MgSO_4$, and concentrated. After chromatography (3:2 hexanes : EtOAc eluent), 0.83 g of hydrazone (**115**) was obtained as a yellow solid (78%). Mp. 81 - 84 °C (lit.[184] Mp. 82°C). ^{1}H NMR (200 MHz, $CDCl_3$) : δ 2.80 - 3.42 (m, 4H, CH_2CH_2), 5.53 (s, 2H, NNH_2), 7.00 - 7.74 (m, 8H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 31.9, 33.9, 125.9, 126.0, 127.0, 127.9, 128.4, 128.5, 129.1, 130.2, 133.6, 137.0, 137.4, 139.9, 149.1.

Diazodibenzosuberone (122)



To a rapidly stirred solution of hydrazone (**115**) (0.83g, 3.7 mmol) in 35 ml anhydrous ether, yellow mercuric oxide (6.0 g, 28 mmol) was added followed by 0.25 g Na_2SO_4. 10 drops of 10% ethanolic KOH was then added and the mixture was stirred for 24 hr. The mixture was decanted from the heavy sludge resulting in a violet colored solution containing the diazo compound **122** which was not isolated but was concentrated to about 10 ml and immediately cooled to 0°C. A small sample (19 mg) was dried and used for spectroscopic analysis. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 3.09 (s, 4H, CH_2CH_2), 7.00 - 7.50 (m, 8H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 35.6, 123.8, 124.7, 126.6, 127.9, 130.2, 132.3, 139.4.

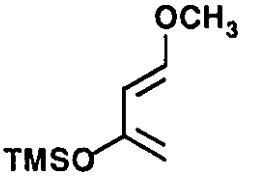
2,? Dichloro-3,3-dibenzosuberonyl episulfide (123)



Thiophosgene (10 drops) in 5.0 ml anhydrous ether was added dropwise to the cooled stirred diazodibenzosuberone **122** solution. Immediate evolution of nitrogen gas was observed. The mixture was allowed to stir for 2 hr, concentrated under vacuo and chromatographed (2:1 hexanes : CH_2Cl_2 eluent) furnishing 0.22 g (~20% based on initial amount of **115**) of **123** as straw yellow crystals. Mp. 113 - 114°C. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 2.98 - 3.16 (m, 2H), 3.64 - 3.82 (m, 2H), 7.11 - 7.41 (m, 8H). ^{13}C NMR (75.4 MHz, $CDCl_3$)

: δ 31.9, 69.0, 82.8, 126.2, 128.9, 129.5, 129.7, 136.5, 138.8. MS m/z (rel. intensity) 306 ($M^{+\cdot}$, 3), 277 (2), 276 (3), 275 (5), 274 ($M^{+\cdot}$ - S, 14), 273 ($M^{+\cdot}$ - SH, 38), 272 ($M^{+\cdot}$ - H_2S, 23), 271 ($M^{+\cdot}$ - Cl, 100), 236 (63), 221 (11), 202 (31), 191 (41). Anal. Calc'd for $C_{16}H_{12}SCl_2$: C, 62.54; H, 3.94. Found: C, 62.14; H, 3.60.

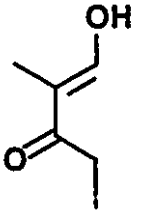
5.16 Preparation of 1-Methoxy-3-trimethylsilyloxy-1,3-butadiene



The siloxydiene was prepared according to the procedure of Danishefsky.[207] Anhydrous powdered $ZnCl_2$ (0.2g, 2 mmol) was added to triethylamine (11.5g, 0.11 mol). The mixture was stirred at room temperature and under an inert atmosphere until the $ZnCl_2$ became suspended in the amine whereupon a white suspension was observed. 1-Methoxy-3-butene-2-one (5g, 0.05 mol) in 15 ml benzene was added followed by 10.85g (0.10 mol) chlorotrimethylsilane. After stirring 0.5 hr, the mixture was heated to 40°C and then left stirring 24 hr. After cooling the mixture, it was transferred to 100ml anhydrous ether and filtered. A brown liquid was obtained after collecting the filtrate and evaporating the ether under reduced pressure. Vacuum distillation of the liquid furnished 3.87g (45%) of 1-methoxy-3-trimethylsilyloxy-1,3-butadiene. Bp. 54 - 55°C (5mm Hg) (lit.[207] 54 - 55°C (5mm Hg)). ^1H NMR (200MHz, $CDCl_3$) : δ 0.22 (s, 9H, OTMS), 3.57 (s, 3H, OCH_3), 4.05 (s, 1H), 4.09 (s, 1H), 5.34 (d, 1H, J = 12.2 Hz), 6.82 (d, 1H, J = 12.4 Hz).

5.17 Preparation of 1-Methoxy-2-methyl-3-trimethylsilyloxy-1,3-pentadiene

1-Hydroxy-2-methyl-pent-1-ene-3-one

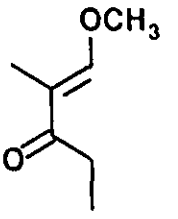


A 1L 3-neck flask was charged with 600ml benzene, 20.45g (0.5 mol) 60% sodium hydride, and 0.5ml methanol. The cooled solution (0°C) was stirred under an inert atmosphere. A mixture of 3-pentanone (55ml, 0.5 mol) and ethyl formate (41ml, 0.5 mol) was added dropwise over a period of 1.5 hr. After addition, the beige pastelike precipitate was stirred for an additional 1.5 hr at room temperature and then diluted with 375ml anhydrous ether. The suspension was then filtered, the crude sodium salt was washed with anhydrous ether. After drying, the yield was 31g (45.6%).

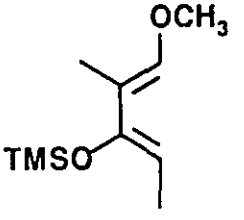
The sodium salt was transferred slowly to 400ml water cooled to 0°C. When the salt was dissolved, the solution was acidified to pH 5 using concentrated HCl. The

mixture was extracted 4 times with 100ml ether each time. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford an amber oil which solidifies on standing. Vacuum distillation (Bp. = 58°C, 12mm Hg) furnished 13.6g (52%) of 1-hydroxy-2-methyl-pent-1-ene-3-one. ^1H NMR (200MHz, $CDCl_3$) : δ 1.12 (t, 3H, J = 7.3 Hz), 1.77 (s, 3H), 2.43 (q, 2H, J = 7.3 Hz), 7.52 (br s, 1H), 7.56 (br s, 1H).

1-Methoxy-2-methyl-pent-1-ene-3-one



A 250ml 3-neck flask was charged with 175ml benzene and 88ml of 3:2 mixture benzene and methanol. To the solution, 13.6g (0.118 mol) of 1-hydroxy-2-methyl-pent-1-ene-3-one was added followed by 0.17g (0.89 mmol) of *p*-toluenesulfonic acid monohydrate. The solution was distilled until half the benzene/methanol azeotrope (Bp. = 59°C) was collected. The flask was replenished with a fresh benzene/methanol mixture and this cycle was repeated four times. Finally, 88ml benzene was added whereupon distillation causes the boiling point to rise to 79°C as the reaction was driven to completion. The reaction was then quenched with 88ml of 1M sodium bicarbonate solution. The phases was separated and the lower aqueous phase was extracted twice with 88ml ether. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under vacuo. The brown oil was vacuum distilled (Bp. = 94°C, 12mm Hg) affording 12.7g (84%) of 1-methoxy-2-methyl-pent-1-ene-3-one. The methoxy ketone was stored over nitrogen at -27°C. ^1H NMR (200MHz, $CDCl_3$) : δ 1.07 (t, 3H, J = 7.4 Hz), 1.68 (s, 3H, CH_3), 2.51 (q, 2H, J = 7.4 Hz), 3.83 (s, 3H, OCH_3), 7.21 (b s, 1H).



The hydroxy ketone was prepared according to the procedure of Danishefsky.[208] A 100ml flask was charged with triethylamine (2.9ml 21 mmol), 1-methoxy-2-methyl-pent-1-ene-3-one (2.00g, 15.6 mmol), and 25ml anhydrous ether then cooled to 0°C. Under an inert atmosphere, trimethylsilyl trifluoromethanesulfonate (TMSOTf) (3.0 ml, 15.6 mmol) was added dropwise over a 10 min. period. The solution went from a yellow color to a red-brown oily precipitate. After allowing the mixture to stir a further 20 min., the oily liquid was separated. The ethereal solution was concentrated under vacuo and the yellow oil was vacuum distilled (Bp. = 83°C, 12mm Hg) (lit.[208] 44 - 46°C (0.7 mm Hg)) yielding 1.57g (50%) of 1-methoxy-2-methyl-3-trimethylsilyloxy-1,3-pentadiene. ^1H

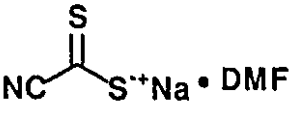
NMR (200MHz, $CDCl_3$) : δ 0.06 (s, 9H, TMS), 1.35 (d, 3H, J = 6.8 Hz), 1.41 (s, 3H), 3.38 (s, 3H, OCH_3), 4.50 (q, 1H, J = 7.0 Hz), 6.1 (br s, 1H).

5.18 Reaction of Thiirane 28 with 1,3-Butadienes

A typical procedure involves dissolving 1 eq. of thiirane **28** in the specified solvent (Table 20) followed by 2.5-3.0 eq. of diene. After stirring at the specified temperature and time, a ^1H NMR spectrum was taken of the crude mixture to detect any appearance of trapped adduct. The corresponding olefin and sulfur were recovered by column chromatography.

5.19 Preparation of Sodium Cyanodithioformate

The preparation of **139** was followed according to the literature.[210] Sodium cyanide (10.0g, 0.20 mmol) was dried over phosphorus pentoxide for 1 hr and then suspended in 50ml dry DMF. Under inert atmosphere and with vigorous stirring, 12ml carbon disulfide was added slowly over a 20 min. period to the cooled (0°C) suspension. After stirring for an additional 30 min., a brown solid precipitated. Isobutanol (35ml) was added to the mixture which was gradually heated until the solid dissolved. Unreacted sodium cyanide was filtered away and the filtrate cooled to yield 42.6g (62%) of **139** as a shiny brown solid. Mp. 62 - 64°C. IR ($CHCl_3$ solution, cm^{-1}) : 1050 (C=S), 2200 (CN).



5.20 Reaction of 139 with 1,3-Butadienes

In a typical reaction **139** (1.0g, 2.9 mmol) was dissolved in 20 ml $CHCl_3$ to which 2,3-diphenyl-1,3-butadiene (0.20g, 0.97 mmol) was added. The mixture was stirred for 1.5 hr at room temperature and the crude was examined by ^1H NMR for any presence of trapped product. Thin layer chromatography revealed the presence of sulfur.

5.21 Chlorination of Tetramethylthiuram Disulfide with 1,3-Butadienes

A typical procedure involves adding 2.0-2.5 eq. of diene to a slurried solution of **141** in CCl_4. One eq. of SO_2Cl_2 in CCl_4 was added dropwise at room temperature. In cases where Cl_2 was used, it was bubbled through the slurry for 20 min. Under conditions specified in Table 21, the initial beige colored mixture gradually transformed to a lemon-colored, one indicating presence of sulfur and *N,N*-dimethylcarbamyl chloride by-product. After filtration through a Schlenck tube under inert atmosphere, only the tetrasulfide product was isolated as a green-yellow oil *via* flash chromatography (hexanes

eluent) which was performed under inert atmosphere and in the absence of light. A small amount of disulfide adduct was also identified in the mixture. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 1.78 (s, 6H), 3.63 (s, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$) : δ 18.1, 42.8, 130.3. MS m/z (rel. intensity) 210 ($M^{+\cdot}$, 3), 146 (39), 82 (94), 67 (100).

5.22 Reaction of *N,N*-dimethylcarbamyl chloride with sulfur

2,3-methyl-1,3-butadiene (2.5g, 30mmol) was added to a solution of *N,N*-dimethylcarbamyl chloride (1.5g, 12mmol) in 35ml CCl_4 followed by elemental sulfur (0.67g, 2.6mmol). The mixture was then stirred at room temperature for 72 hr and a ^{1}H NMR spectrum was taken of the crude material showing only starting materials. Heating the mixture at reflux for 24 hr also showed no reaction.

5.23 Reaction of 28 with methylbenzenes

A typical procedure involved dissolving 31mg of thiirane **28** in 15ml of toluene, 1,2,4-trimethylbenzene, *o*-xylene, *m*-xylene, or *p*-xylene. The solution was then heated at 80°C for two hours, then cooled and the solvent removed under vacuo. The residual material was dissolved in $CDCl_3$ and a ^{1}H NMR spectrum was recorded.

APPENDIX I. X-Ray structure determination of compound **110**.

Atomic coordinates and temperature factors are reported in Table XR-1. Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer controlled by TEXRAY software using the θ/2θ scan mode and are shown in Table XR-2.

Table XR-1. Atomic coordinates (x, y, z) and temperature factors (B_{eq}) for compound **110**. Estimated σs refer to the last digit.

Atom	x	y	z	B_{eq}
Cl 1	0.0877(3)	0.3652(11)	0.0534(3)	5.4(4)
Cl 2	-0.0202(3)	0.4118(11)	0.1232(3)	5.5(4)
S	0.0426(3)	0.8129(11)	0.0785(3)	4.4(4)
C 1	0.0524(12)	0.543(4)	0.1048(11)	4.4(15)
C 2	0.0895(12)	0.685(4)	0.1503(9)	4.2(15)
C 3	0.1638(6)	0.676(3)	0.1537(7)	3.6(3)
C 4	0.1966(9)	0.8525(22)	0.1334(6)	6.9(3)
C 5	0.2647(9)	0.8483(23)	0.1377(6)	6.4(3)
C 6	0.3000(6)	0.668(3)	0.1621(7)	5.0(3)
C 7	0.2672(9)	0.4909(22)	0.1823(7)	6.8(3)
C 8	0.1990(9)	0.4951(23)	0.1781(7)	6.1(3)
C 9	0.0665(8)	0.728(3)	0.2127(6)	4.3(3)
C10	0.0771(7)	0.5720(22)	0.2611(9)	6.2(3)
C11	0.0576(7)	0.609(3)	0.3210(7)	5.7(3)
C12	0.0275(8)	0.802(3)	0.3326(6)	6.7(3)
C13	0.0169(7)	0.9581(23)	0.2843(9)	9.6(3)
C14	0.0364(7)	0.9210(25)	0.2243(7)	5.3(3)
Cl 1A	0.6579(4)	-0.3601(14)	-0.0320(3)	8.2(5)
Cl 2A	0.5726(4)	-0.4533(15)	0.0591(4)	9.5(6)
S A	0.5933(4)	0.0110(14)	0.0270(4)	7.5(5)
C 1A	0.6250(15)	-0.252(4)	0.0354(12)	6.3(19)
C 2A	0.6619(11)	-0.117(5)	0.0817(12)	5.2(16)
C 3A	0.7308(6)	-0.058(3)	0.0698(7)	5.0(3)
C 4A	0.7429(8)	0.139(3)	0.0425(7)	6.7(3)
C 5A	0.8065(9)	0.1933(21)	0.0342(6)	6.0(3)
C 6A	0.8581(6)	0.051(3)	0.0532(7)	5.6(3)
C 7A	0.8460(8)	-0.146(3)	0.0805(7)	7.8(3)
C 8A	0.7824(9)	-0.2009(21)	0.0888(6)	5.3(3)
C 9A	0.6575(7)	-0.143(3)	0.1520(5)	3.4(3)
C10A	0.6796(7)	-0.3271(24)	0.1867(8)	6.6(3)
C11A	0.6777(7)	-0.3386(24)	0.2531(8)	6.2(3)
C12A	0.6536(7)	-0.166(3)	0.2847(5)	6.2(3)
C13A	0.6315(7)	0.018(3)	0.2500(9)	7.8(3)
C14A	0.6334(7)	0.0291(23)	0.1836(8)	8.3(3)

Table XR-2. Crystal data for the structure determination of compound **110**.

