C. Heitner Ph.D.

Photocycloaddition Reactions of Thianaphthene-1 1-dioxide

Ph. D. Cyril Heitner Department of Chemistry

The Photocycloaddition Reactions of Thianaphthene-1,1-dioxide.

ABSTRACT

The structure of the two photodimers of thianaphthene-1,1-dioxide has been elucidated as head-to-head and head-to-tail, anti. This reaction has been found to proceed via an attack by the triplet excited state of thianaphthene-1,1-dioxide on the ground state molecule with a quantum yield (Ω_{DIM}) of 0.18. The quantum yield for attack of the triplet excited state on the ground state ($\Omega_c + \Omega_c'$) was found to be 1.0 by comparing the quantum yield of the unsensitized dimerization ($\Omega_{DIM} = 0.18$) with that of benzophenone sensitized dimerization. Thus the quantum yield of the intersystem crossing from singlet to triplet excited state (Ω_{isc}) is 0.18.

A solvent effect on the ratio of head-to-head, anti to head-to-tail, anti was attributed to a preferential solvation of the more polar transition state.

The Photocycloaddition Reactions of Thianaphthene-1,1-dioxide

by

Cyril Heitner

A Thesis presented to
the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements of
the degree of Doctor of Philosophy

Department of Chemistry
McGill University
Montreal, Canada. March 1971.

© Cyril Heitner 1971

TO MY DEAREST NORMA, DAWN AND TARA

TABLE OF CONTENTS

Page

CHAPTER V

LIST OF TABLES

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to those who have helped make this research a success, particularly the following:

Dr. David N. Harpp, for his patience, encouragement, and advice;

Dr. P.G. Farrell, Dr. D.F.R. Gilson, Dr. W.C. Galley and Dr. T.H. Chan for valued discussions;

The National Research Council of Canada, for the financial support in the form of a bursary (1968-1970);

Mr. Victor T.C. Yu and Mr. Peter Currie for technical assistance;

Mr. Manuel Bernhaut, for expertly typing the manuscript;

My wife Norma, for many long hours of proof reading.

CHAPTER 1

INTRODUCTION

Photodimerization (1) (photocycloaddition of like compounds) has been known for about 100 years. However, like other fields of photochemistry, very little concern was shown for this reaction until the mid-1950's. The study has been hampered by a lack of chemical and physical methods of analysis with which complete structure elucidations can be facilitated. The rapid growth in the study of photodimerization reactions (indeed all photochemistry) has been characterized by a better understanding of energy transfer (photosensitization), kinetic relationships, solvent and substitution effects.

Listed in the following Table I, are typical photodimerization reactions representing a variety of substituent types and substitution patterns of the olefinic bond.

Structure Elucidation - Chemical Degradation

The problems associated with the determination of a structure and stereochemistry about the cyclobutane ring of the photodimers are formidable. Chemical degradation through well defined routes to known derivatives provides,

Table I

Photodimerization Reactions

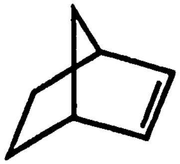
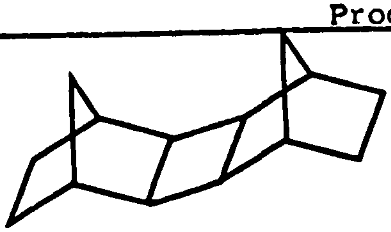
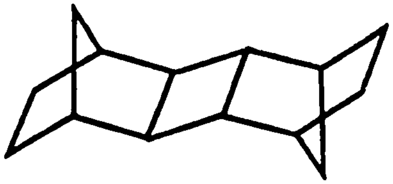
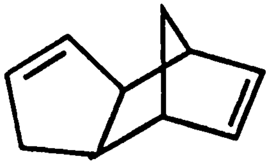
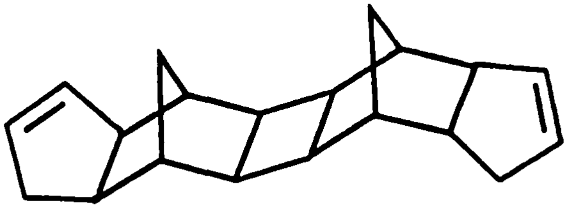
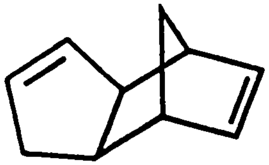
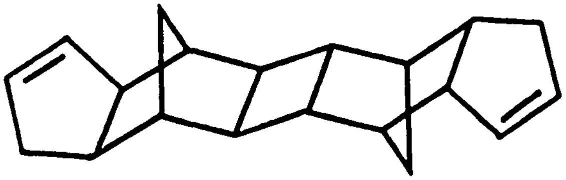
No.	Ref.	Substrate	Conditions	Products	
1	2-5	 1	hν acetophenone sensitizer	 2	 3
2a	5,6	 4	hν acetophenone sensitizer	 5	
2b	5,6	 4	hν CuBr $(C_2H_5)_2O$	 6	

Table I

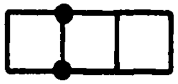
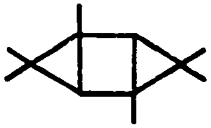
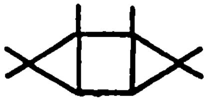
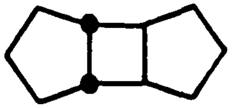
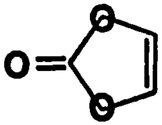
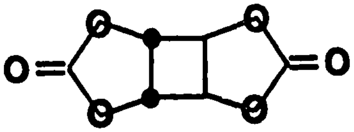
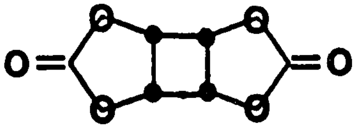
No.	Ref.	Substrate	Conditions	Products	
3	7	 7	hν acetone sensitizer	 8	
4	8	 9	hν acetone sensitizer	 10	 11
5	9	 12	hν acetone sensitizer	 13	
6	10	 14	hν acetone sensitizer	 15	 16

Table I

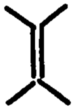
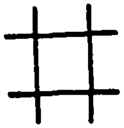
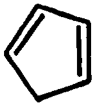
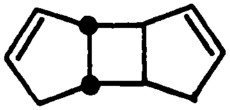
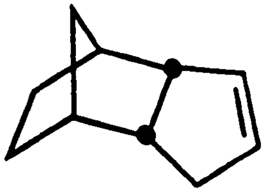
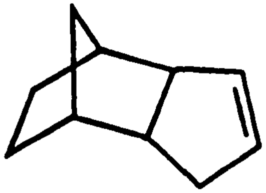
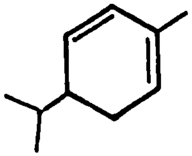
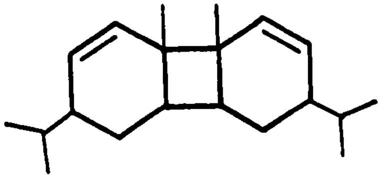
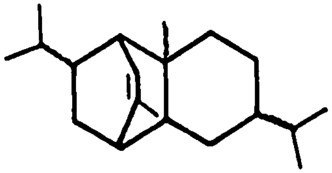
No.	Ref.	Substrate	Conditions	Products
7	11	 17	hν quartz	 18
8	12	 19	hν acetophenone sensitizer	 20  21  22
9	13	 23	hν napthalene sensitizer	 24 & 25  26

Table I

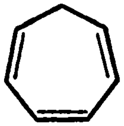
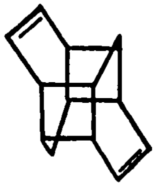
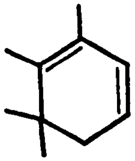
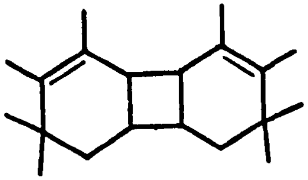
No.	Ref.	Substrate	Conditions	Products
10	14	 27	hν benzophenone sensitizer	 28 3 unidentified dimers
11	15	 29	hν	 30

Table I

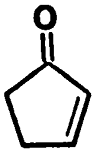
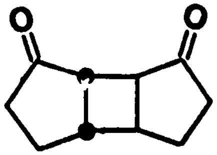
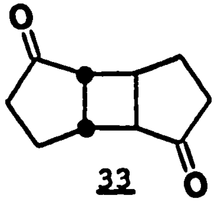
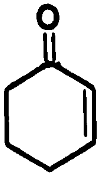
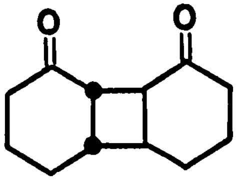
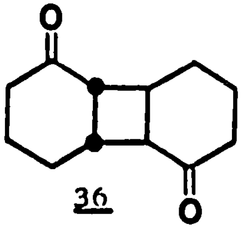
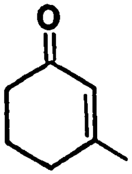
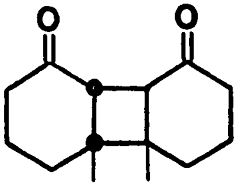
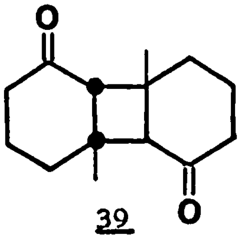
No.	Ref.	Substrate	Conditions	Products	
12	16-18	 31	hν (pyrex)	 32	 33
13	19	 34	hν (pyrex)	 35	 36
14	20	 37	hν	 38	 39

Table I

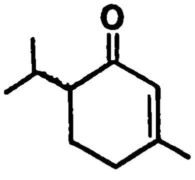
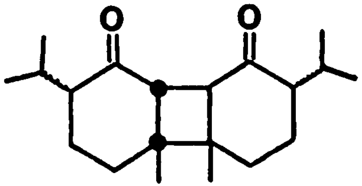
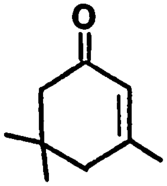
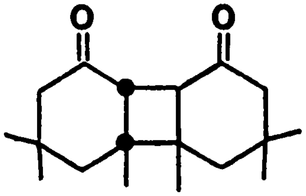
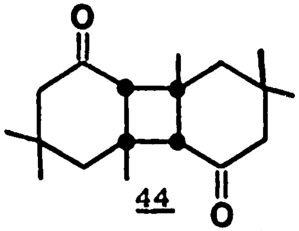
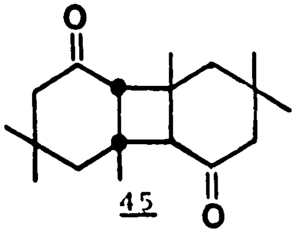
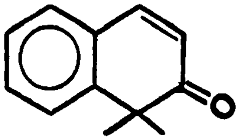
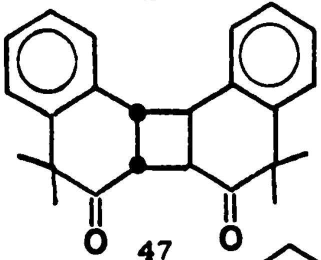
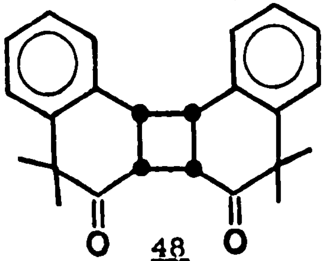
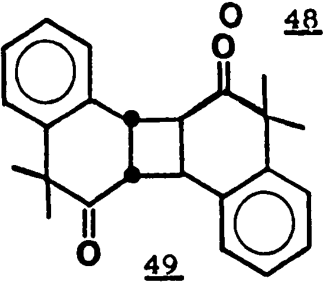
No.	Ref.	Substrate	Conditions	Products
15	21	 40	hν	 41 two other head-to-head dimers
16	22-24	 42	hν	 43  44  45
17	25	 46	hν	 47  48  49

Table I

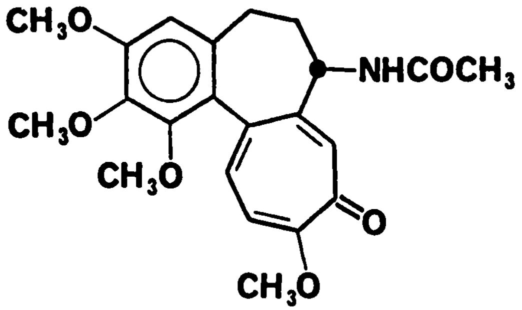
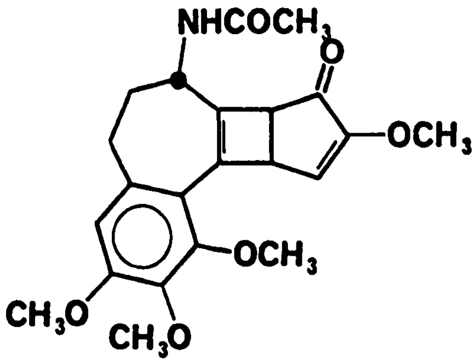
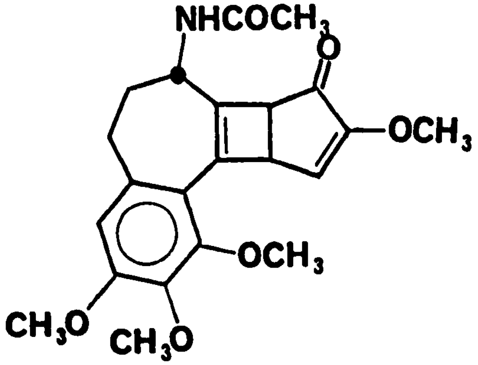
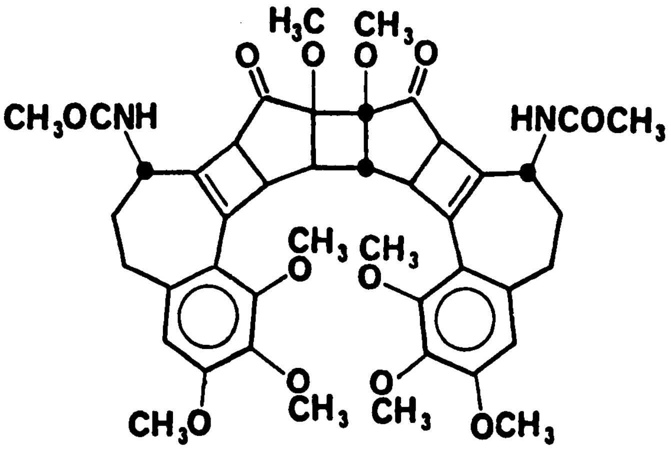
No.	Ref.	Substrate	Conditions	Products
18	26	 50	hν	 51
		 51		 52

Table I

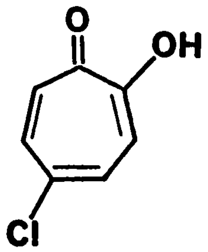
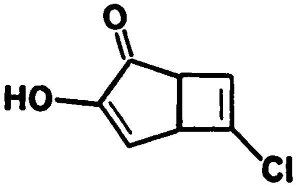
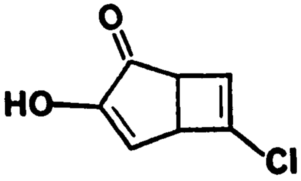
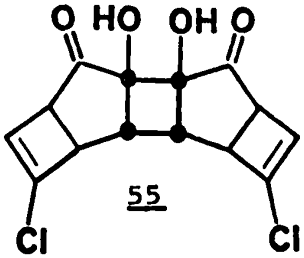
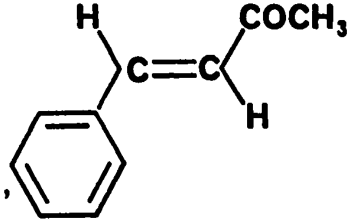
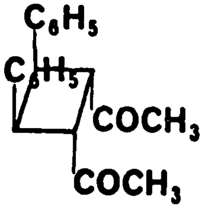
No.	Ref.	Substrate	Conditions	Products
19	27	 53	hν	 54
		 54		 55
20	28, 29		hν solid	 71

Table I

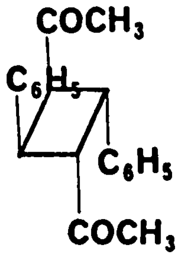
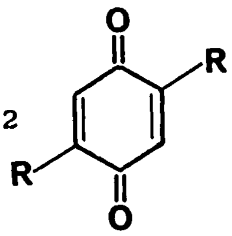
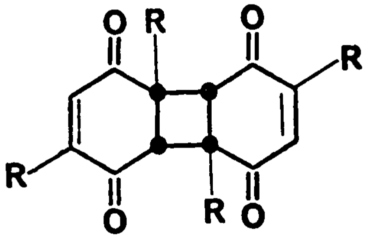
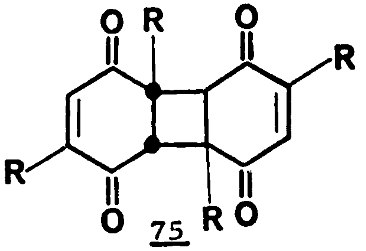
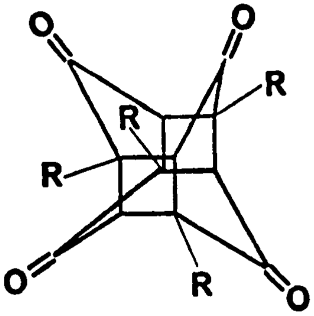
No.	Ref.	Substrate	Conditions	Products
20	28,29	70	hν liquid	 72
21	30-32	 73	hν solid	 74  75  76

Table I

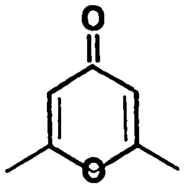
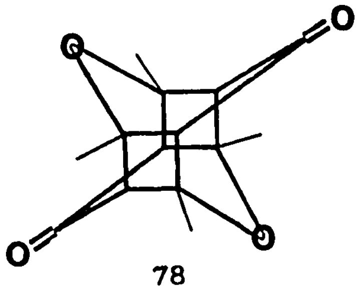
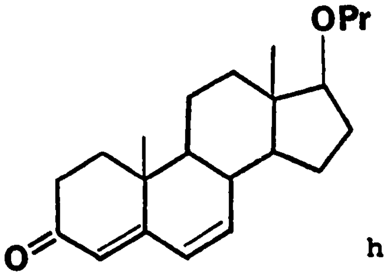
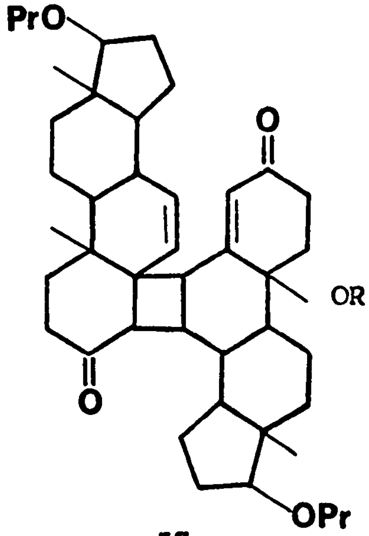
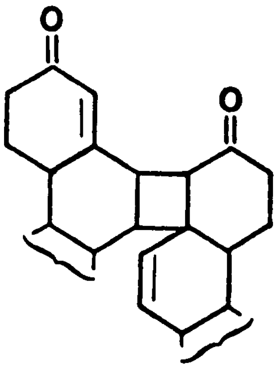
No.	Ref.	Substrate	Conditions	Products
22	33,34	 77	hν	 78
23	35,36	 56	hν	 57 OR  57