Compound **110**	
Chemical Formula	$C_{14}H_{10}SCl_2$
Formula Weight	281.20
X-ray crystal dimension (mm)[a]	0.40 x 0.15 x 0.05
Radiation	Graphite-monochromated CuK_α
Crystal system	monoclinic
Space group	$P2_1$
Lattice constants	
a (Å)	20.646(6)
b (Å)	6.244(3)
c (Å)	20.880(6)
β (°)	99.263(23)
V (Å^3)	2656.5(16)
Z	8
F (000)	1162.33
Density (calc'd) (g cm^{-3})	1.406
μ (mm^{-1})	0.571
λ (Å)	1.54056
2θ max (°)	80.0
h, k, l ranges	-16 16, 0 5, 0 17
No. of reflections measured	1638
No. of unique reflections	1564
No. of reflections with $I_{net} > 2.5\sigma(I_{net})$	827
For significant reflections	RF = 0.091[b], R_w = 0.083[c], G_OF = 2.37[d]
Maximum shift / σ ratio	0.022
Deepest hole in D-map (e / Å^3)	-0.400
Highest peak in D-map (e / Å^3)	0.450
Drop of standard intensities	25% for each crystal
Method of structure determination	Solved by direct methods[216]
Method of structure refinement	NRCVAX system programs[217]

216 G. M. Sheldrick, *Crystallographic Computing 3*, G. M. Sheldrick, M. Kruger, and R. Doddard, Eds., Oxford University Press: Oxford, England, 1985, pp 175-189.

217 E. J. Gabe, Y. LePage, J.-P. Charland, F. L. Lee, and P. S. White, *J. Appl. Cryst.*, 22, 384 (1989).

[a] cell dimensions were obtained from 20 reflections with 2θ angle in the range 40.00 - 50.00°. No correction was made for absorption.

[b] $RF = \Sigma (F_o - F_c) / \Sigma (F_o)$

[c] $R_w = (\Sigma [w(F_o - F_c)^2 / \Sigma (wF_o^2)])^{1/2}$

[d] $G_oF = (\Sigma[w(F_o - F_c)^2 / (\#\text{ reflections} - \#\text{ parameters})])^{1/2}$

The dihedral angles between the planes of the phenyl groups in **110** were determined from the equations in Table XR-3.

Table XR-3. Distances (Å) to the Least-squares planes. Phenyl groups were idealized as rigid groups and all are perfectly planar.

Plane no. 1

Equation of the plane :- 1.04(16)x + 2.39(4)y + 19.18(6)z = 4.39(4)

Distances(Å) to the plane from the atoms in the plane.

C 3	0.000(23)	C 4	0.000(22)
C 5	0.000(22)	C 6	0.000(23)
C 7	0.000(22)	C 8	0.000(22)

χ^2 for this plane 0.000

Plane no. 2

Equation of the plane : 17.57(8)x + 2.49(4)y + 4.17(15)z = 3.87(5)

Distances(Å) to the plane from the atoms in the plane.

C 9	0.000(22)	C10	0.000(22)
C11	0.000(20)	C12	0.000(24)
C13	0.000(23)	C14	0.000(19)

χ^2 for this plane 0.000

Plane no. 3

Equation of the plane : 0.23(15)x + 2.58(4)y + 18.73(7)z = 1.32(12)

Distances(Å) to the plane from the atoms in the plane.

C 3A	0.000(23)	C 4A	0.000(20)
C 5A	0.000(23)	C 6A	0.000(23)
C 7A	0.000(20)	C 8A	0.000(23)

χ^2 for this plane 0.000

Plane no. 4

Equation of the plane : 18.61(6)x + 2.42(4)y + 0.95(16)z = 12.03(5)

Distances(Å) to the plane from the atoms in the plane.

C 9A	0.000(22)	C10A	0.000(20)
C11A	0.000(20)	C12A	0.000(24)
C13A	0.000(22)	C14A	0.000(21)

χ^2 for this plane 0.000

Dihedral angle between planes A and B.

A	B	Angle(°)
1	2	64.9(6)
1	3	4.0(6)
1	4	73.7(6)
2	3	61.0(6)
2	4	9.0(6)
3	4	69.8(6)

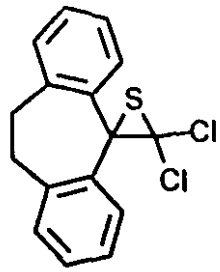
APPENDIX II. X-Ray structure determination of compound **123**.

Atomic coordinates and temperature factors are reported in Table XR-4. Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer controlled by TEXRAY software using the ω scan mode and are shown in Table XR-5.

Table XR-4. Atomic coordinates (x, y, z) and temperature factors (B_{eq}) for compound **123**. Estimated σs refer to the last digit.

Atom	x	y	z	B_{eq}
S	0.62296(19)	0.6257(3)	0.06797(7)	5.15(9)
Cl 1	0.54225(18)	1.0721(3)	0.09744(7)	5.68(9)
Cl 2	0.75718(18)	1.0136(3)	0.01891(6)	5.54(9)
C 1	0.6712(6)	0.8961(10)	0.07392(22)	4.4(3)
C 2	0.7574(6)	0.7600(9)	0.11535(23)	3.7(3)
C 3	0.9152(7)	0.7150(10)	0.10565(23)	4.0(3)
C 4	0.9485(7)	0.5357(12)	0.0762(3)	5.5(4)
C 5	1.0918(9)	0.4897(14)	0.0675(3)	7.2(5)
C 6	1.1976(9)	0.6260(18)	0.0864(4)	7.7(6)
C 7	1.1643(8)	0.8035(15)	0.1158(3)	6.8(5)
C 8	1.0231(7)	0.8520(12)	0.1267(3)	5.2(4)
C 9	1.0055(8)	1.0434(14)	0.1629(4)	7.7(5)
C10	0.8679(9)	1.1112(11)	0.1805(3)	7.2(4)
C11	0.7803(6)	0.9424(10)	0.2072(3)	4.6(3)
C12	0.7550(7)	0.9529(11)	0.2638(3)	5.2(4)
C13	0.6760(7)	0.8005(13)	0.2879(3)	5.2(4)
C14	0.6217(7)	0.6345(11)	0.2568(3)	4.9(3)
C15	0.6462(6)	0.6201(9)	0.20059(24)	4.1(3)
C16	0.7255(6)	0.7735(9)	0.17594(23)	3.6(3)

Table XR-5. Crystal data for the structure determination of compound **123**.

Compound **123**	
Chemical Formula	$C_{16}H_{12}SCl_2$
Formula Weight	307.23
X-ray crystal dimension (mm)[a]	0.50 x 0.35 x 0.20
Radiation	Graphite-monochromated MoK_α
Crystal system	monoclinic
Space group	$P2_1$
Lattice constants	
a (Å)	9.351(4)
b (Å)	6.3151(19)
c (Å)	24.077(6)
β (°)	94.03(3)
V (Å^3)	1418.3(8)
Z	4
F (000)	633.63
Density (calc'd) (g cm^{-3})	1.439
μ (mm^{-1})	0.58
λ (Å)	0.70930
2θ max (°)	44.9
h, k, l ranges	-10 10, 0 6, 0 25
No. of reflections measured	1973
No. of unique reflections	1841
No. of reflections with $I_{net} > 2.5\sigma(I_{net})$	1053
For significant reflections	RF = 0.045[b], R_w = 0.040[c], G_oF = 1.40[d]
For all reflections	RF = 0.106, R_w = 0.044
Maximum shift / σ ratio	0.005
Deepest hole in D-map (e / Å^3)	-0.270
Highest peak in D-map (e / Å^3)	0.390
Merging R	1.5%
Drop of standard intensities	1%
Method of structure determination	Solved by direct methods[216]
Method of structure refinement	NRCVAX system programs[217]

[a] cell dimensions were obtained from 25 reflections with 2θ angle in the range 20.00 - 25.00°. No correction was made for absorption.

[b] $RF = \Sigma (F_o - F_c) / \Sigma (F_o)$

[c] $R_w = (\Sigma [w(F_o - F_c)^2 / \Sigma (wF_o^2)])^{1/2}$

[d] $G_oF = (\Sigma [w(F_o - F_c)^2 / (\#\ \text{reflections} - \#\ \text{parameters})])^{1/2}$

The dihedral angles between the planes of the phenyl groups in **123** were determined from the equations in Table XR-6.

Table XR-6. Distances (Å) to the Least-squares planes.

Plane no. 1

Equation of the plane : 0.33(3)x - 3.289(19)y + 20.43(4)z = 0.11(4)

Distances(Å) to the plane from the atoms in the plane.

C 3	-0.004(8)	C 4	-0.005(9)
C 5	0.014(11)	C 6	-0.012(13)
C 7	-0.007(11)	C 8	0.011(10)

χ^2 for this plane 4.580

Plane no. 2

Equation of the plane : 7.681(15)x - 3.292(15)y + 4.17(7)z = 3.758(24)

Distances(Å) to the plane from the atoms in the plane.

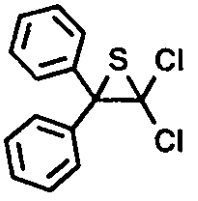
C11	-0.003(8)	C12	0.004(9)
C13	-0.001(9)	C14	-0.001(8)
C15	0.000(7)	C16	0.001(7)

χ^2 for this plane 0.409

Dihedral angle between planes A and B

A	B	Angle(°)
1	2	60.1(3)

Compound **110**



a) Table of Bond Distances (Å) and Bond Angles(^{o})
b) Table of Torsion Angles(^{o})
c) Table of Observed and Calculated Structure Factors
d) Table of Calculated Hydrogen Atom Parameters
e) Table of Anisotropic u(i, j) Values

Table 3. Bond Distances(A) and Angles(Degrees)

Cl(1)-C(1)	1.781(23)
Cl(2)-C(1)	1.80(3)
S-C(1)	1.773(24)
S-C(2)	1.830(22)
C(1)-C(2)	1.43(3)
C(2)-C(3)	1.52(3)
C(2)-C(9)	1.48(3)
Cl(1A)-Cl(2A)	2.854(12)
Cl(1A)-C(1A)	1.79(3)
Cl(2A)-C(1A)	1.78(3)
S(A)-C(1A)	1.76(3)
S(A)-C(2A)	1.852(24)
C(1A)-C(2A)	1.41(4)
C(2A)-C(3A)	1.53(3)
C(2A)-C(9A)	1.49(3)

C(1)-S-C(2)	46.6(11)	C(1A)-S(A)-C(2A)	45.7(13)
Cl(1)-C(1)-Cl(2)	106.2(13)	Cl(1A)-C(1A)-Cl(2A)	106.0(14)
Cl(1)-C(1)-S	116.3(13)	Cl(1A)-C(1A)-S(A)	117.0(14)
Cl(1)-C(1)-C(2)	124.1(19)	Cl(1A)-C(1A)-C(2A)	122.1(22)
Cl(2)-C(1)-S	116.1(13)	Cl(2A)-C(1A)-S(A)	116.9(18)
Cl(2)-C(1)-C(2)	121.1(17)	Cl(2A)-C(1A)-C(2A)	121.2(19)
S-C(1)-C(2)	68.8(14)	S(A)-C(1A)-C(2A)	70.4(15)
S-C(2)-C(1)	64.6(12)	S(A)-C(2A)-C(1A)	63.9(15)
S-C(2)-C(3)	116.8(14)	S(A)-C(2A)-C(3A)	115.8(16)
S-C(2)-C(9)	116.0(16)	S(A)-C(2A)-C(9A)	119.4(16)
C(1)-C(2)-C(3)	115.8(19)	C(1A)-C(2A)-C(3A)	116.6(22)
C(1)-C(2)-C(9)	118.9(20)	C(1A)-C(2A)-C(9A)	119.8(22)
C(3)-C(2)-C(9)	115.4(16)	C(3A)-C(2A)-C(9A)	113.0(17)
C(2)-C(3)-C(4)	119.3(16)	C(2A)-C(3A)-C(4A)	120.7(16)
C(2)-C(3)-C(8)	120.6(16)	C(2A)-C(3A)-C(8A)	119.3(17)
C(2)-C(9)-C(10)	118.4(16)	C(2A)-C(9A)-C(10A)	122.3(17)
C(2)-C(9)-C(14)	121.6(15)	C(2A)-C(9A)-C(14A)	117.6(17)

Table of Torsion Angles in Degrees

C 2	S	C 1	CL 1	-118.6(15)					
C 2	S	C 1	CL 2	115.3(14)	C 2	S	C 1	C 2	0.0(11)
C 1	S	C 2	C 1	0.0(12)	C 1	S	C 2	C 3	107.5(16)
C 1	S	C 2	C 9	-111.3(16)	CL 1	C 1	C 2	S	108.1(16)
CL 1	C 1	C 2	C 3	-0.8(6)	CL 1	C 1	C 2	C 9	-144.8(22)
CL 2	C 1	C 2	S	-108.5(16)	CL 2	C 1	C 2	C 3	142.6(21)
CL 2	C 1	C 2	C 9	-1.5(6)	S	C 1	C 2	S	0.0(3)
S	C 1	C 2	C 3	-108.9(19)	S	C 1	C 2	C 9	107.0(19)
S	C 2	C 3	C 4	40.3(9)	S	C 2	C 3	C 8	-141.2(19)
C 1	C 2	C 3	C 4	113.4(21)	C 1	C 2	C 3	C 8	-68.1(16)
C 9	C 2	C 3	C 4	-101.3(18)	C 9	C 2	C 3	C 8	77.3(15)
S	C 2	C 9	C10	150.7(19)	S	C 2	C 9	C14	-31.0(8)
C 1	C 2	C 9	C10	76.7(17)	C 1	C 2	C 9	C14	-105.0(20)
C 3	C 2	C 9	C10	-67.5(14)	C 3	C 2	C 9	C14	110.8(19)
C 2A	S A	C 1A	CL 1A	-116.9(17)					
C 2A	S A	C 1A	CL 2A	115.8(17)	C 2A	S A	C 1A	C 2A	0.0(13)
C 1A	S A	C 2A	C 1A	0.0(14)	C 1A	S A	C 2A	C 3A	108.5(18)
C 1A	S A	C 2A	C 9A	-111.1(18)	CL 1A	C 1A	C 2A	S A	110.2(19)
CL 1A	C 1A	C 2A	C 3A	2.9(6)	CL 1A	C 1A	C 2A	C 9A	-139.4(24)
CL 2A	C 1A	C 2A	S A	-110.2(19)	CL 2A	C 1A	C 2A	C 3A	142.5(24)
CL 2A	C 1A	C 2A	C 9A	0.2(6)	S A	C 1A	C 2A	S A	0.0(4)
S A	C 1A	C 2A	C 3A	-107.3(21)	S A	C 1A	C 2A	C 9A	110.4(22)
S A	C 2A	C 3A	C 4A	27.5(9)	S A	C 2A	C 3A	C 8A	-154.9(21)
C 1A	C 2A	C 3A	C 4A	99.7(22)	C 1A	C 2A	C 3A	C 8A	-82.6(20)
C 9A	C 2A	C 3A	C 4A	-115.5(21)	C 9A	C 2A	C 3A	C 8A	62.2(14)
S A	C 2A	C 9A	C10A	140.5(20)	S A	C 2A	C 9A	C14A	-42.9(10)
C 1A	C 2A	C 9A	C10A	65.5(17)	C 1A	C 2A	C 9A	C14A	-117.9(23)
C 3A	C 2A	C 9A	C10A	-78.0(16)	C 3A	C 2A	C 9A	C14A	98.5(19)

Table S-1. Observed and Calculated Structure Factors for C14 H10 S C12

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig
-16,	0,	1	
2	525	531	358
4	33	13	4869*
6	34	243	5531*
8	239	236	287
-16,	1,	1	
7	34	104	2340*
8	178	190	977*
-15,	0,	1	
1	32	222	3874*
3	352	305	241
5	303	327	205
7	402	459	227
9	158	267	1122*
-15,	1,	1	
1	222	253	269
2	277	297	224
3	82	38	1790*
4	212	195	288
5	33	208	5091*
6	358	277	230
7	367	384	234
8	34	121	4722*
9	80	146	2035*
10	34	19	5448*
-15,	2,	1	
1	34	31	5091*
2	34	20	4777*
3	34	45	4980*
4	384	354	266
5	34	21	2889*
6	77	169	2334*
7	108	148	1574*
-14,	0,	1	
2	258	182	162
4	305	266	175
6	31	310	4370*
8	64	279	1448*
10	33	269	5060*
12	279	307	240
-14,	1,	1	
1	133	32	297*
2	211	215	197
3	31	9	3144*
4	80	92	1320*
5	73	121	982*
6	332	305	212
7	235	212	188
8	33	177	3665*
9	33	117	5226*
10	77	99	1428*
11	528	369	328
-14,	2,	1	
1	35	65	2017*
2	33	37	4999*
3	348	379	241
4	235	271	262
5	33	67	4452*
6	33	93	5278*
7	293	325	221
8	209	223	299
9	289	259	230
-13,	0,	1	
7	378	409	205
9	139	18	787*
11	224	312	268
13	231	244	249
-13,	1,	1	
1	30	105	3414*
2	30	145	3790*
3	271	191	190
4	198	204	204
5	105	32	973*
6	409	339	278
7	42	108	1760*
8	378	300	182
9	91	112	537*
10	33	142	4862*
11	147	273	1100*
12	191	12	307
-13,	2,	1	
1	249	154	177
2	253	214	169
3	97	89	1092*
4	218	238	204
5	32	19	2430*
6	168	129	237
7	32	27	2753*
8	187	159	298
9	33	145	4732*
10	169	82	933*
11	161	79	1045*
-13,	3,	1	
1	156	169	395*
2	110	172	1507*
3	127	35	641*
4	193	110	324
5	186	45	327
6	149	18	1004*
7	69	142	1080*
-12,	0,	1	
2	126	122	1182*
4	209	184	282
6	379	452	259
8	30	153	3568*
10	447	511	296
12	49	189	3090*
14	34	61	5035*
-12,	1,	1	
7	30	115	3859*
8	30	134	2076*
9	368	374	189
10	146	30	751*
11	285	298	193
12	99	57	953*
13	138	110	796*
-12,	2,	1	
1	140	106	280
2	404	305	184
3	104	119	944*
4	78	60	526*
5	31	11	3696*
6	31	24	3631*
7	443	450	294
8	32	15	3423*
9	217	219	262
10	33	35	3217*
11	202	177	302
12	34	116	5251*
-12,	3,	1	
1	312	319	197
2	152	218	1014*
3	149	125	944*
4	117	209	1366*
5	224	189	263
6	33	112	4660*
7	34	14	4690*
8	362	348	210
9	34	128	4637*
-11,	0,	1	
1	26	78	5491*
3	263	272	220
5	81	344	1894*
7	475	516	269
9	807	823	296
11	722	760	217
13	260	275	232
15	254	205	239
-11,	1,	1	
1	551	682	330
2	27	76	6008*
3	352	453	213
4	78	28	1908*
5	211	232	266
6	322	352	207
7	28	93	5612*
8	45	131	3615*
9	398	418	206
10	309	324	192
11	187	183	215
12	32	77	3553*
13	146	27	1073*
14	138	52	411*
-11,	2,	1	
1	239	205	259
2	352	426	250
3	29	219	6270*
4	203	35	285
5	216	126	288
6	30	16	1968*
7	37	13	2637*
8	275	264	182
9	32	110	3458*
10	32	2	3641*
11	411	314	213
12	122	323	990*
13	50	51	2192*
-11,	3,	1	
1	442	460	298
2	158	38	260
3	206	199	205
4	424	396	296
5	196	151	220
6	489	489	339
7	132	4	1107*
8	33	312	5701*
9	34	90	4202*
10	34	77	3383*
-10,	0,	1	
2	931	898	225
4	137	116	1046*
6	686	656	255
8	166	112	329
10	176	219	993*
12	139	105	708*
14	33	110	1976*
-10,	1,	1	
1	709	662	257
2	646	633	270
3	541	535	299
4	387	366	243
5	393	385	266
6	47	95	3332*
7	201	222	284
8	383	348	244
9	133	228	1316*
10	191	197	201
11	334	267	229

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
-10,	1, 1			6	25	59	5488*	12	30	255	5823*	3	33	129	4876*
2	287	304	179	7	337	354	224	14	418	355	255	4	205	250	279
13	292	356	192	8	27	122	5639*	16	242	252	236	5	175	224	313
14	35	8	4382*	9	82	21	741*	-8,	1, 1			6	33	58	3867*
15	346	390	240	10	567	569	329	1	1064	1047	162	7	176	175	318
-10,	2, 1			11	30	7	2820*	2	894	863	184	8	34	94	4056*
1	27	50	5475*	12	236	238	165	3	469	534	261	-7,	0, 1		
2	170	17	868*	13	105	45	896*	4	330	279	202	1	232	228	167
3	27	165	5930*	14	33	43	4297*	5	107	159	632*	3	20	200	5259*
4	241	298	250	15	220	265	258	6	146	312	1014*	5	334	367	226
5	129	156	1328*	-9,	2, 1			7	427	411	245	7	618	598	203
6	29	98	5706*	1	26	107	5796*	8	491	460	322	9	204	156	249
7	216	215	285	2	256	253	215	9	472	418	227	11	28	5	5304*
8	183	172	203	3	73	51	2006*	10	315	370	224	13	460	417	238
9	137	119	712*	4	101	128	1446*	11	167	141	941*	15	391	475	224
10	31	80	3353*	5	175	119	321	12	30	105	3150*	-7,	1, 1		
11	32	104	3507*	6	303	263	207	13	315	320	169	1	674	731	192
12	149	27	932*	7	113	141	607*	14	32	28	2330*	2	913	862	154
13	81	342	2250*	8	424	326	229	15	143	43	363*	3	120	88	835*
-10,	3, 1			9	30	11	2268*	16	196	22	287	4	778	757	174
1	111	241	605*	10	31	183	3687*	-8,	2, 1			5	745	748	187
2	31	57	3216*	11	82	54	1129*	1	830	808	233	6	254	308	177
3	61	92	1710*	12	79	181	642*	2	659	658	261	7	867	849	199
4	106	107	964*	13	33	22	4651*	3	92	11	1424*	8	97	2	596*
5	289	274	186	14	34	26	4620*	4	554	523	289	9	98	72	943*
6	136	117	816*	-9,	3, 1			5	117	88	873*	10	27	47	5161*
7	175	151	225	1	361	392	215	6	26	165	5213*	11	110	44	1338*
8	33	80	4637*	2	168	134	229	7	27	2	5286*	12	29	119	5253*
9	33	115	4503*	3	30	78	3894*	8	133	149	1089*	13	149	161	238
10	36	138	4498*	4	292	280	183	9	29	9	5269*	14	267	335	163
11	34	142	4417*	5	153	159	250	10	83	90	1008*	15	133	263	973*
-10,	4, 1			6	383	357	212	11	332	343	214	16	34	89	4450*
1	34	182	4498*	7	136	129	772*	12	32	84	3024*	-7,	2, 1		
2	34	204	5413*	8	175	132	225	13	278	313	198	1	878	842	206
3	34	9	4717*	9	79	66	1308*	14	34	86	3066*	2	98	232	1393*
4	34	146	4666*	10	68	234	1505*	15	199	106	271	3	154	175	323*
5	34	29	4686*	11	125	155	1187*	-8,	3, 1			4	820	873	216
-9,	0, 1			12	213	261	276	1	29	46	5881*	5	25	168	5799*
1	532	480	232	-9,	4, 1			2	138	292	1224*	6	420	370	245
3	147	65	733*	1	33	168	4526*	3	436	487	241	7	26	34	5606*
5	297	326	206	2	272	248	210	4	29	172	5952*	8	247	282	230
7	539	489	299	3	267	288	231	5	622	558	300	9	163	2	883*
9	384	415	204	4	33	211	4924*	6	30	7	3555*	10	29	74	5700*
11	188	78	330	5	34	54	4653*	7	334	353	231	11	95	65	359*
13	115	144	936*	6	165	104	1063*	8	280	255	178	12	118	40	779*
15	293	283	191	7	34	121	4275*	9	102	37	369*	13	97	47	384*
-9,	1, 1			-8,	0, 1			10	32	43	4094*	14	139	45	965*
1	253	338	209	2	511	492	224	11	33	67	3676*	15	52	2	2905*
2	468	399	319	4	796	794	171	12	241	266	240	-7,	3, 1		
3	385	388	218	6	602	609	266	-8,	4, 1			1	28	71	5367*
4	177	237	303	8	442	406	228	1	138	120	1055*	2	258	262	224
5	105	226	1359*	10	546	548	306	2	33	64	4535*	3	321	404	218

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	-7, 3, 1			5	275	267	187	6	258	235	171	2	83	114	794*
4	499	473	346	6	25	129	5383*	7	331	328	184	4	828	807	121
5	499	607	350	7	25	64	5392*	8	111	132	808*	6	1531	1494	111
6	29	2	5316*	8	302	379	207	9	249	331	211	8	383	374	180
7	204	130	175	9	119	243	1226*	10	100	169	1338*	10	905	872	197
8	459	554	287	10	28	143	5304*	11	101	71	940*	12	96	89	987*
9	322	318	194	11	178	167	178	12	117	184	1161*	14	327	318	199
10	435	442	295	12	31	91	2074*	13	163	133	182	16	299	271	203
11	41	3	3280*	13	32	85	2139*	14	31	146	3188*		-4, 1, 1		
12	296	266	195	14	139	197	1060*	16	152	132	882*	1	398	374	214
13	34	78	4154*	15	34	281	4590*		-5, 2, 1			2	304	278	196
	-7, 4, 1				-6, 3, 1			1	394	366	195	3	120	90	258*
1	345	362	194	1	324	209	226	2	22	6	4476*	4	1206	1155	114
2	328	294	194	2	133	72	1001*	3	730	708	182	5	671	556	159
3	467	529	301	3	530	509	313	4	273	203	190	6	855	852	146
4	111	132	652*	4	27	9	5150*	5	23	46	5686*	7	611	612	194
5	119	160	668*	5	145	135	380*	6	349	369	231	8	104	104	353*
6	300	330	209	6	343	298	240	7	140	84	348*	9	321	280	206
7	33	3	4340*	7	217	128	261	8	111	163	1267*	10	441	451	234
8	34	12	4616*	8	178	146	191	9	157	3	329*	11	83	124	902*
9	120	129	616*	9	49	122	1341*	10	290	241	202	12	485	450	230
	-6, 0, 1			10	31	110	3017*	11	88	4	1145*	13	379	380	164
2	1067	1065	123	11	222	248	170	12	30	96	2870*	14	293	276	200
4	395	296	246	12	54	29	2693*	13	150	129	220	15	252	226	166
6	884	886	151	13	228	226	237	14	378	355	251	16	137	46	892*
8	23	122	5348*		-6, 4, 1			15	130	182	396*	17	112	82	1214*
10	99	23	776*	1	453	508	264		-5, 3, 1				-4, 2, 1		
12	76	141	990*	2	31	10	3294*	1	26	74	5250*	1	249	188	177
14	104	49	756*	3	81	147	1156*	2	497	499	314	2	617	564	187
16	68	18	1981*	4	32	88	3102*	3	127	101	1027*	3	520	460	209
	-6, 1, 1			5	32	222	3385*	4	140	68	940*	4	44	78	1578*
1	179	209	207	6	185	238	245	5	409	446	269	5	915	923	159
2	19	60	5111*	7	84	142	666*	6	271	323	210	6	236	254	205
3	522	430	214	8	33	202	4972*	7	139	152	741*	7	24	25	3807*
4	338	266	219	9	34	35	4174*	8	396	362	238	8	395	401	271
5	702	647	178	10	34	157	4446*	9	346	365	201	9	179	141	283
6	487	506	239		-5, 0, 1			10	401	322	249	10	243	253	212
7	854	872	176	1	2524	2378	88	11	32	68	2167*	11	29	75	4939*
8	299	305	192	3	485	386	184	12	33	134	3923*	12	30	25	2431*
9	556	591	282	5	294	214	209	13	34	71	4133*	13	31	13	2827*
10	674	587	253	7	90	14	996*		-5, 4, 1			15	42	110	2991*
11	28	5	5072*	9	248	226	200	1	390	384	192	16	37	136	3702*
12	301	288	210	11	471	457	230	2	65	2	545*		-4, 3, 1		
13	71	106	1246*	13	119	84	1191*	3	360	345	195	1	586	645	271
14	143	193	250	15	107	41	755*	4	360	346	211	2	25	176	5320*
15	262	287	212	17	100	5	655*	5	201	214	193	3	141	225	994*
16	136	274	809*		-5, 1, 1			6	297	287	195	4	26	247	5631*
	-6, 2, 1			1	1137	1120	122	7	32	40	4715*	5	252	313	222
1	343	359	197	2	590	613	175	8	33	17	4094*	6	457	485	235
2	415	432	212	3	400	354	233	9	230	193	235	7	466	608	260
3	211	191	189	4	1321	1245	120	10	34	140	4530*	8	29	28	4987*
4	23	237	5906*	5	950	914	140		-4, 0, 1			9	592	526	181