Table I

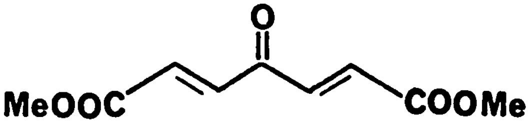
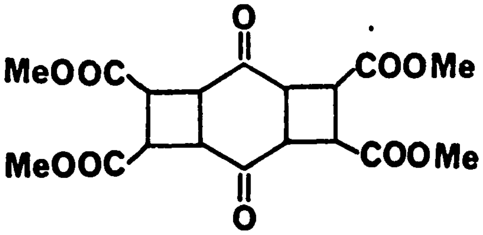
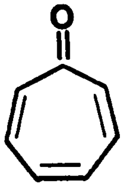
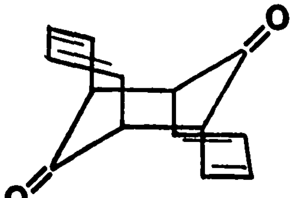
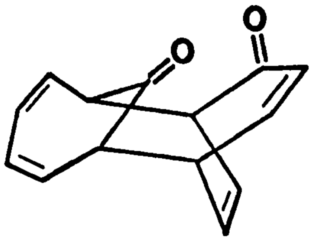
No.	Ref.	Substrate	Conditions	Products
24	37,38	 <u>79</u>	hν	 <u>80</u>
25	39	 <u>81</u>	hν H_2SO_4	 <u>82</u>
26	40	<u>81</u>	hν fluorenone sensitizer	 <u>83</u>

Table I

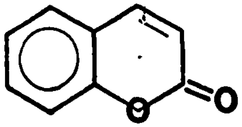
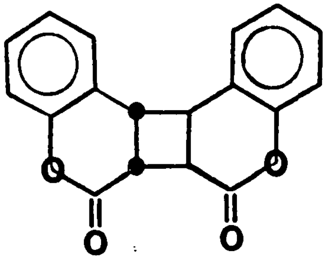
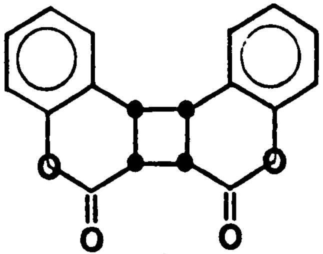
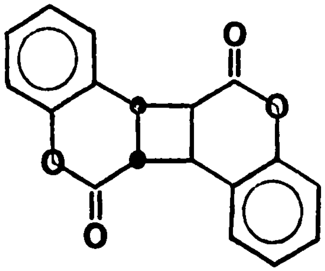
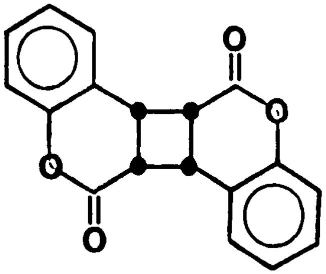
No.	Ref.	Substrate	Conditions	Products
27	41-45	 84	hν	 85  86  87  88

Table I

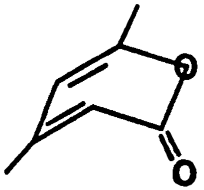
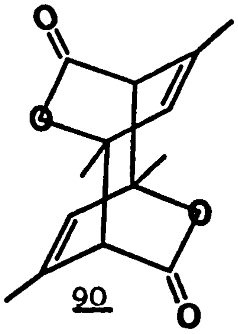
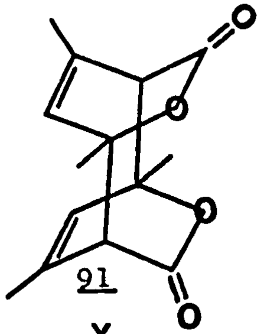
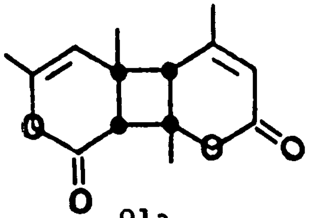
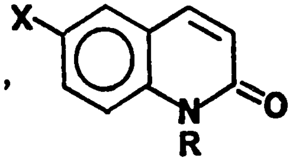
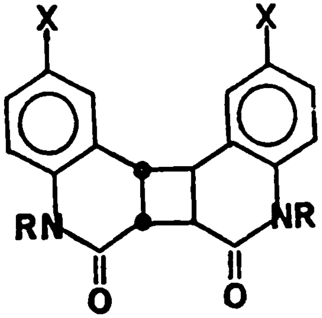
No.	Ref.	Substrate	Conditions	Products
28	46	 89	hν C_6H_6	 90  91  91a
29	47,49, 88,89	 92 a) R = H, X = H b) R = CH_3 X = H c) R = CH_3 X = Cl d) R = CH_3 X = CH_3	hν	 93 a) R = H, X = H b) R = CH_3 X = H c) R = CH_3 X = Cl d) R = CH_3 X = CH_3

Table I

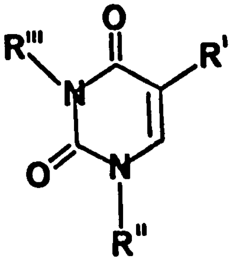
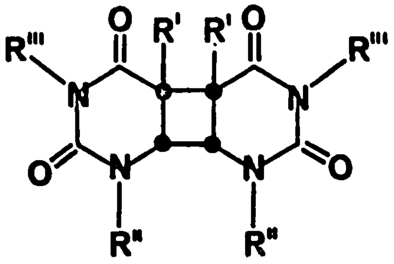
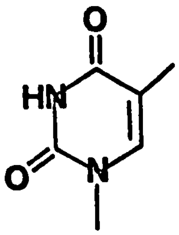
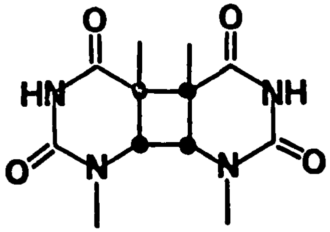
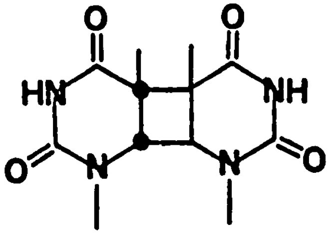
No.	Ref.	Substrate	Conditions	Products
30	50-54	 94 a) R_1 = H, R_2 = H, R_3 = H b) R_1 = ribosyl, R_2 = H, R_3 = H c) R_1 = H, R_2 = H, R_3 = CH_3 d) R_1 = H, R_2 = CH_3, R_3 = CH_3	hν H_2O (ice)	 95
31	53	 96	hν H_2O	 97  98

Table I

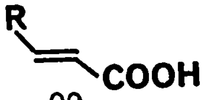
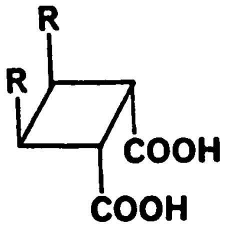
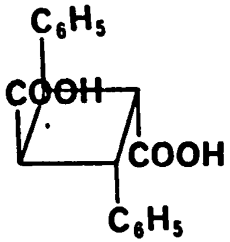
No.	Ref.	Substrate	Conditions	Products
32	55-65	 99 a C_6H_5 b  c  d 	hν	 100
33	55-65	99a	hν crystals	 101a

Table I

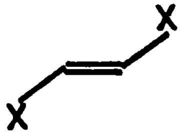
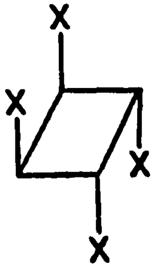
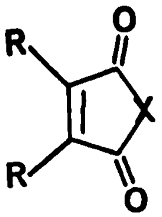
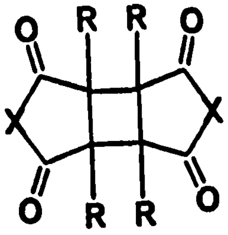
No.	Ref.	Substrate	Conditions	Products
34	66,67	 102 a) X = CO_2CH_3 b) X = CN	hυ solid	 103
35	68-70	 104 a) R = H, X = O b) R = CH_3, X = O c) R = H, CH_3, X = O d) R = H, X = N-Ø e) R = H, X = N-C_6H_{11} f) R = CH_3, X = NH	hυ	

Table I

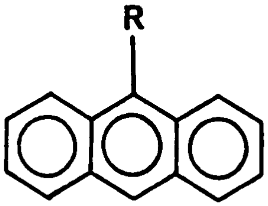
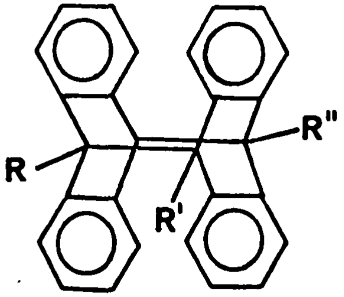
No.	Ref.	Substrate	Conditions	Products
36	71-75	 106 a) $R = H$ b) $R = CHO, CO_2C_2H_5, CH_2OH$ c) $R = Br$	hν	 107 a) $R_1 = R_2 = R_3 = H$ b) $R_1 = R_2 = CHO, CO_2C_2H_5, CH_2OH;$ $R_3 = H$ c) $R_1 = R_3 = Br; R_2 = H$