STRUCTURE FACTORS FOR C14 H10 S C12

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig
	-4, 3, 1		
0	31	81	2779*
1	352	330	204
12	33	31	2626*
13	34	6	3683*
14	50	147	1061*
	-4, 4, 1		
1	550	584	205
2	30	45	3132*
3	153	158	209
4	31	98	2808*
5	129	186	647*
6	180	166	185
7	294	248	178
8	228	268	234
9	33	68	4165*
10	128	35	1061*
	-4, 5, 1		
1	98	188	1635*
2	34	74	4792*
	-3, 0, 1		
1	1466	1417	67
3	223	176	152
5	479	413	171
7	20	130	4151*
9	388	430	251
11	287	372	200
13	269	331	208
15	32	4	2336*
17	248	313	213
	-3, 1, 1		
1	1204	1144	94
2	499	456	149
3	16	58	4557*
4	236	149	145
5	547	568	169
6	19	32	4260*
7	369	390	260
8	935	923	144
9	973	938	188
10	402	442	243
11	690	762	256
12	28	131	5089*
13	184	243	296
14	193	254	154
15	82	4	684*
16	88	82	1047*
17	34	194	4355*
	-3, 2, 1		
1	517	528	196
2	128	171	700*
3	864	894	147
4	374	332	254
5	618	636	182
6	517	570	210
7	292	254	199
8	907	939	211
9	246	248	212
10	463	497	329
11	85	27	1556*
12	30	119	2698*
13	51	66	1527*
14	32	42	2571*
15	33	99	4372*
16	58	7	1548*
	-3, 3, 1		
1	25	30	5312*
2	25	169	5680*
3	253	288	201
4	167	258	303
5	63	62	2172*
6	234	153	225
7	265	364	205
8	361	256	230
9	522	451	192
10	142	130	214
11	356	287	174
12	447	491	231
13	90	141	750*
14	537	578	293
	-3, 4, 1		
1	287	290	175
2	127	135	233
3	228	141	158
4	302	340	198
5	387	387	170
6	272	231	162
7	542	542	200
8	33	44	4044*
9	33	129	3772*
10	204	244	256
11	102	57	692*
	-3, 5, 1		
1	178	285	301
2	34	38	4354*
3	98	49	631*
	-2, 0, 1		
2	1320	1348	61
4	503	533	134
6	436	430	191
8	457	422	201
10	345	295	223
12	491	499	322
14	155	101	163
16	33	246	3972*
	-2, 1, 1		
1	807	776	100
2	558	545	131
3	450	355	164
4	471	459	167
5	890	910	120
6	570	608	174
7	110	150	771*
8	370	344	176
9	214	292	216
10	141	237	895*
11	948	990	204
12	110	83	825*
13	468	437	322
14	199	117	138
15	52	76	1455*
16	366	381	260
17	152	6	306*
	-2, 2, 1		
1	321	311	200
2	276	286	183
3	20	91	4142*
4	405	395	238
5	386	337	231
6	289	292	189
7	135	192	971*
8	582	615	260
9	318	305	190
10	98	15	1348*
11	29	21	5056*
12	88	17	542*
13	242	257	164
14	129	82	216
15	241	253	203
16	34	164	3762*
	-2, 3, 1		
1	207	152	233
2	354	381	225
3	254	246	197
4	146	116	849*
5	252	266	198
6	263	316	194
7	437	393	235
8	134	82	1047*
9	29	77	5058*
10	30	159	2519*
11	189	199	152
12	73	24	1911*
13	71	101	1078*
14	34	167	4475*
	-2, 4, 1		
2	217	144	138
3	78	102	490*
4	174	154	161
5	518	503	190
6	279	275	152
7	262	254	159
8	32	176	4141*
9	33	186	4166*
10	107	171	902*
11	291	342	183
	-2, 5, 1		
1	155	236	348*
2	165	65	306
3	72	1	1964*
4	162	91	325*
	-1, 0, 1		
3	1152	1190	68
5	3198	3079	78
7	230	208	150
9	773	764	157
11	56	135	2167*
13	212	160	228
15	379	334	219
17	34	15	3672*
	-1, 1, 1		
1	808	775	91
2	767	771	99
3	528	508	139
4	78	116	882*
5	272	292	160
6	1321	1338	107
7	627	635	160
8	1279	1257	125
9	493	481	278
10	237	163	196
11	26	109	4868*
12	28	79	4536*
13	29	86	5026*
14	177	113	150
15	366	318	222
16	33	7	3292*
17	34	64	3894*
	-1, 2, 1		
1	659	653	158
2	199	197	154
3	720	689	147
4	62	205	1393*
5	436	395	209
6	67	183	1298*
7	438	390	292
8	114	241	1114*
9	26	8	4727*

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	-1, 2, 1			5	18	44	2934*	9	200	264	233		1, 3, 1		
0	27	167	4738*	6	853	851	89	10	191	214	234	0	162	285	824*
1	120	206	670*	7	21	73	2719*	11	34	153	4589*	1	402	433	242
12	249	263	166	8	661	667	113		0, 5, 1			2	359	391	207
13	137	87	193	9	23	200	3760*	1	269	301	201	3	664	738	248
15	130	216	977*	10	691	705	164	2	34	86	1901*	4	484	527	300
16	34	163	3847*	11	218	218	158	3	172	309	276	5	155	3	785*
	-1, 3, 1			12	346	352	164	4	257	297	161	6	27	33	4732*
1	120	15	725*	13	330	366	115		1, 0, 1			7	35	214	2859*
2	24	72	5223*	14	437	407	135	1	231	231	104	8	301	417	188
3	571	589	260	16	426	445	172	3	276	287	179	9	216	206	138
4	386	348	246		0, 2, 1			5	92	29	734*	10	321	252	180
5	26	98	4840*	0	489	449	184	7	647	673	151	11	239	181	137
6	27	180	5210*	1	517	490	125	11	241	152	192	12	119	13	1132*
7	27	109	5062*	2	19	42	2952*	13	349	327	231	13	34	237	2229*
8	101	144	1298*	3	1287	1287	79	15	422	367	204		1, 4, 1		
9	29	108	5087*	4	389	367	159	17	242	224	196	0	29	16	5128*
10	209	222	147	5	336	329	130		1, 1, 1			2	30	32	2652*
11	177	140	154	6	32	63	1052*	0	757	753	92	3	132	73	211
12	341	410	235	7	267	259	132	1	140	148	144	4	267	322	181
13	376	428	206	8	25	110	3387*	2	1132	1112	85	5	384	321	229
14	34	296	3935*	9	26	6	3369*	3	854	831	103	6	70	64	1150*
	-1, 4, 1			10	27	57	3408*	4	848	874	113	7	308	246	192
1	346	351	229	11	82	187	955*	5	18	17	4166*	8	233	261	216
3	298	380	203	12	162	184	147	6	433	486	207	9	235	297	231
4	189	211	148	13	305	287	127	7	376	400	174	10	199	283	278
5	253	189	156	14	288	294	140	8	22	7	3762*		1, 5, 1		
6	88	225	926*	15	77	152	768*	9	24	117	4931*	0	163	239	880*
7	268	203	176		0, 3, 1			10	154	91	292	1	34	119	4014*
8	108	304	709*	1	55	193	1557*	11	270	283	184	2	156	162	343*
9	119	220	605*	2	448	473	209	12	358	328	234	3	99	67	1444*
10	56	335	1833*	3	239	221	141	13	479	444	191	4	402	370	223
11	158	82	304	4	136	103	286*	14	447	388	200		2, 0, 1		
	-1, 5, 1			5	730	737	156	15	384	457	213	0	443	444	83
1	106	9	1215*	6	253	258	137	16	146	110	311*	2	1195	1275	70
2	34	15	3904*	7	243	275	148		1, 2, 1			4	598	657	131
3	101	278	1339*	8	209	222	175	0	706	680	147	6	1132	1203	114
4	34	74	4383*	9	30	163	2294*	1	585	572	162	8	197	230	161
	0, 0, 1			10	359	295	134	2	1398	1433	110	10	605	531	254
2	935	919	39	11	381	378	156	3	20	25	4168*	12	28	136	5214*
4	68	63	324*	12	33	72	2761*	4	1100	1085	124	14	353	266	228
6	333	332	133	13	236	234	147	5	102	10	816*	16	127	3	367*
8	984	996	90	14	228	171	205	6	183	150	180		2, 1, 1		
10	1035	1057	130		0, 4, 1			7	550	634	263	0	1850	1875	76
12	223	254	155	0	390	391	233	8	397	451	242	1	891	874	98
14	209	185	105	1	75	23	683*	9	351	377	225	2	789	821	112
16	88	188	483*	3	450	392	135	10	386	445	270	3	328	290	227
	0, 1, 1			4	216	248	119	11	94	132	586*	4	858	824	120
1	255	234	116	5	516	454	129	12	745	643	153	5	1253	1276	109
2	944	939	61	6	146	80	177	13	414	406	218	6	1042	1063	123
3	599	619	88	7	76	52	451*	14	539	541	294	7	78	25	405*
4	175	200	104	8	33	21	1729*	15	34	14	3826*	9	426	469	219

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	2, 1, 1			0	34	29	4211*	3	408	367	252	14	99	219	1396*
0	53	75	2357*	1	268	246	204	4	559	563	276	15	110	115	591*
11	27	115	5378*	2	34	187	3953*	5	64	17	2053*		4, 2, 1		
12	29	26	4613*	3	34	73	4849*	6	28	146	5212*	0	108	32	865*
13	325	283	183		3, 0, 1			7	278	192	197	1	766	730	164
14	149	130	188	1	634	608	99	8	30	92	5546*	2	149	100	242
15	478	556	320	3	126	110	199	9	92	15	836*	3	337	354	217
16	96	140	954*	5	824	873	129	10	152	55	191	4	352	396	216
	2, 2, 1			7	557	570	190	11	171	101	280	5	161	241	814*
0	478	501	203	9	571	594	261	12	119	145	424*	6	24	43	5339*
1	222	211	146	11	327	362	197	13	34	79	4003*	7	856	951	220
2	127	64	660*	13	30	91	2622*		3, 4, 1			8	214	235	246
3	92	164	924*	15	109	173	701*	0	77	23	1045*	9	28	153	5597*
4	146	149	221		3, 1, 1			1	30	46	1870*	10	29	94	5476*
5	223	239	157	0	56	18	1200*	2	30	95	2698*	11	30	21	2523*
6	306	338	210	1	242	260	146	3	234	261	145	12	326	286	191
7	367	424	248	2	881	893	114	4	105	45	607*	13	105	85	625*
8	226	244	219	3	886	946	121	5	518	465	199	14	145	86	889*
9	103	173	491*	4	545	569	172	6	32	78	2985*		4, 3, 1		
10	208	166	247	5	76	89	1097*	7	270	292	202	0	25	13	5156*
11	29	30	4986*	6	117	122	276*	8	33	66	4259*	1	642	656	251
12	617	549	162	7	22	51	4062*	9	141	89	360*	2	364	346	225
13	173	113	162	8	23	127	5152*	10	34	58	4095*	3	65	61	1987*
14	80	227	1614*	9	25	57	5119*		3, 5, 1			4	34	21	1516*
15	34	17	4023*	10	401	463	251	0	223	226	246	5	144	205	985*
	2, 3, 1			11	28	15	4835*	1	34	117	4109*	6	351	420	218
0	155	152	831*	12	492	536	339	2	34	2	2550*	7	329	360	211
1	24	3	5055*	13	325	312	190		4, 0, 1			8	435	418	223
2	498	425	280	14	303	292	168	0	590	633	131	9	356	246	178
3	68	108	1851*	15	233	171	206	2	1574	1609	91	10	32	111	2894*
4	26	154	5105*	16	140	51	346*	4	3315	3358	95	11	82	55	939*
5	135	37	368*		3, 2, 1			6	1560	1635	121	12	83	22	1486*
6	112	89	839*	0	328	314	202	8	23	197	5443*		4, 4, 1		
7	121	163	421*	1	607	574	174	10	480	400	310	0	30	60	2951*
8	243	159	230	2	1280	1364	130	12	309	242	205	1	344	318	200
9	220	190	134	3	274	326	175	14	118	118	740*	2	39	104	967*
10	38	25	2033*	4	897	959	147	16	66	189	1605*	3	78	86	482*
11	174	150	179	5	270	318	183		4, 1, 1			4	76	149	456*
12	33	173	3984*	6	468	494	307	0	144	157	211	5	480	502	218
13	186	130	277	7	757	793	209	1	50	43	1601*	6	99	118	799*
	2, 4, 1			8	423	395	241	2	406	394	213	7	280	341	191
1	167	191	172	9	118	225	1213*	3	1056	1051	124	8	34	157	3977*
2	51	27	1423*	10	140	63	374*	4	192	136	175	9	227	197	235
3	385	335	228	11	30	29	2489*	5	234	272	166		4, 5, 1		
4	31	125	2554*	12	70	11	625*	6	84	105	644*	0	268	330	213
5	156	69	211	13	106	24	576*	7	81	92	1085*		5, 0, 1		
6	184	159	186	14	151	143	791*	8	226	254	213	1	1194	1128	106
7	188	124	164	15	103	19	952*	9	309	295	217	3	964	972	129
8	95	80	790*		3, 3, 1			10	238	273	223	5	269	248	180
9	228	246	243	0	25	233	5544*	11	421	435	260	7	502	547	284
10	202	300	262	1	279	306	182	12	263	278	184	9	1122	1119	190
	2, 5, 1			2	189	160	267	13	113	29	668*	11	406	429	279

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	5, 0, 1			1	273	356	192	4	28	173	5259*	9	373	336	241
	118	204	824*	2	31	99	3071*	5	29	60	5149*	10	253	266	158
	222	221	232	3	362	332	209	6	131	133	249	11	297	338	200
	5, 1, 1			4	282	313	169	7	31	32	1721*	12	322	285	228
0	906	908	136	5	57	109	1251*	8	31	142	3088*	13	139	84	1021*
1	486	433	200	6	120	23	1180*	9	32	99	3352*		7, 3, 1		
2	944	948	137	7	33	204	2202*	10	154	88	820*	0	28	7	5228*
3	735	774	165	8	111	42	697*	11	117	103	1183*	1	167	112	869*
4	544	570	200		6, 0, 1				6, 4, 1			2	82	4	1742*
5	278	254	180	0	18	59	5055*	0	416	342	262	3	29	149	5271*
6	112	132	886*	2	780	797	160	1	31	179	3201*	4	139	27	1091*
7	84	75	687*	4	1113	1118	145	2	32	117	3286*	5	219	210	171
8	130	144	992*	8	1063	1101	194	3	32	100	3464*	6	31	75	3432*
9	133	12	1023*	10	673	582	258	4	32	118	2735*	7	412	340	272
10	205	147	263	12	301	293	184	5	204	318	286	8	169	160	238
11	29	121	5230*	14	33	95	4398*	6	33	44	4352*	9	33	104	4600*
12	31	149	2880*		6, 1, 1			7	34	13	4308*	10	34	83	5221*
13	204	95	165	0	865	848	150	8	186	136	309	11	199	147	280
14	33	219	4111*	1	109	102	333*		7, 0, 1				7, 4, 1		
15	136	79	934*	2	20	178	5142*	1	277	272	183	0	352	328	198
	5, 2, 1			3	222	237	174	3	373	405	209	1	32	19	3769*
0	289	307	163	4	22	75	4947*	5	557	584	263	2	32	16	2602*
1	528	517	217	5	284	359	172	7	357	338	235	3	55	107	1479*
2	22	249	4776*	6	409	337	237	9	28	102	5224*	4	33	193	5023*
3	314	355	200	7	220	255	229	11	187	136	186	5	137	119	1055*
4	721	750	222	8	134	109	997*	13	288	269	203	6	34	97	4447*
5	429	471	230	9	327	321	210		7, 1, 1			7	34	54	4804*
6	907	947	219	10	263	306	229	0	170	139	226		8, 0, 1		
7	153	197	340*	11	152	137	208	1	21	24	4825*	0	806	834	168
8	495	557	334	12	31	34	3061*	2	53	107	1975*	2	380	368	218
9	218	172	257	13	409	429	266	3	332	309	197	4	595	607	263
10	30	18	3185*	14	89	83	1492*	4	246	217	203	6	824	812	229
11	246	191	151		6, 2, 1			5	24	85	5170*	8	998	1046	228
12	309	332	219	0	570	563	222	6	25	86	5609*	10	653	629	209
13	283	216	195	1	432	431	177	7	26	112	5354*	12	90	120	1072*
14	395	440	234	2	333	348	200	8	174	128	303		8, 1, 1		
	5, 3, 1			3	255	299	195	9	211	269	273	0	1537	1516	143
0	521	521	308	4	298	357	207	10	87	175	1122*	1	275	304	180
1	26	217	5349*	5	144	110	351*	11	78	149	925*	2	142	128	897*
2	237	266	228	6	123	99	1125*	12	192	128	190	3	138	9	365*
3	250	250	222	7	246	218	231	13	33	127	4941*	4	97	88	1372*
4	373	427	242	8	112	33	956*	14	162	45	811*	5	25	83	2045*
5	134	101	1026*	9	30	107	5271*		7, 2, 1			6	181	70	290
6	29	21	5055*	10	198	195	181	0	24	130	5690*	7	27	8	5101*
7	655	587	177	11	370	372	203	1	560	701	284	8	28	46	3749*
8	400	379	252	12	42	15	2323*	2	440	395	233	9	423	382	252
9	225	256	160	13	283	262	198	3	500	523	327	10	101	64	851*
10	33	159	4254*		6, 3, 1			4	26	58	5678*	11	32	85	2385*
11	162	46	865*	0	421	484	277	5	290	316	192	12	33	75	4965*
12	130	16	1047*	1	69	194	2104*	6	574	643	297	13	34	159	3440*
	5, 4, 1			2	27	107	5437*	7	315	347	224		8, 2, 1		
0	357	401	211	3	55	63	2662*	8	337	398	217	0	234	220	230