Table I

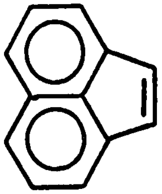
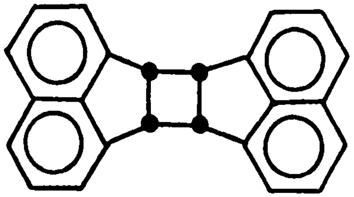
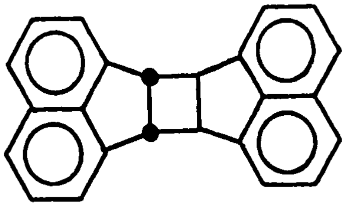
No.	Ref.	Substrate	Conditions	Products
37	76-79, 93	 108	hν	 109  110

Table I

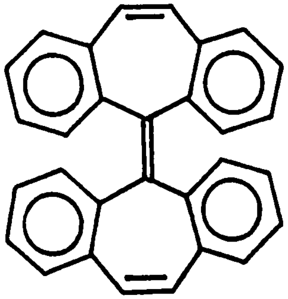
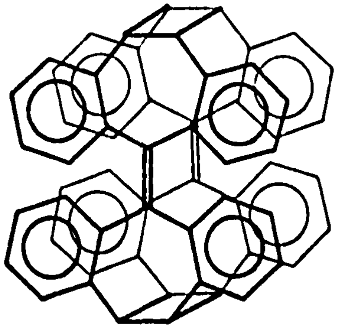
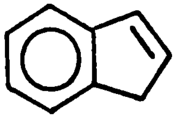
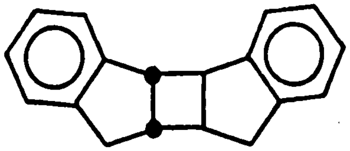
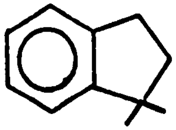
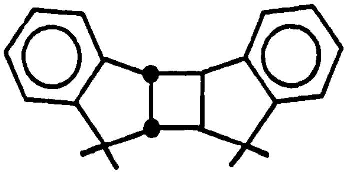
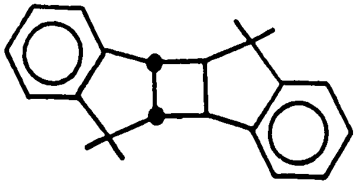
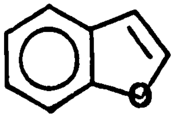
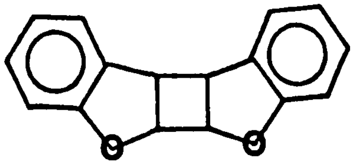
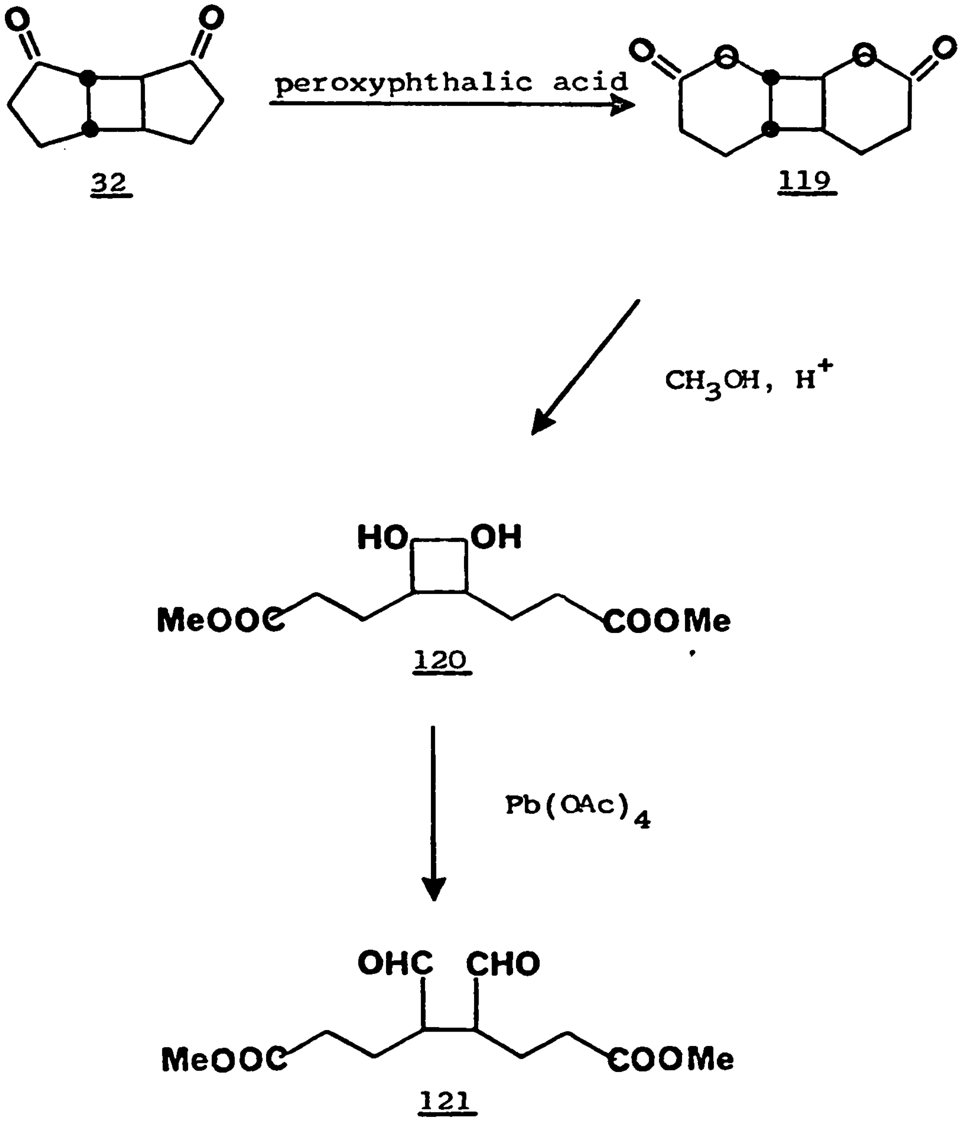
No.	Ref.	Substrate	Conditions	Products
38	79	 111	hν	 112
39	80-82	 113	hν benzophenone sensitizer	 114

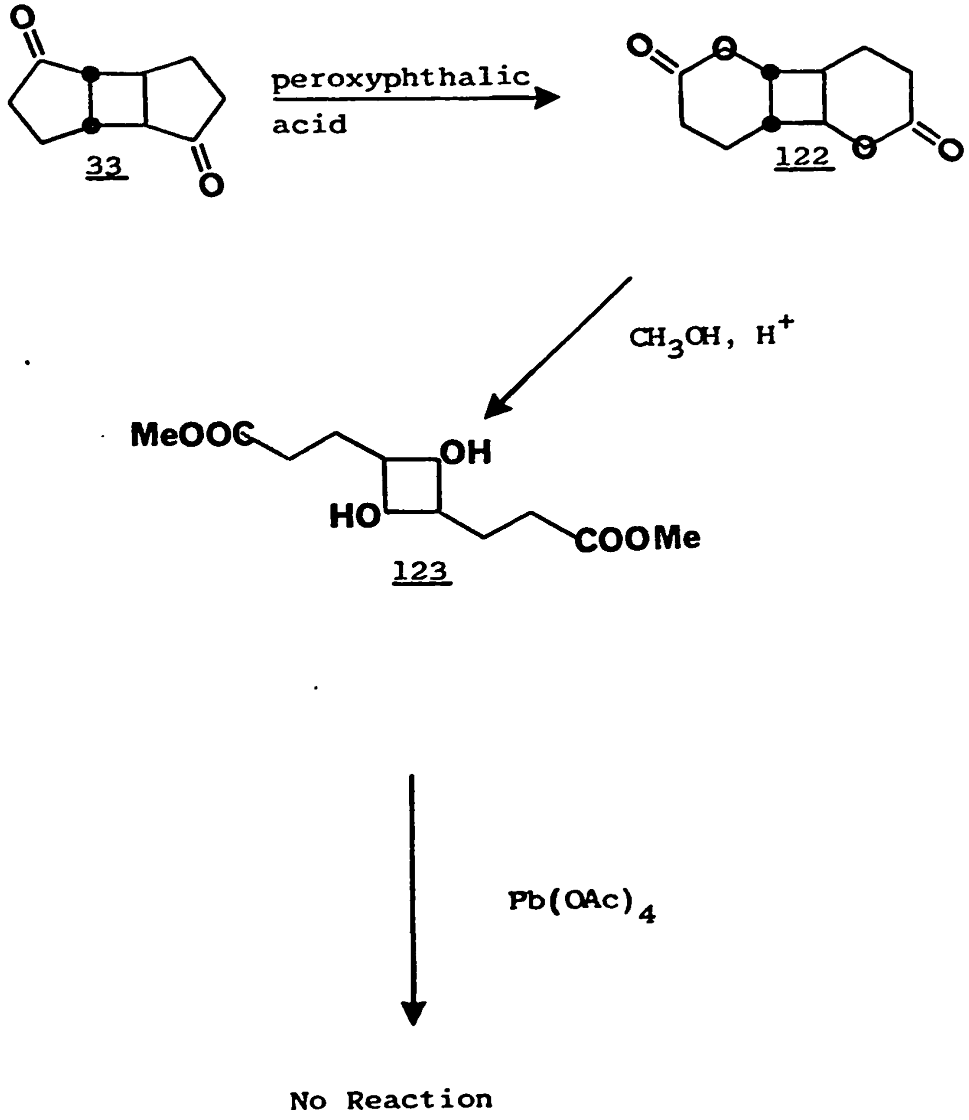
Table I

No.	Ref.	Substrate	Conditions	Products	
40	83	 115	hυ acetophenone sensitizer	 116	 117
41	84	 117	hυ benzophenone sensitizer	 118	

Scheme 1


32
peroxyphthalic acid
119
CH3OH, H+
HO
OH
MeOOC
COOMe
120
Pb(OAc)4
OHC
CHO
MeOOC
COOMe
121

Scheme 2


33
peroxyphthalic acid
122
CH3OH, H+
MeOOC
OH
HO
COOMe
123
Pb(OAc)4
No Reaction

by far, the best evidence for structure and stereochemistry. The following are selected examples of such degradation.

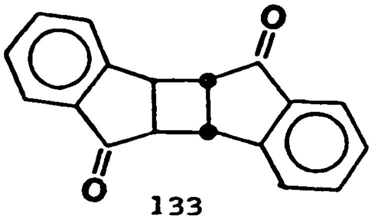
The first involves the photodimer of cyclopentenone (see equation 12, Table I (16)). Schemes 1 and 2 establish the gross structure of photodimers of cyclopentenone; 32 being head-to-head and 33 head-to-tail.

The reaction scheme 3 establishes that the head-to-tail photodimer 33 has anti stereochemistry. Unfortunately, the head-to-head dimer was not subjected to the same degradation route (16).

Both the structure and stereochemistry of the cyclopentenone dimers were determined via analysis of the nmr spectra of their respective dilactones 119 and 122 (16).

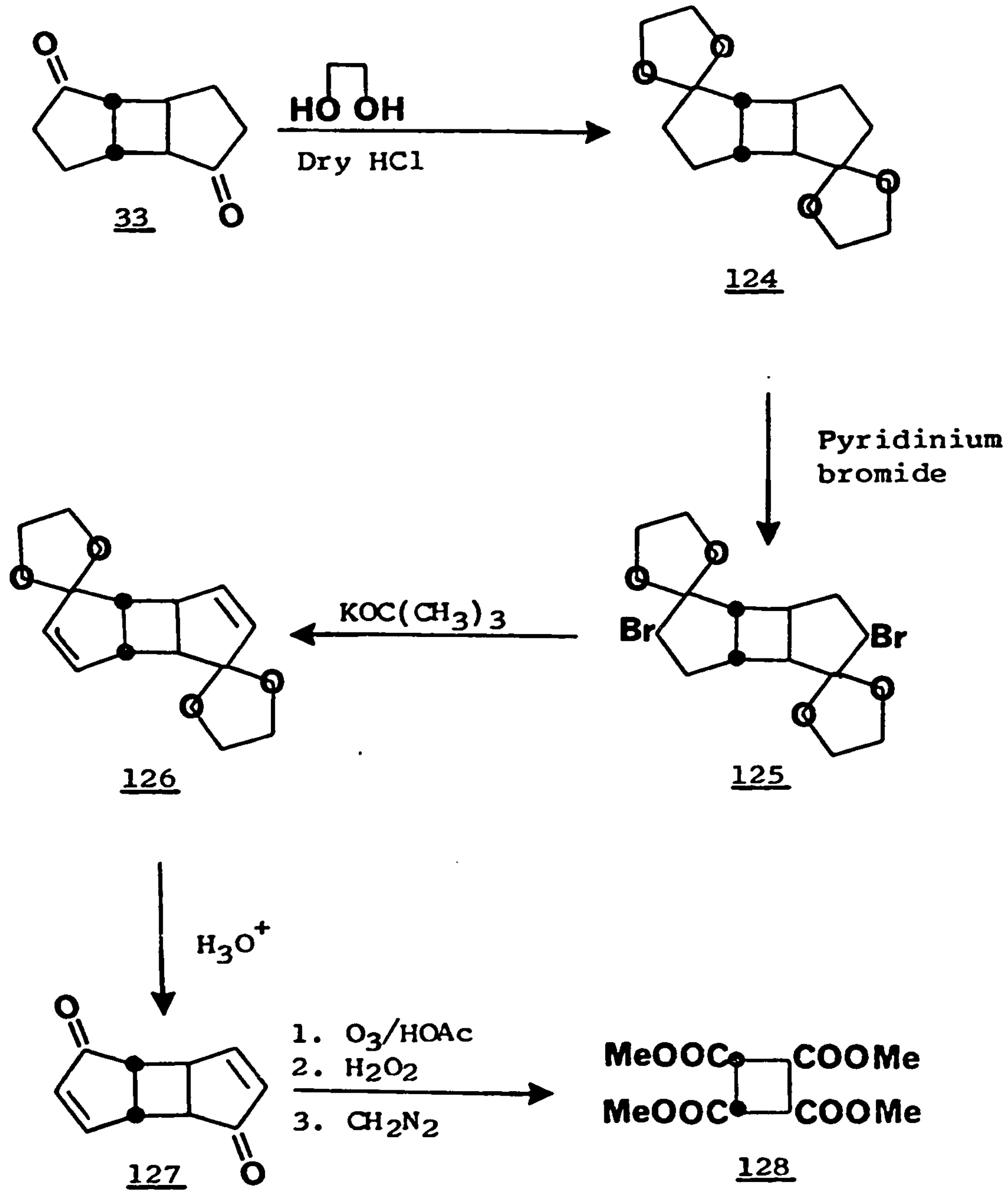
The elucidation of structure and stereochemistry of indene photodimers (81,82) is represented by the following scheme 4.

The formation of 128 from indene photodimer 114 indicates anti stereochemistry. The truxone corresponding to 114 is not known. The only reported truxone with anti stereochemistry is α truxone 133 with mp 294° - 295.5°.

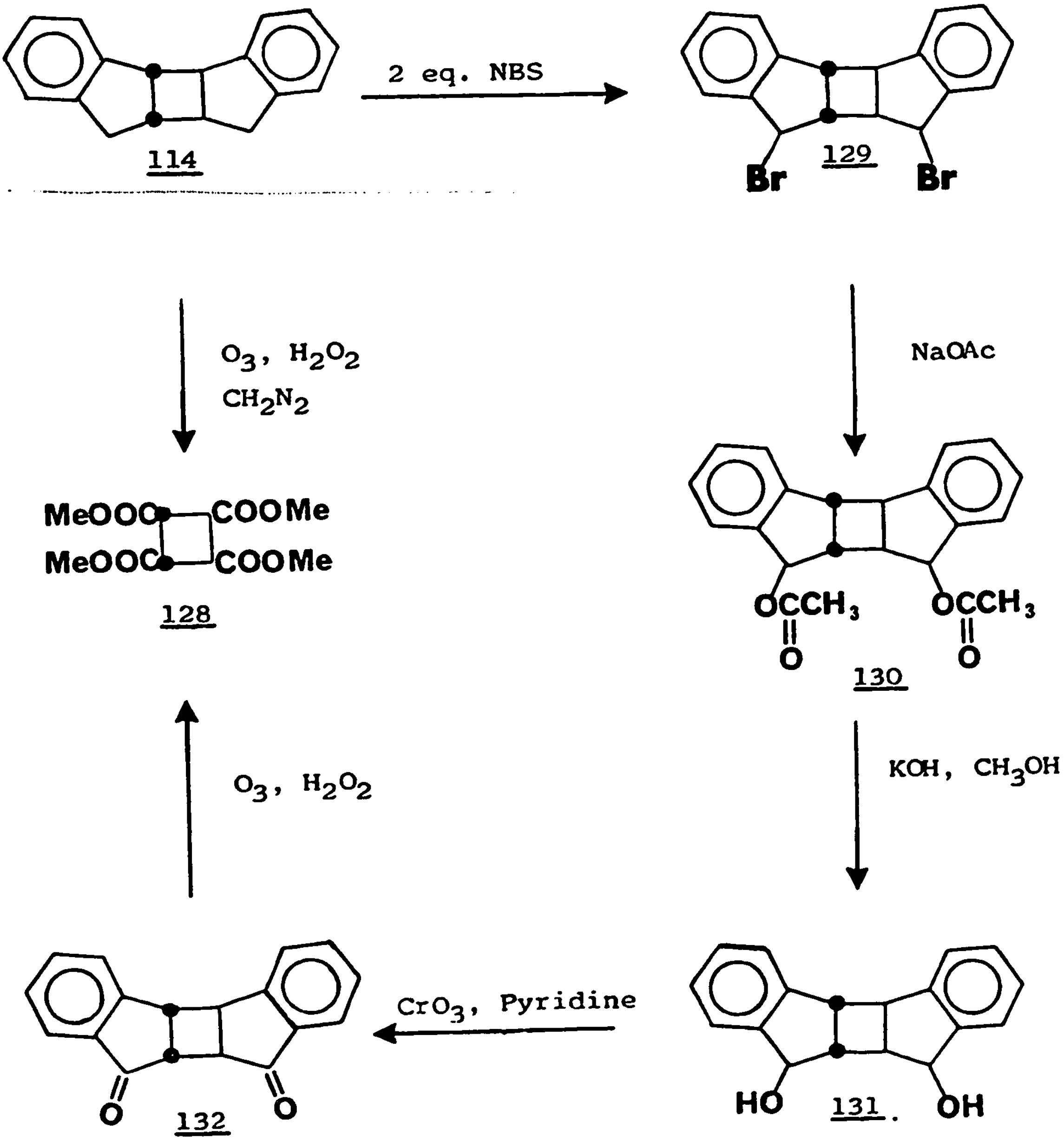


133

Scheme 3


33
HO OH
Dry HCl
124
Pyridinium bromide
Br
Br
125
KOC(CH3)3
126
H3O+
127
1. O3/HOAc
2. H2O2
3. CH2N2
MeOOC
COOMe
MeOOC
COOMe
128

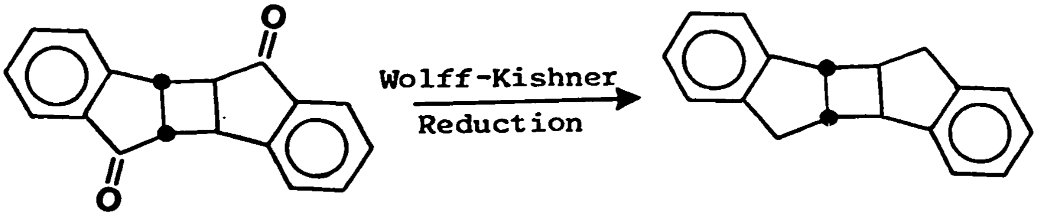
Scheme 4



114
2 eq. NBS
129
Br
Br
NaOAc
O_3, H_2O_2
CH_2N_2
MeOOC
COOMe
MeOOC
COOMe
128
OCCH$_3$
O
OCCH$_3$
O
130
KOH, CH_3OH
O_3, H_2O_2
CrO_3, Pyridine
O
O
132
HO
131
OH

Since 132 has a mp 221° - 223°, the only structure it could have would be head-to-head, anti. The photodimer of indene 114 would also be head-to-head, anti.