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig
8, 2, 1			
1	25	72	5750*
2	26	141	5524*
3	296	189	198
4	426	521	273
5	296	336	200
6	28	82	3849*
7	199	142	306
8	30	70	3236*
9	31	127	3075*
10	129	18	297*
11	237	285	240
12	34	75	1848*
8, 3, 1			
0	421	405	284
1	443	380	272
2	29	69	5386*
3	521	567	236
4	207	245	184
5	113	139	674*
6	119	126	875*
7	115	115	945*
8	93	92	1052*
9	34	78	4552*
10	56	187	1568*
8, 4, 1			
0	79	68	960*
1	111	49	1411*
2	204	81	273
3	356	374	228
4	34	20	4646*
5	267	382	234
6	47	32	2395*
9, 0, 1			
1	391	399	255
3	156	160	910*
5	524	506	302
7	28	23	5400*
9	113	24	314*
11	208	193	195
13	466	436	260
9, 1, 1			
0	550	518	290
1	24	68	5650*
2	703	685	240
3	196	259	277
4	214	237	262
5	436	390	258
6	304	289	194
7	458	469	264
8	136	53	258
9	80	47	1181*
10	32	77	3319*
11	166	49	304
12	34	57	4976*
9, 2, 1			
0	235	237	229
1	124	120	659*
2	27	115	5613*
3	149	34	990*
4	282	285	213
5	180	211	341
6	30	13	3038*
7	295	302	200
8	263	250	182
9	199	156	200
10	403	314	260
11	34	150	3098*
9, 3, 1			
0	221	163	172
1	323	299	196
2	385	420	218
3	31	83	3589*
4	117	211	937*
5	48	128	2058*
6	32	71	3488*
7	164	117	889*
8	244	195	239
9	34	50	4610*
9, 4, 1			
0	116	249	1003*
1	194	408	980*
2	117	139	933*
3	285	333	223
4	304	324	214
10, 0, 1			
0	383	373	266
2	859	883	220
4	27	154	5315*
6	28	178	5776*
8	362	389	232
10	32	84	3482*
12	34	306	5019*
10, 1, 1			
0	98	162	1044*
1	905	898	227
2	96	72	1052*
3	231	218	256
4	581	536	300
5	28	22	5267*
6	29	152	5958*
7	307	290	189
8	199	140	191
9	292	268	196
10	33	184	4732*
11	74	107	784*
10, 2, 1			
0	27	220	5978*
1	286	241	209
2	188	258	323
3	34	222	4779*
4	416	502	296
5	30	102	2585*
6	131	113	293*
7	45	144	1723*
8	32	24	3372*
9	166	33	932*
10	34	96	4552*
10, 3, 1			
0	31	94	3321*
1	350	346	227
2	220	210	194
3	121	55	865*
4	57	275	2222*
5	162	173	336*
6	142	36	979*
7	34	19	3297*
8	34	160	4404*
10, 4, 1			
0	34	127	3564*
1	34	153	4978*
2	34	11	4793*
11, 0, 1			
1	26	59	5601*
3	229	190	256
5	53	20	2929*
7	208	230	191
9	32	105	2399*
11	238	164	247
11, 1, 1			
0	27	246	6032*
1	27	91	3970*
2	612	582	301
3	252	200	237
4	283	287	231
5	523	541	262
6	198	247	203
7	72	34	819*
8	32	82	3565*
9	33	153	5040*
10	34	107	5267*
11	83	51	1320*
11, 2, 1			
0	29	70	5432*
1	141	163	824*
2	335	313	182
3	247	294	165
4	31	74	4005*
5	306	364	194
6	32	24	3161*
7	357	349	225
8	33	94	4960*
9	34	31	4888*
11, 3, 1			
0	338	278	226
1	340	353	202
2	467	394	261
3	151	57	928*
4	127	37	441*
5	34	2	4947*
6	274	242	208
12, 0, 1			
6	202	155	194
8	216	202	270
10	326	310	206
12, 1, 1			
3	327	320	186
4	695	672	211
5	31	66	3220*
6	161	226	268
7	365	346	186
8	348	321	204
9	34	3	4900*
12, 2, 1			
0	244	194	169
1	30	45	3403*
2	479	495	261
3	381	398	228
4	74	201	1681*
5	148	164	279
6	305	312	216
7	52	36	3002*
8	263	260	228
12, 3, 1			
0	145	57	408*
1	153	340	1160*
2	33	161	5170*
3	152	11	1036*
4	111	81	749*
5	345	285	241
13, 0, 1			
3	30	12	3719*
5	32	32	3571*
7	33	29	4523*
9	34	41	4897*
13, 1, 1			
0	96	184	1109*
1	85	122	863*

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig
13, 1, 1			
2	31	54	2539*
3	300	294	213
4	274	229	174
5	146	146	283
6	393	418	258
7	264	309	239
8	58	139	1445*
13, 2, 1			
0	94	34	1062*
1	206	127	194
2	250	253	184
3	316	378	210
4	293	328	215
5	33	223	3581*
6	34	159	5184*
7	164	64	360*
13, 3, 1			
0	549	537	343
1	163	6	1024*
2	124	173	955*
3	48	231	2145*
14, 0, 1			
0	31	8	3243*
2	233	167	180
4	139	80	900*
6	221	250	268
14, 1, 1			
0	31	22	3321*
1	345	334	237
2	130	284	1006*
3	272	295	192
4	225	194	273
5	82	63	1772*
6	262	179	229
7	34	91	5091*
14, 2, 1			
0	33	153	4708*
1	136	237	1110*
2	79	118	1392*
3	34	138	5057*
4	240	250	276
5	34	48	5121*
15, 0, 1			
1	192	158	303
3	425	464	286
5	34	47	5632*
15, 1, 1			
0	212	193	280
1	111	235	1456*
2	416	315	297
3	150	335	824*
4	34	11	4768*
5	103	34	1490*
15, 2, 1			
0	354	280	232
1	34	173	3445*
2	237	207	270
16, 0, 1			
0	431	401	244
2	34	49	3280*

Table S-2. Calculated Hydrogen Atom Parameters

	x	y	z	Biso
H 4	0.1693(13)	0.993 (3)	0.1145(10)	7.7(3)
H 5	0.2901(13)	0.985 (3)	0.1220(10)	6.8(3)
H 6	0.3527(6)	0.664 (5)	0.1654(11)	5.1(3)
H 7	0.2945(13)	0.351 (3)	0.2012(10)	6.7(3)
H 8	0.1737(13)	0.359 (3)	0.1937(10)	7.3(3)
H10	0.1004(10)	0.423 (3)	0.2521(13)	6.8(3)
H11	0.0659(11)	0.488 (4)	0.3585(10)	5.8(3)
H12	0.0124(12)	0.831 (5)	0.3791(8)	7.3(3)
H13	-0.0064(11)	1.107 (3)	0.2932(14)	9.7(3)
H14	0.0282(11)	1.042 (3)	0.1869(10)	6.6(3)
H 4A	0.7029(10)	0.249 (4)	0.0278(11)	8.1(3)
H 5A	0.8158(14)	0.346 (3)	0.0131(9)	6.3(3)
H 6A	0.9073(7)	0.093 (5)	0.0468(11)	6.6(3)
H 7A	0.8860(10)	-0.256 (4)	0.0952(11)	9.6(3)
H 8A	0.7731(14)	-0.3531(25)	0.1099(9)	5.8(3)
H10A	0.6982(11)	-0.461 (3)	0.1622(12)	7.8(3)
H11A	0.6948(11)	-0.481 (3)	0.2800(12)	6.1(3)
H12A	0.6521(12)	-0.175 (5)	0.3361(6)	7.0(3)
H13A	0.6129(11)	0.151 (3)	0.2745(13)	9.1(3)
H14A	0.6163(11)	0.171 (3)	0.1567(12)	9.0(3)

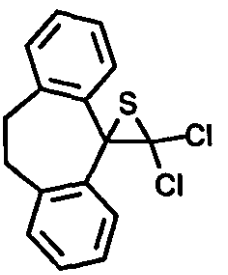
Hydrogen positions calculated assuming a C-H distance of 1.08 A.
Biso(H) is from Uiso(H) = 0.01 + Ueq(C) for the attached carbon.

Table S-3. Anisotropic u(i,j) values *100.
E.S.Ds. refer to the last digit printed

	u11	u22	u33	u12	u13	u23
Cl 1	7.8(6)	6.3(5)	6.4(5)	-0.4(5)	1.3(4)	-1.1(5)
Cl 2	4.9(5)	6.1(6)	9.8(6)	-1.5(5)	0.7(4)	0.0(5)
S	5.1(5)	5.2(5)	6.6(5)	-0.2(5)	0.9(4)	2.0(4)
C 1	6.8(22)	5.5(20)	4.9(18)	1.7(19)	1.8(16)	-2.0(17)
C 2	7.9(21)	5.7(20)	2.3(15)	-0.5(19)	0.1(15)	-2.7(16)
Cl 1A	14.6(9)	9.9(7)	6.3(5)	-2.3(7)	0.0(5)	-0.7(5)
Cl 2A	9.9(8)	13.9(9)	12.2(7)	-6.2(7)	1.0(6)	0.9(7)
S A	10.5(8)	9.4(8)	8.1(6)	1.5(7)	0.3(6)	0.8(6)
C 1A	12.4(29)	4.9(22)	6.1(21)	-5.1(23)	0.2(21)	-0.6(17)
C 2A	3.7(18)	9.5(24)	6.2(19)	-0.4(19)	-0.5(15)	0.6(19)

Anisotropic Temperature Factors are of the form
Temp=-2*Pi*Pi*(h*h*u11*astar*astar+---+2*h*k*u12*astar*bstar+---)

Compound **123**



a) Table of Bond Distances (Å) and Bond Angles(^{o})
b) Table of Torsion Angles(^{o})
c) Table of Observed and Calculated Structure Factors
d) Table of Calculated Hydrogen Atom Parameters
e) Table of Anisotropic u(i, j) Values

Table 3. Bond Distances(A) and Angles(Degrees)

S-C(1)	1.769(6)	C(6)-C(7)	1.373(15)
S-C(2)	1.844(6)	C(7)-C(8)	1.398(11)
Cl(1)-C(1)	1.763(6)	C(8)-C(9)	1.506(12)
Cl(2)-C(1)	1.761(6)	C(9)-C(10)	1.448(12)
C(1)-C(2)	1.507(8)	C(10)-C(11)	1.514(10)
C(2)-C(3)	1.536(8)	C(11)-C(12)	1.400(9)
C(2)-C(16)	1.512(8)	C(11)-C(16)	1.383(9)
C(3)-C(4)	1.383(10)	C(12)-C(13)	1.367(10)
C(3)-C(8)	1.397(10)	C(13)-C(14)	1.366(11)
C(4)-C(5)	1.402(10)	C(14)-C(15)	1.390(9)
C(5)-C(6)	1.365(15)	C(15)-C(16)	1.380(8)

C(1)-S-C(2)	49.2(3)	C(5)-C(6)-C(7)	120.1(7)
S-C(1)-Cl(1)	117.3(3)	C(6)-C(7)-C(8)	121.8(8)
S-C(1)-Cl(2)	118.2(3)	C(3)-C(8)-C(7)	117.6(7)
S-C(1)-C(2)	68.0(3)	C(3)-C(8)-C(9)	126.9(6)
Cl(1)-C(1)-Cl(2)	109.5(3)	C(7)-C(8)-C(9)	115.3(7)
Cl(1)-C(1)-C(2)	119.6(4)	C(8)-C(9)-C(10)	122.9(6)
Cl(2)-C(1)-C(2)	119.1(4)	C(9)-C(10)-C(11)	115.7(6)
S-C(2)-C(1)	62.8(3)	C(10)-C(11)-C(12)	120.8(6)
S-C(2)-C(3)	116.2(4)	C(10)-C(11)-C(16)	120.2(5)
S-C(2)-C(16)	116.8(4)	C(12)-C(11)-C(16)	119.0(6)
C(1)-C(2)-C(3)	118.7(5)	C(11)-C(12)-C(13)	120.9(6)
C(1)-C(2)-C(16)	118.3(5)	C(12)-C(13)-C(14)	119.9(6)
C(3)-C(2)-C(16)	114.5(5)	C(13)-C(14)-C(15)	120.3(6)
C(2)-C(3)-C(4)	118.9(6)	C(14)-C(15)-C(16)	120.2(5)
C(2)-C(3)-C(8)	120.5(6)	C(2)-C(16)-C(11)	118.6(5)
C(4)-C(3)-C(8)	120.6(6)	C(2)-C(16)-C(15)	121.6(5)
C(3)-C(4)-C(5)	119.9(7)	C(11)-C(16)-C(15)	119.8(5)
C(4)-C(5)-C(6)	119.8(8)		

Table S-4. Torsion Angles in Degrees

C 2	S	C 1	CL 1	-113.0(4)	C 2	S	C 1	CL 2	112.3(4)
C 2	S	C 1	C 2	0.0(3)	C 1	S	C 2	C 1	0.0(3)
C 1	S	C 2	C 3	-110.4(4)	C 1	S	C 2	C16	109.7(4)
C 1	CL 1	CL 2	C 1	0.0(3)	CL 2	CL 1	C 1	S	-138.4(3)
CL 2	CL 1	C 1	CL 2	0.0(1)	CL 2	CL 1	C 1	C 2	142.7(4)
CL 1	CL 2	C 1	S	138.0(3)	CL 1	CL 2	C 1	CL 1	0.0(1)
CL 1	CL 2	C 1	C 2	-142.9(4)	S	C 1	C 2	S	0.0(1)
S	C 1	C 2	C 3	106.5(5)	S	C 1	C 2	C16	-107.4(5)
CL 1	C 1	C 2	S	109.8(4)	CL 1	C 1	C 2	C 3	-143.7(6)
CL 1	C 1	C 2	C16	2.4(2)	CL 2	C 1	C 2	S	-111.0(4)
CL 2	C 1	C 2	C 3	-4.5(2)	CL 2	C 1	C 2	C16	141.6(6)
S	C 2	C 3	C 4	-20.1(3)	S	C 2	C 3	C 8	160.5(6)
C 1	C 2	C 3	C 4	-91.9(6)	C 1	C 2	C 3	C 8	88.7(6)
C16	C 2	C 3	C 4	120.8(7)	C16	C 2	C 3	C 8	-58.6(5)
S	C 2	C16	C11	-151.1(6)	S	C 2	C16	C15	30.2(3)
C 1	C 2	C16	C11	-79.2(5)	C 1	C 2	C16	C15	102.2(6)
C 3	C 2	C16	C11	68.3(5)	C 3	C 2	C16	C15	-110.3(6)
C 2	C 3	C 4	C 5	-179.2(8)	C 8	C 3	C 4	C 5	0.2(4)
C 2	C 3	C 8	C 7	-179.1(8)	C 2	C 3	C 8	C 9	4.2(4)
C 4	C 3	C 8	C 7	1.5(4)	C 4	C 3	C 8	C 9	-175.2(8)
C 3	C 4	C 5	C 6	-2.2(5)	C 4	C 5	C 6	C 7	2.4(4)
C 5	C 6	C 7	C 8	-0.6(4)	C 6	C 7	C 8	C 3	-1.3(5)
C 6	C 7	C 8	C 9	175.7(10)	C 3	C 8	C 9	C10	-0.4(4)
C 7	C 8	C 9	C10	-177.2(10)	C 8	C 9	C10	C11	51.5(5)
C 9	C10	C11	C12	112.1(8)	C 9	C10	C11	C16	-67.1(6)
C10	C11	C12	C13	-180.0(8)	C16	C11	C12	C13	-0.8(4)
C10	C11	C16	C 2	1.1(4)	C10	C11	C16	C15	179.8(7)
C12	C11	C16	C 2	-178.1(7)	C12	C11	C16	C15	0.6(3)
C11	C12	C13	C14	0.6(4)	C12	C13	C14	C15	-0.2(4)
C13	C14	C15	C16	0.0(4)	C14	C15	C16	C 2	178.4(7)
C14	C15	C16	C11	-0.2(4)					