Scheme 5



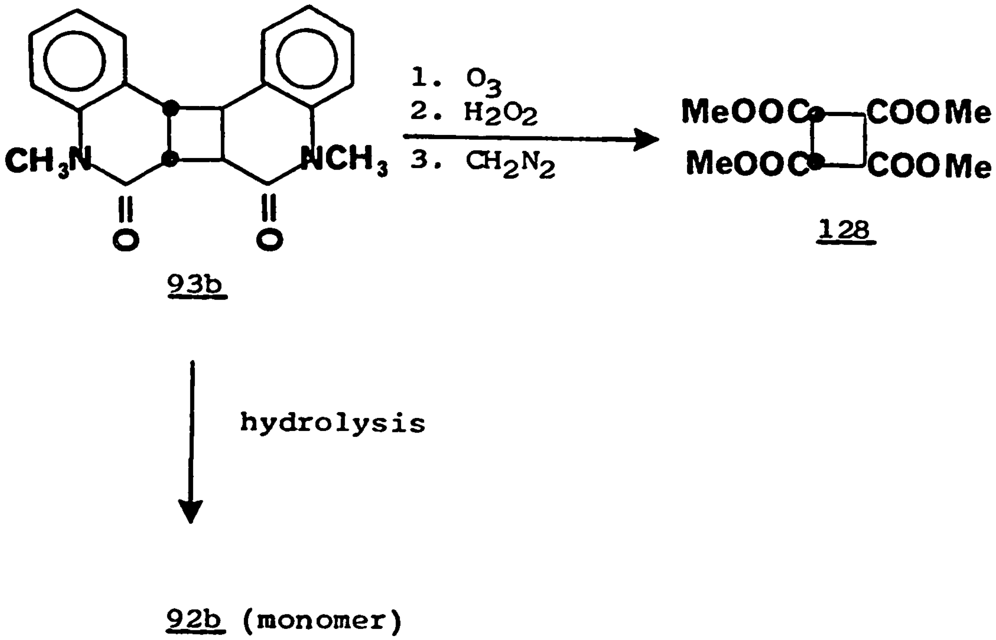
133

134

As a corollary (82), it was observed that truxone 133 upon Wolff-Kishner reduction produced truxane 134 with a higher melting point (143°) than that of indene photodimer 114 (116°). This confirms the structure assignment as stated above.

Unfortunately there are a few photodimers that undergo monomerization when attempts at chemical degradations are made. An example of this is the photodimer of N-methylcarbostyril, (93b) which undergoes monomerization when attempts at amide hydrolysis are made (48) (Scheme 6). Physical methods must be used to supply additional evidence to that obtained by chemical degradation.

Scheme 6



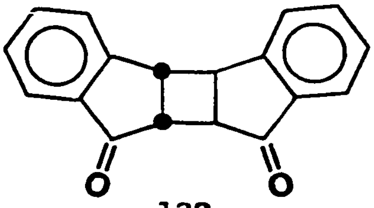
The above reaction (Scheme 6) establishes the fact that 93b has anti sterochemistry. Evidence for the gross structure was obtained by determining its dipole moment; it is smaller for the head-to-tail, anti dimer than for the head-to-head, anti dimer because the effects of the polar group are cancelled. The dipole moment of 93b was found to be 5.28 D in benzene (48). It would be expected that a head-to-tail dimer would have a much lower dipole moment. Thus from the above data a head-to-head, anti structure is assigned.

These measurements, however, as evidence for structure (head-to-head versus head-to-tail), would be stronger if the dipole moment of the head-to-head dimer were compared with that of the head-to-tail dimer.

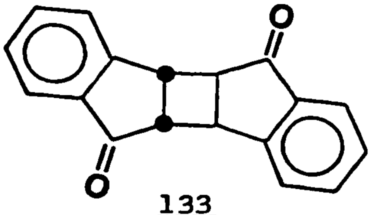
Structure Elucidation - Spectroscopic Methods

Infrared and Raman Spectroscopy

Vibrational spectroscopy offers a means of identifying a molecule with a centre of symmetry. The different vibrational selection rules for infrared and Raman transitions through the Rule of Mutual Exclusion (85) serves as a theoretical basis for detecting the presence or absence of a centre of symmetry. The cyclobutane ring dimers with head-to-head or head-to-tail configuration exist in either a planar or puckered conformation, depending on the nature of the substituents on the cyclobutane ring. However, head-to-tail, anti dimers with a planar cyclobutane ring possess an inversion centre. Ziffer and Levin (86) have examined several pairs of structurally known photodimers (32, 33, 35, 36, 38, 39, 43, 44, 45, 132, 133). For comparison purposes one member of each pair was a head-to-tail, anti dimer which could contain a centre of inversion, while the other member contained no centre of symmetry.



132



133

Table II

COMPARISON OF THE RAMAN AND INFRARED FREQUENCY COINCIDENCES

(C) (86)

COMPOUND	RAMAN	ir	C	COMPOUND	RAMAN	ir	C
33	24	24	6	32	31	36	26
35	24	46	10	34	33	42	24
38	34	34	7	37	41	46	28
133	26	42	10	132	24	43	16
44	41	48	16	43	37	42	23
45	33	41	9				

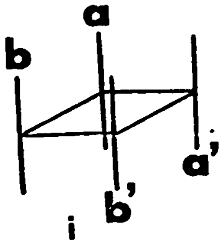
Table II illustrates that all the head-to-tail, anti dimers have smaller numbers of infrared absorptions coincident with Raman displacement bands than the head-to-head and head-to-tail, syn isomers of each pair. However, there are complicating effects. As the molecule increases in size through the addition of more units of atoms; the chances for accidental coincidences increase.

Also, it is possible that a small percentage of molecules exist in the puckered conformation. These complicating effects serve to increase the number of coincidences. This effect is evident as the infrared and Raman spectra of dimer pairs 33, 32 to 133 and 132 (Table II) are observed. Vibrational spectra can be useful only if the number of coincidences in the infrared and Raman spectra of one photodimer are compared with that of one or more different isomeric photodimers. Thus, the Rule of Mutual Exclusion can be used only to confirm the presence of a head-to-tail, anti dimer; it cannot be used to prove its absence.

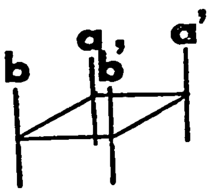
Nuclear Magnetic Resonance Spectroscopy

The coupling constants of protons in cyclobutane rings have been summarized (87), and it has been observed that coupling constants for cis protons (J_{cis}, 6 to 12 Hz) are larger than the corresponding trans protons (J_{trans}, 2 to 8 Hz). However, these constants vary over a large range so that overlap between values occurs. Thus a single coupling constant is insufficient to establish the stereochemistry of the protons being studied.

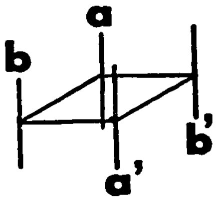
The nmr of coumarin dimer 86 and substituted carbostyril dimers 93b, 93c, and 93d were analysed by computer (89). The results are summarized in Table III.



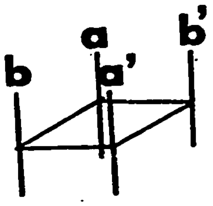
i



ii



iii



iv

Table III (89)

COMPOUND	$J_{aa'}$	J_{ab}	$J_{ab'}$	$J_{bb'}$
86	8.28	8.56	1.47	9.97
93b	2.97	8.77	-1.35	7.87
93c	2.76	8.99	-0.94	7.43
93d	2.65	8.77	-0.94	7.53

Structures iii and iv can be eliminated because $J_{aa'}$ and $J_{bb'}$ would involve cross ring coupling which rarely is higher than 2 Hz. Compound 86 would correspond to ii because of the high value for $J_{aa'}$ as compared to that of 93b, 93c and 93d. Because $J_{aa'}$ is small compared with J_{ab}, compound 93b, 93c and 93d correspond to i. Protons a and b, the protons on the six-four ring junctions, are assumed to be cis (89).

Also, the similarity of corresponding coupling constants of 93c with those of 93d and those of 93b confirms the assignment of head-to-head, anti structure i (see number 29, Table I). Assignments for 86 and 93b made with nmr analysis agree with those made by chemical degradation and dipole moment measurements (41-45, 47, 49).

Thus the analysis of nmr signals of cyclobutane protons can be used to assign head-to-head, anti structures but cannot be used to prove the absence of such dimers. The review by Fleming and Williams (87) was examined carefully and it is possible to find several examples of cis and trans coupling constants of protons on the same ring which overlap in value. If there is a large difference in the coupling constants of protons on the same cyclobutane ring, assignments could be made with confidence. However, if the difference is small or non-existent then no assignment should be made.

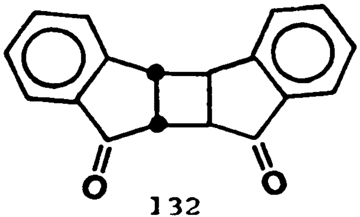
Also, structural evidence for syn dimers exists if there is a positive cross-ring coupling constant ($J_{ab'}$) and all anti dimers have a negative $J_{ab'}$ (89). More studies on other photodimers systems are necessary, however.

The structure of photodimers of 1,1-dimethylindene, 116, 117 have been elucidated by comparing the nmr signals of the cyclobutane protons with those of the coumarin photodimers 85 and 87 (83). Observation of the nmr signals for cyclobutane protons in many photodimer systems, however, (16, 25, 81) has shown that the multiplicity of the signals vary for different dimer systems of the same configuration. Coumarin photodimers are a poor choice for comparison because electronegativity affects the magnitude of coupling constants as well as chemical shift. The only valid comparison made was between indene dimers 116 and 114. Chemical degradation studies must be made to confirm the structures assigned.

Another region of the nmr spectrum that can be useful in determining some aspects of dimer structure has thus far been ignored. Photodimers which have aromatic rings can yield nmr signals that can give evidence for determining stereochemistry. The aromatic proton signals occur in several systems at τ = 2.1-2.7 for head-to-head, anti dimers and at τ = 3.0-3.2 for head-to-head, syn dimers (25, 48, 79, 81). (chart 1).

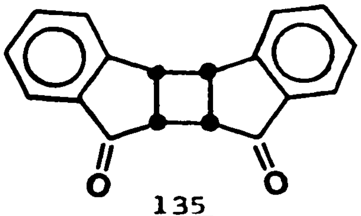
A study of molecular models explains the upfield shift for some of the aromatic protons on going from anti

Chart 1



132

τ = 2.1-2.6

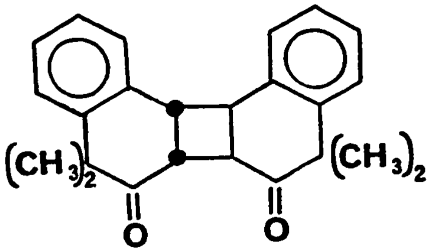


135

τ = 2.5-3.0

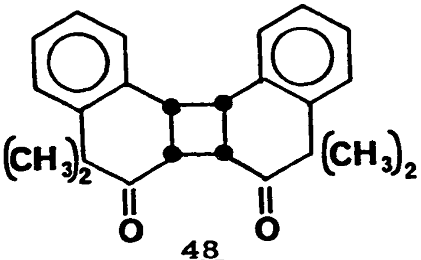
(81)

Chart 1



47

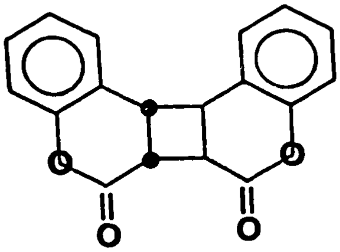
τ = 2.67



48

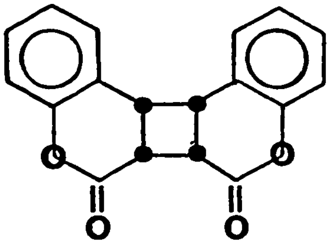
τ = 2.7-3.2

(25)



85

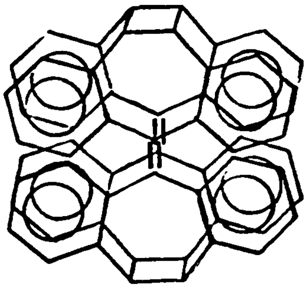
τ = 2.72



86

τ = 3.00

(48)



112

τ = 2.68-3.17

(79)

to syn stereochemistry. For the syn isomer the benzene rings are at close proximity to each other causing some of the aromatic protons to be shielded by the other benzene ring.

This phenomenon can best be used when comparisons between syn and anti dimers are made. However, if the chemical shift is quite low ($\tau = 2.0\text{-}2.4$) one can come to a safe conclusion that the dimer has anti stereochemistry. A corresponding conclusion for the syn dimer alone cannot be made because there is one example of an anti dimer having aromatic proton signals at $\tau = 3.00$ (N-methylcarbostyril).

Chemical Ionization Mass Spectrometry

Chemical ionization mass spectrometry is a form of mass spectrometry wherein the unknown compound is admitted into an ionization chamber where a known compound is present. The ionization of the compound is effected by the presence of ions from the known compound. In most cases methane at a pressure of 0.8 to 1.0 mm is used. At these pressures the species CH_5^+ and $C_2H_5^+$ serve as the major protonating species (90).

It has been observed that there are differences in C.I. spectra of head-to-head and head-to-tail photodimers of several cycloalkenones (91). Table IV illustrates that in all cases the quasimolecular ion peak ($(M+1)^+$) is the

Table IV (91)

Compound	Structure*	QM $(M + 1)^+$ m/e (relative abundance)	$(M/2 + 1)^+$ m/e (relative abundance)
32	HH	165 (100)	83 (11)
33	HT	165 (57)	83 (100)
35	HH	193 (100)	97 (4)
36	HT	193 (100)	97 (55)
38	HH	221 (100)	111 (12)
39	HT	221 (5)	111 (100)
43	HH	277 (100)	139 (27)
44	HT	277 (4)	139 (100)
45	HT	277 (5)	139 (100)
41	HH	305 (100)	153 (11)
132	HH	261 (100)	131 (58)
133	HT	261 (64)	131 (100)

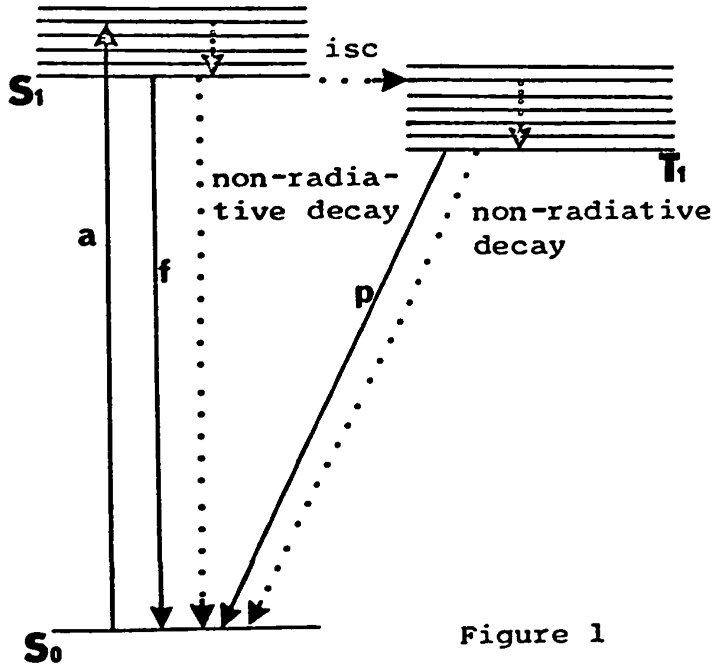
*HH is the head-to-head dimer and HT is the head-to-tail dimer.

base peak in all head-to-head dimers and the $(M/2+1)^+$ peak in most of the head-to-tail dimers. A noted exception is the cyclohexenone photodimer 36.

This method is a rapid and clean way to determine the gross structure of photodimers capable of protonation via CH_5^+ and $C_2H_5^+$ ions.

Thus a combination of all these techniques (vibrational and nmr spectra and chemical ionization spectrometry) should at least in some instances allow for photodimer structure determination and thus avoid the tedium associated with obtaining evidence via chemical degradation.

Kinetics and Mechanism



S_0, ground state.

S_1, singlet excited state.

T_1, triplet excited state.

f, fluorescence.

p, phosphorescence.

a, absorption.

Figure 1

One of the first steps in determining the mechanism and kinetic parameters of photodimerization reactions is to characterize the excited state. Photochemical reactions occur via singlet, triplet or thermally excited ground states (figure 1). Most photodimerizations have been shown to occur via the triplet excited state; tetramethylethylene (11), coumarin to a head-to-head syn dimer (43) and acenaphthene to its syn dimer (93) are noted exceptions. Reactions in which the triplet excited state is an intermediate are induced in presence of triplet sensitizers, are inhibited by triplet quenchers (oxygen, piperylene, and α-methylstilbene) and exhibit linear Stern-Volmer plots (17-19, 24).

Until now the only detailed mechanistic work done on alkene dimerization have been with those of cyclopentenone (18, 92), cyclohexenone (19, 92) and isophorone (24). It has been proposed (19) that photodimerization occurs via an attack by a triplet excited state molecule on a ground state molecule (Scheme 7).

The linearity of the reciprocal of the quantum yield for photodimerization vs the reciprocal of the olefin concentration (1/Q vs 1/(O)) is taken as strong evidence that the above mechanism is operative. The intercept of this plot is the quantum yield of intersystem crossing from the singlet to the triplet excited state and the slope is $k_3/k_4 \times 1/Q_{isc}$.

Chapman (24) has observed that the ratio of head-to-head to head-to-tail dimerization of isophorone is a function of a solvent polarity, as illustrated in Table V (22-24).