Table S-1. Observed and Calculated Structure Factors for C16 H12 S Cl2

STRUCTURE FACTORS FOR C16 H12 S C12

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
-10,	0,	1		5	192	204	107	10	79	98	99	8	36	39	411*
2	58	49	161*	6	44	28	438*	12	97	93	79	9	68	54	349*
4	22	24	1076*	7	20	65	1218*	14	227	231	136	10	103	106	90
-9,	0,	1		8	102	106	89	16	20	40	1345*	11	56	106	511*
2	146	146	94	9	68	14	105	18	156	159	101	12	21	52	1183*
4	114	117	87	10	79	74	99	-7,	1,	1		13	42	80	527*
6	82	76	110	11	20	28	523*	1	89	99	84	14	41	42	404*
8	58	74	422*	12	98	96	91	2	159	173	112	15	87	85	106
10	158	184	104	13	21	23	1174*	3	256	256	116	-7,	4,	1	
12	113	117	96	14	120	91	82	4	39	81	590*	1	103	114	94
-9,	1,	1		15	42	24	258*	5	164	163	103	2	21	20	1117*
1	139	162	89	16	22	2	1397*	6	112	117	78	3	21	18	1159*
2	87	102	104	-8,	2,	1		7	29	82	796*	4	21	23	1227*
3	49	9	476*	1	57	71	393*	8	18	31	807*	5	137	142	94
4	35	17	651*	2	79	72	105	9	129	136	85	6	60	31	146*
5	21	53	1263*	3	20	22	1028*	10	19	34	1237*	7	83	62	108
6	30	36	845*	4	80	72	102	11	168	172	93	8	59	66	154*
7	21	50	1167*	5	108	105	85	12	33	61	359*	9	21	15	1014*
8	42	26	527*	6	149	171	101	13	46	50	170*	10	69	56	133
9	94	85	94	7	143	129	101	14	102	100	85	11	104	110	100
10	56	16	414*	8	49	57	169*	15	48	65	177*	-6,	0,	1	
11	38	38	596*	9	47	53	529*	16	110	128	90	2	116	105	82
12	22	20	1013*	10	21	32	1066*	17	127	124	85	4	301	315	99
-9,	2,	1		11	143	145	101	18	21	7	1052*	6	343	345	99
1	114	105	90	12	21	40	1277*	19	22	74	1178*	8	224	213	109
2	37	54	707*	13	46	38	533*	-7,	2,	1		10	17	16	1154*
3	34	18	722*	14	62	58	152*	1	93	97	93	12	144	141	99
4	122	114	87	15	64	55	410*	2	216	231	141	14	269	281	117
5	157	153	95	-8,	3,	1		3	215	199	90	16	243	231	136
6	33	18	748*	1	170	150	112	4	116	134	82	18	77	97	118
7	55	83	451*	2	78	82	123	5	107	101	81	20	113	120	94
8	46	4	338*	3	21	78	1105*	6	104	101	84	-6,	1,	1	
9	22	3	1287*	4	21	5	1151*	7	126	122	81	1	220	200	105
10	22	9	1324*	5	21	9	1220*	8	281	309	140	2	50	6	278*
-9,	3,	1		6	111	117	84	9	221	187	121	3	147	145	98
1	22	48	1082*	7	21	37	1170*	10	53	62	418*	4	102	105	71
2	22	53	1234*	8	44	32	568*	11	20	41	1184*	5	155	153	98
3	71	59	386*	9	85	94	116	12	48	10	435*	6	232	214	102
-8,	0,	1		10	30	17	302*	13	29	48	341*	7	242	239	118
2	200	200	103	11	59	53	443*	14	26	15	861*	8	62	66	113
4	212	215	142	12	25	1	1050*	15	59	44	374*	9	331	340	110
6	58	9	343*	-8,	4,	1		16	61	57	349*	10	18	23	1154*
8	103	103	82	1	84	66	110	17	86	84	111	11	203	200	95
10	20	14	1110*	2	22	13	1249*	18	26	65	444*	12	56	7	135*
12	160	168	99	3	22	13	1032*	-7,	3,	1		13	125	127	83
14	31	37	420*	4	22	26	1178*	1	19	15	1081*	14	40	40	534*
16	137	127	96	5	70	60	130	2	116	127	81	15	19	34	1144*
-8,	1,	1		-7,	0,	1		3	58	69	418*	16	53	125	509*
1	111	131	85	2	56	32	121*	4	45	19	503*	17	168	163	115
2	119	119	82	4	156	169	100	5	173	188	116	18	20	29	1053*
3	183	188	113	6	278	310	124	6	20	21	1100*	19	21	2	1148*
4	69	65	118	8	262	265	124	7	96	98	94	20	21	15	1176*

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
-6, 1, l				10	160	154	102	1	183	194	122	10	52	35	399*
1	22	39	1299*	11	48	69	506*	2	137	120	94	11	34	39	612*
-6, 2, l				12	21	63	1393*	3	189	193	119	12	102	106	87
1	36	55	514*	13	38	5	319*	4	129	135	84	13	56	24	137*
2	43	56	454*	14	22	59	1185*	5	16	18	993*	14	21	15	719*
3	64	64	106	15	22	18	1114*	6	97	99	66	15	113	101	86
4	199	212	122	-6, 5, l				7	107	111	72	16	165	156	109
5	26	45	753*	1	67	60	138*	8	77	79	86	17	22	14	1024*
6	187	168	126	2	40	31	388*	9	23	53	354*	-5, 5, l			
7	18	13	1167*	3	134	122	86	10	45	14	146*	1	161	160	106
8	135	145	90	4	21	12	1249*	11	193	205	136	2	128	124	89
9	233	244	126	5	154	144	102	12	159	166	108	3	80	69	115
10	18	5	1250*	6	44	37	612*	13	18	26	1213*	4	55	25	147*
11	147	140	103	7	33	23	285*	14	200	197	104	5	35	8	611*
12	69	56	111	8	48	92	604*	15	140	137	81	6	54	48	164*
13	85	66	97	9	40	25	415*	16	260	271	138	7	142	148	99
14	95	88	89	-5, 0, l				17	20	39	1216*	8	56	76	453*
15	194	193	111	2	269	266	92	18	20	17	995*	9	112	106	96
16	48	39	324*	4	125	133	85	19	51	15	400*	10	56	22	411*
17	76	62	108	6	127	133	76	20	21	14	1164*	11	22	19	1045*
18	21	16	1068*	8	193	180	117	21	72	76	382*	12	45	16	339*
19	88	87	108	10	441	445	94	-5, 3, l				-4, 0, l			
20	45	38	579*	12	493	487	98	1	130	140	84	2	196	213	87
-6, 3, l				14	164	191	107	2	47	29	277*	4	79	75	61
1	210	237	104	16	110	110	75	3	85	89	87	6	547	527	73
2	184	175	109	18	44	2	309*	4	255	270	115	8	589	581	78
3	99	107	85	20	127	117	80	5	61	8	329*	10	427	442	85
4	18	0	1116*	22	105	93	93	6	187	204	101	12	16	34	964*
5	98	103	90	-5, 1, l				7	176	168	103	14	216	220	124
6	131	116	83	1	322	317	87	8	88	80	92	16	277	251	106
7	186	181	108	2	46	84	320*	9	305	322	117	18	164	158	90
8	196	201	105	3	227	228	94	10	185	210	113	20	20	16	730*
9	88	96	105	4	15	19	979*	11	131	124	92	22	102	106	93
10	142	129	84	5	116	104	68	12	19	6	1130*	24	54	64	512*
11	43	8	287*	6	258	261	94	13	55	23	140*	-4, 1, l			
12	120	131	86	7	207	217	103	14	19	84	1216*	1	1026	1037	70
13	95	97	99	8	16	8	995*	15	20	17	1021*	2	13	59	1106*
14	28	1	746*	9	16	12	1135*	16	60	23	354*	3	407	401	75
15	21	25	1073*	10	42	18	409*	17	21	13	1142*	4	636	624	71
16	21	13	984*	11	351	342	101	18	21	19	1120*	5	63	51	81
17	39	75	667*	12	96	106	81	19	70	58	118	6	315	304	85
18	22	37	1070*	13	260	274	115	20	22	2	1072*	7	203	202	101
-6, 4, l				14	257	249	126	-5, 4, l				8	24	20	395*
1	46	5	472*	15	108	101	77	1	109	108	85	9	148	148	79
2	29	39	368*	16	139	155	91	2	215	221	141	10	388	389	90
3	61	64	356*	17	30	61	701*	3	19	38	1047*	11	313	325	97
4	20	8	1162*	18	62	102	412*	4	19	25	1098*	12	157	161	101
5	60	46	330*	19	43	16	224*	5	147	145	93	13	202	191	119
6	55	38	392*	20	25	11	733*	6	61	20	355*	14	76	79	96
7	20	54	1179*	21	158	168	100	7	44	79	356*	15	240	227	119
8	20	8	1077*	22	21	14	1148*	8	55	44	350*	16	200	206	136
9	95	90	94	-5, 2, l				9	108	111	83	17	160	154	90

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	-4, 1, 1			20	40	29	598*	16	368	376	103	22	21	53	1148*
18	67	47	114	21	51	8	398*	18	161	166	93	23	63	51	382*
19	78	86	102		-4, 4, 1			20	19	7	1058*		-3, 3, 1		
20	45	32	166*	1	28	5	683*	22	140	158	97	1	105	106	67
21	137	143	89	2	18	66	1347*	24	87	80	100	2	480	476	84
22	21	65	1121*	3	194	208	133		-3, 1, 1			3	276	280	102
23	37	70	734*	4	131	129	93	1	77	91	58	4	364	361	87
24	22	44	1112*	5	137	125	92	2	530	533	63	5	161	136	90
	-4, 2, 1			6	95	92	82	3	97	87	63	6	111	86	72
1	421	416	81	7	47	7	274*	4	389	386	71	7	125	123	78
2	326	341	90	8	64	68	123	5	536	531	68	8	368	375	95
3	21	39	261*	9	106	116	82	6	199	182	86	9	129	120	89
4	359	340	85	10	19	15	1060*	7	562	584	71	10	262	263	112
5	30	61	470*	11	19	34	1132*	8	75	68	67	11	181	179	90
6	65	53	83	12	64	60	328*	9	112	108	80	12	17	31	1055*
7	70	66	80	13	135	130	85	10	464	451	80	13	159	160	109
8	159	159	87	14	60	8	350*	11	99	75	65	14	33	61	474*
9	104	108	70	15	97	104	99	12	69	41	75	15	246	262	130
10	156	145	91	16	168	165	107	13	163	154	92	16	177	182	116
11	60	67	111	17	40	22	399*	14	95	83	69	17	98	102	93
12	237	257	121	18	47	17	283*	15	181	190	124	18	35	28	579*
13	157	151	103		-4, 5, 1			16	95	97	83	19	88	86	104
14	48	54	415*	1	20	35	1228*	17	344	360	117	20	134	117	95
15	222	217	142	2	20	86	1229*	18	32	46	664*	21	21	37	1164*
16	243	256	135	3	53	33	349*	19	96	92	86	22	69	73	137
17	208	205	109	4	31	79	720*	20	29	11	780*		-3, 4, 1		
18	67	107	367*	5	134	112	90	21	48	85	528*	1	61	38	317*
19	20	56	987*	6	20	23	1136*	22	81	70	104	2	157	160	100
20	20	47	1108*	7	140	133	98	23	63	4	356*	3	230	212	110
21	76	73	113	8	22	36	911*	24	52	64	308*	4	101	106	80
22	54	14	159*	9	106	102	87		-3, 2, 1			5	96	106	82
23	22	53	1166*	10	84	81	107	1	546	520	73	6	298	309	124
	-4, 3, 1			11	37	12	564*	2	85	75	62	7	27	16	708*
1	155	149	102	12	46	8	359*	3	389	365	77	8	90	87	85
2	54	100	322*	13	55	16	282*	4	13	32	1001*	9	18	53	1144*
3	145	151	82	14	148	142	98	5	171	173	105	10	61	4	305*
4	306	316	104		-4, 6, 1			6	353	368	83	11	19	63	1218*
5	261	258	110	1	47	80	422*	7	219	216	99	12	118	126	75
6	341	319	96	2	54	46	385*	8	243	234	93	13	30	39	550*
7	256	239	104	3	99	94	97	9	28	21	479*	14	20	42	1173*
8	17	13	1022*	4	22	48	837	10	100	95	67	15	61	75	139*
9	102	98	72	5	50	60	535*	11	116	120	77	16	20	9	1011*
10	157	150	111	6	109	98	99	12	157	159	89	17	21	42	1166*
11	98	93	81	7	44	2	291*	13	159	147	91	18	154	144	109
12	124	127	85		-3, 0, 1			14	101	92	73	19	22	69	1353*
13	18	7	766*	2	617	606	59	15	17	54	1229*		-3, 5, 1		
14	56	42	145*	4	185	193	80	16	312	316	113	1	147	135	102
15	62	72	138*	6	270	266	72	17	103	94	81	2	50	45	152*
16	47	49	438*	8	374	359	73	18	47	25	390*	3	19	18	1085*
17	47	56	489*	10	143	150	82	19	111	116	80	4	88	85	94
18	137	138	91	12	244	250	98	20	112	132	84	5	82	65	99
19	21	6	945*	14	371	357	94	21	74	77	121	6	19	52	1101*

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
-3,	5, 1			17	139	142	94	18	214	245	112	8	29	12	546*
7	64	52	124	18	18	52	1216*	19	67	53	376*	9	108	102	94
8	20	7	1038*	19	18	41	1171*	20	20	45	1211*	10	56	36	436*
9	27	10	303*	20	110	102	82	21	106	120	95	11	22	21	1013*
10	20	23	1110*	21	162	175	97	22	21	42	1063*	-1,	0, 1		
11	197	204	115	22	20	96	1173*	-2,	4, 1			2	1008	987	35
12	35	25	275*	23	146	154	90	1	16	52	1201*	4	749	736	44
13	164	150	108	24	21	44	1288*	2	340	338	101	6	98	111	66
14	86	83	117	25	108	96	87	3	131	130	80	8	141	151	93
15	35	23	710*	-2,	2, 1			4	343	351	108	10	13	5	928*
16	22	83	1233*	1	65	45	69	5	125	121	80	12	740	721	75
-3,	6, 1			2	72	63	60	6	252	241	121	14	91	103	62
1	94	71	96	3	12	27	890*	7	212	209	130	16	218	218	119
2	21	10	1137*	4	691	676	66	8	60	40	119	18	159	186	108
3	21	84	1321*	5	148	162	106	9	259	251	109	20	351	367	120
4	21	16	1119*	6	272	258	84	10	18	11	1060*	22	63	47	128*
5	73	92	141	7	237	228	87	11	92	95	92	24	54	46	433*
6	21	19	1226*	8	467	480	78	12	51	95	468*	-1,	1, 1		
7	56	32	413*	9	178	182	110	13	88	76	92	1	747	736	44
8	52	25	448*	10	49	22	278*	14	133	127	92	2	38	56	226*
9	91	87	112	11	119	101	77	15	90	110	97	3	464	451	51
10	83	70	119	12	85	75	73	16	137	134	94	4	279	272	60
-2,	0, 1			13	49	3	307*	17	42	44	213*	5	381	390	60
2	919	922	47	14	32	55	515*	18	21	25	1045*	6	747	749	57
4	56	62	72	15	141	152	93	19	88	88	109	7	153	123	94
6	522	514	58	16	17	11	1041*	20	22	7	1131*	8	661	652	64
8	382	395	67	17	29	12	659*	-2,	5, 1			9	437	459	71
10	647	613	70	18	122	84	85	1	84	67	96	10	357	351	80
12	56	44	89	19	104	97	84	2	104	133	89	11	646	637	74
14	138	157	94	20	89	76	93	3	18	67	1195*	12	267	263	87
16	119	117	76	21	78	84	121	4	19	13	996*	13	475	481	81
18	218	209	123	22	130	126	91	5	53	22	364*	14	215	209	103
20	275	261	123	23	51	60	454*	6	33	41	561*	15	28	96	653*
22	149	155	105	24	55	72	306*	7	55	19	331*	16	17	8	1049*
24	45	27	262*	-2,	3, 1			8	19	15	1135*	17	17	2	986*
-2,	1, 1			1	160	156	109	9	152	140	94	18	39	35	465*
1	538	537	55	2	229	241	94	10	20	56	1083*	19	117	114	82
2	233	234	68	3	262	253	88	11	93	105	100	20	43	75	510*
3	532	528	56	4	124	129	86	12	20	24	1130*	21	171	152	111
4	179	188	87	5	25	38	412*	13	49	24	370*	22	52	84	267*
5	955	942	58	6	116	117	71	14	69	90	401*	23	88	78	93
6	296	293	68	7	44	35	378*	15	45	17	190*	24	45	39	540*
7	552	566	65	8	473	482	89	16	67	101	366*	25	26	23	742*
8	519	521	68	9	232	222	107	17	56	36	446*	-1,	2, 1		
9	174	165	93	10	250	251	108	-2,	6, 1			1	11	34	999*
10	316	315	81	11	227	200	105	1	202	200	112	2	121	119	63
11	234	240	86	12	100	100	75	2	99	105	99	3	514	510	63
12	218	217	97	13	49	36	271*	3	63	18	320*	4	170	147	83
13	157	157	111	14	141	140	92	4	38	73	646*	5	270	274	75
14	235	239	108	15	105	124	88	5	111	104	94	6	145	138	103
15	186	188	123	16	202	231	105	6	31	14	636*	7	250	243	83
16	126	123	78	17	196	202	111	7	100	127	108	8	460	466	77

STRUCTURE FACTORS FOR C16 H12 S C12

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	-1, 2, 1			11	58	74	134*	24	134	127	62	24	75	88	123
9	70	61	74	12	164	156	115		0, 1, 1				0, 3, 1		
10	562	571	79	13	54	94	399*	1	550	568	30	1	374	385	56
11	61	53	89	14	64	66	352*	2	949	960	30	2	250	252	64
12	182	193	117	15	177	160	106	3	216	211	40	3	294	297	59
13	16	10	900*	16	27	66	413*	4	590	601	36	4	78	73	65
14	16	14	947*	17	126	123	85	5	408	412	40	5	279	285	63
15	104	111	75	18	42	51	507*	6	315	314	45	6	404	404	60
16	245	237	120	19	21	28	1022*	7	939	940	41	7	86	82	65
17	43	9	414*	20	34	21	395*	8	241	243	55	8	68	63	56
18	39	40	508*		-1, 5, 1			9	610	616	47	9	116	110	50
19	43	6	250*	1	42	78	473*	10	201	208	64	10	227	216	75
20	204	205	106	2	18	2	995*	11	283	277	59	11	136	137	65
21	141	125	93	3	18	11	1155*	12	42	17	112*	12	443	455	69
22	49	69	453*	4	62	82	346*	13	288	301	63	13	17	2	630*
23	121	99	83	5	144	129	84	14	291	293	66	14	201	210	94
24	44	16	336*	6	59	61	133*	15	360	367	70	15	18	27	864*
	-1, 3, 1			7	19	70	1253*	16	47	33	126*	16	374	391	83
1	445	433	77	8	51	84	458*	17	179	191	67	17	167	177	75
2	49	65	269*	9	43	2	452*	18	213	210	86	18	57	70	129*
3	110	116	77	10	19	35	982*	19	40	12	164*	19	105	93	59
4	357	330	84	11	20	28	1052*	20	152	148	69	20	20	44	883*
5	154	165	82	12	20	13	1226*	21	40	2	201*	21	89	79	102
6	446	460	82	13	20	48	1087*	22	63	60	121	22	107	119	69
7	152	156	91	14	35	24	651*	23	20	12	726*	23	119	105	61
8	312	314	94	15	133	128	86	24	98	95	93		0, 4, 1		
9	180	177	122	16	21	28	690*	25	136	138	64	0	69	57	84
10	75	53	82	17	133	130	92		0, 2, 1			1	171	172	70
11	121	106	84		-1, 6, 1			0	746	751	58	2	82	82	71
12	188	171	121	1	43	47	349*	1	505	499	43	3	269	267	71
13	117	121	79	2	138	139	88	2	513	529	43	4	130	135	63
14	371	386	111	3	114	109	84	3	603	608	44	5	93	83	54
15	251	271	136	4	90	98	103	4	555	555	45	6	329	322	72
16	65	77	325*	5	56	22	441*	5	393	399	49	7	35	36	172*
17	232	233	105	6	114	107	88	6	68	65	48	8	270	286	80
18	153	153	105	7	72	62	125	7	72	76	61	9	75	85	96
19	87	94	102	8	21	80	1253*	8	118	116	50	10	116	116	52
20	20	59	1332*	9	21	54	1275*	9	423	436	55	11	125	117	60
21	50	73	466*	10	21	2	1213*	10	50	57	93	12	59	51	124*
22	47	37	284*	11	40	75	488*	11	219	220	75	13	171	176	74
23	22	5	1169*	12	45	26	307*	12	332	322	63	14	167	167	74
	-1, 4, 1				0, 0, 1			13	281	291	73	15	42	61	216*
1	16	13	922*	4	608	629	29	14	167	175	74	16	105	107	63
2	173	167	92	6	1146	1115	35	15	86	91	78	17	29	7	245*
3	66	60	93	8	326	326	45	16	131	134	58	18	34	66	443*
4	28	34	567*	10	700	687	47	17	18	61	800*	19	21	2	738*
5	55	32	118*	12	336	332	57	18	235	240	93	20	42	44	417*
6	190	174	88	14	26	53	365*	19	55	74	237*		0, 5, 1		
7	231	238	118	16	72	74	62	20	63	62	88	1	52	74	144*
8	328	326	109	18	28	30	447*	21	98	96	84	2	114	125	58
9	105	100	73	20	192	187	77	22	25	77	727*	3	139	127	65
10	274	276	117	22	299	300	93	23	50	40	264*	4	180	187	75

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	0, 5, 1			10	403	393	77	9	289	292	96	15	21	15	1161*
5	150	159	71	11	138	148	83	10	206	226	116	16	57	10	397*
6	19	48	544*	12	278	283	85	11	164	160	90	17	66	63	152*
7	79	82	76	13	308	310	89	12	140	135	83		1, 6, 1		
8	19	12	799*	14	16	0	567*	13	17	51	1156*	0	36	74	660*
9	42	34	167*	15	541	550	92	14	109	111	75	1	46	80	523*
10	25	11	467*	16	261	271	117	15	84	86	93	2	47	47	177*
11	20	18	723*	17	196	189	131	16	145	142	91	3	54	39	143*
12	40	24	269*	18	221	215	123	17	148	148	99	4	20	35	1087*
13	31	19	441*	19	18	38	1108*	18	20	74	1349*	5	21	64	1066*
14	44	46	333*	20	19	1	1113*	19	126	129	82	6	21	19	1124*
15	80	67	78	21	70	76	363*	20	127	126	87	7	55	44	150*
16	21	48	519*	22	126	118	81	21	205	208	120	8	104	108	102
17	41	26	414*	23	63	56	137*	22	98	71	103	9	53	95	502*
	0, 6, 1			24	22	40	1187*		1, 4, 1			10	60	109	488*
0	78	76	108	25	102	76	89	0	310	311	95	11	57	20	438*
1	118	111	58		1, 2, 1			1	144	134	94		2, 0, 1		
2	77	62	77	0	13	36	812*	2	86	103	77	0	644	658	47
3	46	84	357*	1	701	699	61	3	171	181	94	2	734	724	49
4	149	139	70	2	67	57	64	4	65	61	95	4	1966	1949	52
5	67	57	120	3	316	327	70	5	16	23	986*	6	507	515	61
6	96	98	91	4	483	502	66	6	313	341	112	8	126	128	77
7	40	52	322*	5	331	342	75	7	85	99	87	10	378	378	80
8	32	44	421*	6	569	574	69	8	17	28	1133*	12	315	304	89
9	87	80	99	7	413	429	77	9	104	117	85	14	63	54	91
10	74	78	108	8	198	189	96	10	270	276	128	16	199	193	114
11	66	76	135*	9	104	105	72	11	180	170	101	18	18	55	1070*
2	22	17	553*	10	30	10	401*	12	354	357	115	20	156	147	108
	1, 0, 1			11	41	30	247*	13	156	137	111	22	163	173	103
2	915	917	37	12	289	289	97	14	187	221	123	24	113	98	87
4	29	19	181*	13	94	88	69	15	56	90	409*		2, 1, 1		
6	1213	1216	53	14	404	403	100	16	57	36	337*	0	872	890	52
8	522	521	62	15	17	14	1135*	17	96	84	94	1	74	72	59
10	352	354	74	16	416	425	101	18	21	36	1093*	2	678	682	54
12	291	276	89	17	102	104	82	19	169	168	108	3	977	963	55
14	15	62	1000*	18	18	26	1117*	20	41	33	266*	4	58	75	74
16	387	389	99	19	19	4	917*		1, 5, 1			5	218	238	77
18	257	255	116	20	44	14	172*	0	34	4	588*	6	43	14	242*
20	136	144	95	21	30	19	405*	1	54	37	341*	7	119	113	75
22	50	55	382*	22	21	3	1112*	2	280	279	135	8	200	198	93
24	66	43	368*	23	21	76	1103*	3	48	4	400*	9	41	37	280*
	1, 1, 1			24	89	75	110	4	228	225	145	10	59	63	84
0	814	806	44		1, 3, 1			5	83	63	103	11	204	201	96
1	150	143	68	0	44	41	261*	6	41	7	248*	12	138	135	74
2	586	586	47	1	180	162	93	7	153	163	98	13	130	135	81
3	281	269	57	2	66	84	75	8	181	182	118	14	146	166	102
4	95	103	61	3	171	165	100	9	154	146	103	15	235	229	120
5	1103	1107	54	4	136	120	83	10	131	126	86	16	276	276	116
6	320	316	68	5	523	526	81	11	20	56	1268*	17	261	244	109
7	598	611	62	6	49	44	114*	12	24	53	602*	18	47	5	165*
8	78	74	56	7	281	269	94	13	20	17	1046*	19	218	200	138
9	98	108	57	8	53	10	274*	14	65	55	350*	20	111	111	86

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	2, 1, 1			21	58	70	451*	10	55	62	476*	11	360	362	96
21	254	283	151	22	122	125	89		3, 0, 1			12	87	88	76
22	94	90	101		2, 4, 1			0	336	321	65	13	213	185	121
23	21	56	1241*	0	225	233	120	2	154	150	91	14	17	53	1051*
24	54	11	273*	1	232	231	113	4	641	628	63	15	133	150	87
	2, 2, 1			2	112	119	72	6	163	181	98	16	165	165	109
0	127	112	71	3	16	14	1089*	8	1125	1113	72	17	104	98	75
1	662	644	66	4	165	181	105	10	897	899	77	18	19	37	1250*
2	437	431	69	5	135	134	88	12	217	206	113	19	57	1	351*
3	170	190	101	6	62	50	325*	14	299	300	111	20	158	170	95
4	830	809	68	7	185	172	95	16	103	94	75	21	108	112	90
5	42	56	302*	8	343	347	112	18	197	191	100	22	95	87	101
6	231	247	90	9	18	20	1169*	20	229	246	155		3, 3, 1		
7	624	632	75	10	138	158	90	22	39	61	602*	0	42	50	237*
8	28	41	208*	11	47	45	162*	24	29	1	813*	1	119	113	80
9	285	281	86	12	66	58	119		3, 1, 1			2	239	235	96
10	105	96	69	13	19	1	996*	0	12	20	1131*	3	105	110	72
11	15	53	1021*	14	31	48	298*	1	736	744	62	4	199	184	106
12	69	66	86	15	39	53	528*	2	12	2	946*	5	81	82	80
13	188	197	121	16	121	116	85	3	151	165	102	6	82	75	79
14	151	156	108	17	66	72	141*	4	62	73	71	7	298	292	106
15	186	190	97	18	58	43	426*	5	425	427	71	8	136	145	85
16	24	15	751*	19	22	56	1436*	6	323	320	79	9	374	353	97
17	197	199	97		2, 5, 1			7	13	22	1009*	10	17	60	1253*
18	202	203	104	0	242	253	145	8	151	127	75	11	236	243	128
19	45	42	400*	1	304	331	128	9	400	417	83	12	56	9	316*
20	20	61	1049*	2	204	212	106	10	112	111	76	13	161	174	95
21	20	10	1075*	3	19	35	1040*	11	236	248	103	14	31	80	534*
22	56	85	470*	4	75	82	120	12	105	105	75	15	67	73	122
23	41	20	349*	5	52	14	149*	13	16	7	994*	16	91	84	89
	2, 3, 1			6	219	223	144	14	167	183	100	17	58	35	308*
0	242	223	94	7	48	80	548*	15	218	223	135	18	20	45	1252*
1	308	317	90	8	136	141	88	16	43	8	429*	19	54	30	432*
2	131	142	85	9	51	4	409*	17	242	231	122	20	140	158	95
3	328	320	87	10	20	31	825*	18	158	141	94	21	22	47	1361*
4	82	73	64	11	20	74	1107*	19	258	250	136		3, 4, 1		
5	400	406	88	12	20	67	1325*	20	34	27	611*	0	199	182	124
6	109	95	78	13	62	53	353*	21	93	70	99	1	17	38	1175*
7	139	155	95	14	21	28	1149*	22	51	85	523*	2	344	350	110
8	87	86	73	15	57	72	396*	23	98	93	101	3	39	84	524*
9	44	28	387*	16	22	1	630*		3, 2, 1			4	171	167	97
10	16	18	971*		2, 6, 1			0	162	164	73	5	17	45	1219*
11	213	202	118	0	31	23	655*	1	555	541	72	6	18	18	1163*
12	17	48	1190*	1	42	34	230*	2	199	187	94	7	237	231	117
13	44	32	155*	2	21	57	1102*	3	13	6	888*	8	23	16	839*
14	34	74	673*	3	40	17	406*	4	254	240	87	9	18	5	1047*
15	38	70	587*	4	21	7	1026*	5	561	553	76	10	84	77	95
16	109	100	76	5	21	13	1016*	6	272	283	93	11	70	93	127
17	48	44	319*	6	21	19	1125*	7	482	509	84	12	43	70	300*
18	139	138	84	7	35	24	682*	8	259	251	92	13	105	104	84
19	52	68	449*	8	98	95	107	9	121	132	82	14	154	153	95
20	70	72	356*	9	22	17	1158*	10	356	358	94	15	20	2	1056*

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	3, 4, 1			7	157	159	106	12	121	109	76	2	317	315	85
6	190	201	125	8	157	166	94	13	23	17	573*	4	216	227	107
17	108	100	93	9	182	168	118	14	46	86	450*	6	240	229	101
18	44	88	304*	10	79	80	81	15	166	172	118	8	57	37	294*
	3, 5, 1			11	16	20	982*	16	44	20	501*	10	184	161	129
0	190	183	107	12	36	40	207*	17	121	122	85	12	487	508	103
1	57	21	335*	13	181	162	91	18	30	26	737*	14	354	374	118
2	104	97	81	14	18	37	1010*	19	64	70	144*	16	104	77	87
3	114	116	82	15	23	10	841*	20	41	58	628*	18	141	136	92
4	19	7	1062*	16	19	13	1034*		4, 4, 1			20	49	24	166*
5	19	18	1237*	17	45	56	473*	0	437	433	105		5, 1, 1		
6	206	181	146	18	20	27	989*	1	127	92	77	0	137	148	92
7	60	79	382*	19	77	89	122	2	18	123	1397*	1	238	231	100
8	24	105	1108*	20	21	76	1237*	3	143	148	97	2	215	239	107
9	100	90	96	21	183	172	120	4	111	118	77	3	122	133	78
10	20	30	1076*	22	35	63	385*	5	146	149	95	4	213	222	112
11	59	84	443*		4, 2, 1			6	82	84	99	5	479	484	88
12	88	87	115	0	389	390	81	7	43	9	393*	6	101	91	67
13	158	166	95	1	228	212	96	8	109	107	80	7	112	118	75
14	47	73	431*	2	36	55	372*	9	139	141	89	8	200	223	120
15	23	8	959*	3	15	92	1026*	10	58	14	408*	9	130	136	92
	3, 6, 1			4	200	212	107	11	109	89	83	10	38	6	425*
0	21	23	1056*	5	408	428	89	12	117	118	82	11	116	97	78
1	21	4	760*	6	167	171	118	13	74	67	116	12	39	31	292*
2	48	53	531*	7	16	18	990*	14	40	20	300*	13	151	159	89
3	64	46	344*	8	208	235	111	15	122	107	84	14	75	49	101
4	83	74	109	9	16	89	1085*	16	21	32	1298*	15	91	89	92
5	44	28	299*	10	89	79	82	17	67	61	137*	16	77	62	104
6	51	31	166*	11	311	289	110		4, 5, 1			17	20	29	731*
7	48	16	490*	12	189	173	127	0	90	88	93	18	60	57	137*
8	45	31	494*	13	196	199	132	1	107	111	81	19	21	54	1162*
	4, 0, 1			14	93	85	90	2	20	39	1104*	20	88	77	100
0	221	209	86	15	21	13	840*	3	20	26	1098*	21	61	106	532*
2	13	4	855*	16	37	51	223*	4	52	86	475*		5, 2, 1		
4	73	71	67	17	96	122	90	5	103	116	94	0	65	83	100
6	434	445	79	18	20	7	1090*	6	142	141	93	1	16	19	1041*
8	621	634	82	19	87	92	109	7	96	92	94	2	122	119	74
10	115	102	76	20	21	4	1101*	8	55	17	388*	3	39	47	412*
12	127	125	87	21	47	6	514*	9	62	25	350*	4	290	301	104
14	290	296	116		4, 3, 1			10	94	100	101	5	452	450	97
16	257	263	123	0	163	177	91	11	54	54	330*	6	253	241	108
18	54	79	272*	1	16	6	1061*	12	128	101	85	7	17	16	1145*
20	49	75	257*	2	441	465	99	13	22	44	1169*	8	17	77	1177*
22	41	1	572*	3	102	115	70		4, 6, 1			9	277	275	115
	4, 1, 1			4	16	31	1017*	0	21	12	874*	10	115	107	79
0	544	544	74	5	119	110	80	1	36	38	630*	11	302	291	111
1	463	475	74	6	155	165	94	2	24	43	1071*	12	177	170	110
2	44	70	223*	7	142	167	93	3	81	64	128	13	75	81	107
3	78	82	67	8	143	150	87	4	22	72	1203*	14	117	144	84
4	157	150	73	9	157	161	103	5	71	70	133	15	212	230	109
5	14	27	1059*	10	18	1	1124*		5, 0, 1			16	121	122	86
6	50	66	106*	11	89	88	90	0	253	267	94	17	132	138	89

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	5, 2, 1			10	103	103	101	17	89	116	120	14	46	38	480*
18	21	19	1025*	11	67	73	149*	18	129	138	92	16	58	131	454*
19	59	81	501*		6, 0, 1				6, 3, 1				7, 1, 1		
20	22	3	1191*	0	161	168	94	0	327	373	128	0	263	268	125
	5, 3, 1			2	287	283	102	1	41	14	232*	1	184	197	104
0	394	388	99	4	89	84	75	2	123	120	86	2	43	47	253*
1	174	152	100	6	288	277	102	3	143	132	97	3	74	75	110
2	304	316	114	8	84	63	79	4	121	123	83	4	250	274	135
3	92	83	79	10	55	79	133*	5	82	86	97	5	18	99	1328*
4	130	153	91	12	271	276	130	6	202	212	141	6	192	193	111
5	18	43	1180*	14	69	39	119	7	47	25	263*	7	281	277	124
6	149	132	106	16	211	204	118	8	51	50	154*	8	147	150	104
7	42	62	272*	18	36	113	781*	9	64	37	350*	9	297	295	137
8	18	68	1172*		6, 1, 1			10	72	64	111	10	68	73	350*
9	18	26	1140*	0	239	244	106	11	50	44	163*	11	33	71	641*
10	61	63	355*	1	322	304	96	12	100	70	89	12	20	23	1180*
11	240	209	127	2	130	118	90	13	36	43	597*	13	21	15	970*
12	81	91	104	3	481	482	96	14	21	7	1016*	14	45	59	513*
13	219	216	154	4	17	63	578*	15	34	32	574*	15	48	3	453*
14	20	79	1286*	5	317	327	104	16	22	3	1105*	16	60	17	325*
15	179	181	121	6	196	212	131		6, 4, 1				7, 2, 1		
16	27	17	503*	7	49	56	282*	0	209	211	105	0	85	80	95
17	21	40	1118*	8	98	97	82	1	189	180	131	1	57	28	360*
18	22	12	1163*	9	70	97	113	2	72	90	124	2	188	172	101
	5, 4, 1			10	18	7	1131*	3	65	63	121	3	50	59	165*
0	141	160	86	11	109	74	78	4	20	41	1128*	4	19	15	1114*
1	233	243	134	12	94	84	87	5	39	31	256*	5	19	35	1174*
2	181	182	97	13	19	28	1270*	6	99	107	92	6	131	136	87
3	45	47	240*	14	25	35	848*	7	20	67	1122*	7	54	72	154*
4	132	127	92	15	28	21	759*	8	21	34	1041*	8	150	159	103
5	61	42	369*	16	31	17	803*	9	55	18	398*	9	148	133	90
6	255	259	144	17	113	87	85	10	56	56	403*	10	30	50	798*
7	19	15	1156*	18	53	26	166*	11	21	48	1334*	11	20	17	1052*
8	104	101	87	19	62	7	365*	12	22	83	1422*	12	60	41	323*
9	20	16	1163*		6, 2, 1			13	96	93	107	13	160	150	112
10	38	33	614*	0	139	107	95		6, 5, 1			14	79	92	129
11	91	85	100	1	74	58	94	0	25	29	1001*	15	98	111	105
12	61	15	405*	2	103	96	72	1	41	28	587*		7, 3, 1		
13	38	7	537*	3	204	220	131	2	72	66	127	0	29	68	782*
14	21	61	1097*	4	317	310	112	3	21	45	1229*	1	186	194	113
15	22	82	1308*	5	29	40	652*	4	115	109	91	2	152	157	98
	5, 5, 1			6	34	39	384*	5	49	11	330*	3	44	15	442*
0	55	75	162*	7	143	130	96	6	22	96	1393*	4	20	15	1113*
1	20	37	1138*	8	18	6	1228*	7	63	77	349*	5	175	193	122
2	20	11	983*	9	167	193	115		7, 0, 1			6	219	234	153
3	51	24	417*	10	61	24	354*	0	232	210	121	7	39	59	314*
4	54	37	406*	11	96	74	83	2	200	196	126	8	20	36	1146*
5	21	74	1105*	12	19	9	498*	4	124	109	85	9	21	30	1040*
6	35	19	635*	13	44	72	342*	6	42	78	491*	10	167	130	119
7	21	16	1156*	14	59	51	394*	8	108	92	80	11	21	23	1118*
8	30	1	746*	15	239	213	157	10	141	131	92	12	64	65	370*
9	131	115	92	16	51	95	543*	12	40	35	271*	13	22	21	1185*

STRUCTURE FACTORS FOR C16 H12 S C12

Columns are 10Fo 10Fc 100Sig, * for Insignificant

l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig	l	kFo	Fc	Sig
	7, 4, 1			3	112	113	77	12	23	28	960*	0	21	7	799*
0	53	28	365*	4	47	30	279*		8, 3, 1			1	135	130	94
1	50	41	459*	5	96	91	87	0	21	9	1009*	2	21	81	1257*
2	67	54	130	6	32	23	479*	1	56	89	444*	3	40	12	576*
3	27	10	847*	7	262	234	135	2	41	25	546*	4	44	59	239*
4	79	78	113	8	48	15	467*	3	100	92	95	5	37	67	708*
5	48	81	555*	9	78	74	114	4	181	175	123	6	21	3	995*
6	56	16	407*	10	21	7	1120*	5	21	11	1102*	7	80	82	116
7	65	37	406*	11	54	31	456*	6	21	66	1146*	8	22	58	800*
8	158	121	113	12	122	112	85	7	21	57	1328*	9	57	49	446*
9	22	6	842*	13	104	94	98	8	140	133	94		9, 2, 1		
	8, 0, 1				8, 2, 1			9	22	39	1165*	0	120	114	84
0	203	197	142	0	52	60	385*		8, 4, 1			1	146	140	91
2	149	154	96	1	36	67	630*	0	62	8	365*	2	61	67	434*
4	58	67	357*	2	20	46	1129*	1	22	32	1088*	3	43	25	266*
6	173	177	114	3	20	11	1035*	2	57	39	428*	4	83	83	113
8	135	126	80	4	111	129	87		9, 0, 1			5	22	56	1137*
10	211	218	112	5	107	105	87	0	20	66	1270*	6	22	28	1170*
12	21	101	1259*	6	20	4	1127*	2	127	115	80	7	40	41	664*
14	44	6	244*	7	21	68	1228*	4	21	100	1298*		9, 3, 1		
	8, 1, 1			8	52	54	171*	6	41	91	584*	0	22	1	1091*
0	30	57	712*	9	35	13	642*	8	21	15	1092*		10, 0, 1		
1	113	116	78	10	63	37	140*		9, 1, 1			0	107	117	104
2	40	59	318*	11	22	46	1301*								

Table S-2. Calculated Hydrogen Atom Parameters

	x	y	z	Biso
H 4	0.863	0.432	0.060	6.4
H 5	1.124	0.351	0.045	8.1
H 6	1.308	0.592	0.079	8.6
H 7	1.252	0.906	0.130	7.6
H 9A	1.055	1.175	0.143	8.5
H 9B	1.069	1.011	0.201	8.5
H10A	0.883	1.245	0.208	8.0
H10B	0.807	1.172	0.144	8.0
H12	0.798	1.082	0.289	6.0
H13	0.654	0.812	0.331	6.0
H14	0.561	0.515	0.277	5.7
H15	0.603	0.488	0.176	4.9

Hydrogen positions calculated assuming C-H of 1.08A. Biso is from Uiso(H) = Ueq(C) + 0.01.

Table S-3. Anisotropic u(i,j) values *100.
E.S.Ds. refer to the last digit printed

	u11	u22	u33	u12	u13	u23
S	6.26(12)	6.61(13)	6.62(12)	-1.93(10)	-0.20(9)	-1.34(10)
Cl 1	6.28(11)	7.40(13)	7.79(12)	1.11(11)	-0.31(9)	-0.37(11)
Cl 2	8.20(12)	7.89(13)	4.88(10)	-1.15(12)	-0.02(9)	1.21(10)
C 1	5.2 (4)	6.0 (5)	5.4 (4)	-0.9 (4)	0.3 (3)	-0.4 (3)
C 2	5.2 (4)	4.3 (4)	4.6 (4)	-1.0 (3)	0.0 (3)	-0.1 (3)
C 3	5.3 (4)	5.6 (5)	4.3 (4)	0.0 (4)	1.0 (3)	0.8 (4)
C 4	7.1 (5)	7.8 (6)	6.3 (5)	0.9 (5)	1.8 (4)	0.7 (4)
C 5	9.1 (6)	11.2 (7)	7.6 (6)	4.1 (6)	3.7 (5)	2.5 (5)
C 6	6.5 (6)	15.7 (11)	7.6 (6)	2.6 (7)	2.8 (5)	5.3 (7)
C 7	5.0 (5)	13.6 (8)	7.3 (5)	-0.6 (6)	0.9 (4)	2.6 (6)
C 8	5.3 (5)	8.3 (6)	6.4 (4)	-1.1 (4)	0.5 (4)	1.6 (4)
C 9	6.5 (5)	9.1 (7)	13.8 (7)	-3.4 (5)	1.4 (5)	-1.3 (6)
C10	10.5 (7)	6.2 (5)	10.8 (6)	-2.8 (5)	1.9 (5)	-1.2 (5)
C11	6.0 (4)	5.5 (5)	5.8 (4)	-0.9 (4)	0.7 (3)	-0.2 (4)
C12	6.5 (5)	8.1 (6)	5.2 (4)	-0.7 (4)	-0.4 (3)	-1.7 (4)
C13	5.5 (5)	8.8 (6)	5.5 (4)	0.7 (5)	1.1 (4)	0.9 (4)
C14	4.9 (4)	7.6 (5)	6.2 (4)	-0.3 (4)	1.3 (4)	1.9 (4)
C15	5.1 (4)	4.8 (4)	5.7 (4)	-1.0 (4)	1.1 (3)	-0.3 (3)
C16	4.5 (4)	4.3 (4)	4.7 (4)	-0.2 (3)	0.8 (3)	0.0 (3)

Anisotropic Temperature Factors are of the form
exp=-2*Pi*Pi*(h*h*u11*astar*astar+---+2*h*k*u12*astar*bstar+---)