Similar effects have been observed for other cyclodimerizations (19). The ratio of head-to-head to head-to-tail dimers was determined in the above three cases by glpc assuming equal response factors for both isomers. This

Scheme 7

	Rate
$O \xrightarrow{h\nu} {}^1O$	I
${}^1O \xrightarrow{k_1} O$	$k_1({}^1O)$
${}^1O \xrightarrow{k_2} {}^3O$	$k_2({}^1O)$
${}^3O \xrightarrow{k_3} O$	$k_3({}^3O)$
${}^3O + O \xrightarrow{k_4} O\text{-}O$	$k_4({}^3O)(O)$

O is olefin ground state, ^1O is olefin singlet excited state, ^3O is olefin triplet state and O-O is olefin dimer.

$$Q = \frac{d(O\text{-}O)}{dt} \div I = k_4 \frac{({}^3O)(O)}{I}$$

Q is the quantum yield of dimerization.

At the stationary state

$$\frac{d({}^3O)}{dt} = k_2({}^1O) - k_3({}^3O) - k_4({}^3O)(O) = 0,$$

and

$$\frac{d({}^1O)}{dt} = I - k_1({}^1O) - k_2({}^1O) = 0.$$

Therefore,

$$I = (k_1 + k_2)({}^1O)$$

and

$$({}^1O) = \frac{I}{k_1 + k_2}.$$

Hence, at the stationary state

$$\frac{d({}^3O)}{dt} = \frac{Ik_2}{k_1 + k_2} - k_3({}^3O) - k_4({}^3O)(O) = 0$$

$$Q_{isc} = \frac{k_2}{k_1 + k_2}$$

Q_{isc} is the quantum yield of intersystem crossing from singlet to triplet excited states.

$$\frac{d({}^3O)}{dt} = IQ_{isc} - k_3({}^3O) - k_4({}^3O)(O) = 0$$

$$({}^3O) = \frac{IQ_{isc}}{k_4(O) + k_3}$$

$$Q = \frac{k_4 IQ_{isc}(O)}{(k_4(O) + k_3)\, I}$$

$$1/Q = 1/Q_{isc} + k_3/Q_{isc}k_4 \cdot 1/(O)$$

Table V (23, 24)

Variation of Isomer Distribution With Solvent for Photodimerization of Isophorone

SOLVENT	HEAD-TO-HEAD DIMER(%)	HEAD-TO-TAIL DIMER(%)
Cyclohexane	20.2	79.8
P-Dioxane	30.6	69.4
Isophorone(neat)	38.7	61.3
Dimethyl Sulfoxide	63.2	36.8
Methanol	79.5	20.5
90% Acetic Acid	81.4	18.6

assumption has not been tested for these isomers and it often turns out that structural isomers do not have identical response factors (118). However, the increase in the relative amounts of head-to-head dimer with increase of polarity of solvent has been noted.

A plot of the reciprocal of quantum yield of each isomeric dimer against the reciprocal of isophorone concentration was linear (24). The above results have been attributed to the formation of two triplet excited states, each of which attacks the ground state molecule to give one of the dimers, according to the mechanism below.

Scheme 8

$$\mathrm{Is} \xrightarrow{h\nu} {}^{1}\mathrm{Is}$$
$${}^{1}\mathrm{Is} \rightarrow {}^{3}\mathrm{Is} + {}^{3}\mathrm{Is'}$$
$${}^{3}\mathrm{Is} \xrightarrow{k_d} \mathrm{Is}$$
$${}^{3}\mathrm{Is'} \xrightarrow{k'_d} \mathrm{Is}$$
$${}^{3}\mathrm{Is} + \mathrm{Is} \xrightarrow{k_r} \text{H-H dimer}$$
$${}^{3}\mathrm{Is'} + \mathrm{Is} \xrightarrow{k_r} \text{H-T dimer}$$
$$1/Q_{HH} = 1/q + k_d/qk_r \cdot 1/(\mathrm{Is})$$
$$1/Q_{HT} = 1/q' + k'_d/q'k'_r \cdot 1/(\mathrm{Is})$$

Is: isophorone

q,q': efficiencies of populating excited states ${}^{3}\mathrm{Is}$ and ${}^{3}\mathrm{Is'}$ respectively.

Q_{HH}, Q_{HT}: quantum yields for the formation of head-to-head and head-to-tail dimers respectively.

Chapman (24) has stated that if the attack by one triplet was involved, K_{sens}/K_o would be the same for both isomers (K_{sens} is rate constant of photodimerization sensitized by benzophenone and K_o is rate constant of unsensitized reaction).

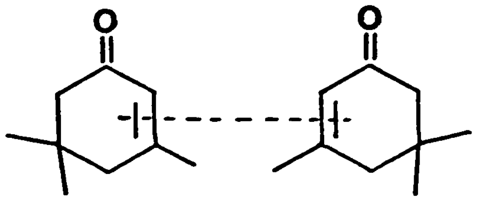
However, it was found that $K_{sens}/K_o = 3.43$ for head-to-head dimerization and $K_{sens}/K_o = 2.40$ for the head-to-tail dimerization. This result was used by Chapman to confirm the attack on ground state isophorone by two different isophorone triplets to give different photodimers. Analysis of the $1/Q$ versus $1/(I)$ plot yield $Q = 0.29$ and $Q = 0.04$ from the intercepts, and $K_d/K_r = 3.2$ and $k'_d/k'_r = 7.4$ from the slopes.

A study of the Stern-Volmer plot (24) for both dimers shows that HH/HT ratios are independent of the extent of quenching. Thus, if two triplet states were involved they would have to have equal lifetimes, to yield the same ratio of dimers. In fact Chapman has even suggested that these two triplets have identical lifetimes. However, due to the different properties attributed to these triplets such a coincidence would be remarkable. Thus, the results from the Stern-Volmer plot appear consistent with attack on the ground state isophorone only one triplet.

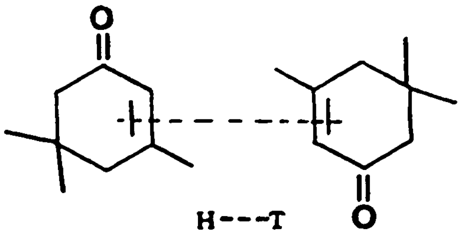
In addition, an alternative mechanism involving one triplet intermediate has been proposed, and can be used to explain the solvent effects observed by Eaton (17), Hammond (19) and Chapman (24), as well as the kinetics observed by Chapman (24).

Scheme 9

	Rate
$\text{Is} \xrightarrow{h\nu} {}^1\text{Is}$	I (Rate of light absorption)
${}^1\text{Is} \xrightarrow{k_1} \text{Is}$	$k_1({}^1\text{Is})$
${}^1\text{Is} \xrightarrow{k_2} {}^3\text{Is}$	$k_2({}^1\text{Is})$
${}^3\text{Is} \xrightarrow{k_3} \text{Is}$	$k_3({}^3\text{Is})$
${}^3\text{Is} + \text{Is} \xrightarrow{k_4} \text{H---H}$	$k_4({}^3\text{Is})(\text{Is})$
	H---H is the metastable precursor to the head-to-head dimer.
${}^3\text{Is} + \text{Is} \xrightarrow{k'_4} \text{H---T}$	$k'_4({}^3\text{Is})(\text{Is})$
	H---T is the metastable precursor to the head-to-tail dimer.
$\text{H---H} \xrightarrow{k_5} \text{HH dimer}$	$k_5(\text{H---H})$
$\text{H---T} \xrightarrow{k'_5} \text{HT dimer}$	$k'_5(\text{H---T})$
$\text{H---H} \xrightarrow{k_6} 2\text{Is}$	$k_6(\text{H---H})$
$\text{H---T} \xrightarrow{k'_6} 2\text{Is}$	$k'_6(\text{H---T})$



H---H



H---T

$$Q_{HH} = \frac{k_5(H\text{---}H)}{I}$$

At the stationary state for the production of H---H,

$$\frac{d(H\text{---}H)}{dt} = k_4(^3Is)(Is) - k_5(H\text{---}H) - k_6(H\text{---}H) = 0$$

$$(H\text{---}H) = k_4(^3Is)(Is)/(k_5 + k_6)$$

$$Q_{HH} = k_4 \cdot k_5/(k_5 + k_6) \cdot \frac{(^3Is)(Is)}{I}$$

$$Q_c = k_5/(k_5 + k_6)$$

Q_c is the efficiency of formation of head-to-head dimer from metastable intermediate H---H.

$$Q_{HH} = Q_c \cdot \frac{k_4(^3Is)(Is)}{I}$$

At the stationary state for the production of ^{3}Is,

$$\frac{d(^3Is)}{dt} = k_2(^1Is) - k_3(^3Is) - k_4(^3Is)(Is) = 0$$

$$(^3Is) = \frac{k_2(^1Is)}{k_3 + k_4(Is)}$$

At the stationary state for the production of ^{1}Is,

$$\frac{d(^1Is)}{dt} = I - k_1(^1Is) - k_2(^1Is) = 0$$

$$(^1Is) = \frac{I}{k_1 + k_2}$$

$$(^3Is) = \frac{k_2/(k_1 + k_2) \cdot I}{k_3 + k_4(Is)}$$

$$Q_{isc} = k_2/(k_1 + k_2)$$

$$(^3Is) = \frac{Q_{isc}I}{k_3 + k_4(Is)}$$

$$Q_{HH} = \frac{Q_{isc}Q_c k_4(Is)}{k_3 + k_4(Is)}$$

$$1/Q_{HH} = \frac{k_4(Is)}{Q_{isc}Q_ck_4(Is)} + \frac{k_3}{Q_{isc}Q_ck_4(Is)}$$

$$1/Q_{HH} = 1/Q_{isc}Q_c + k_3/k_4Q_{isc}Q_c \cdot 1/(Is)$$

Similarly,

$$1/Q_{HT} = 1/Q_{isc}Q'_c + k_3/k'_4Q_{isc}Q_c \cdot 1/(Is)$$

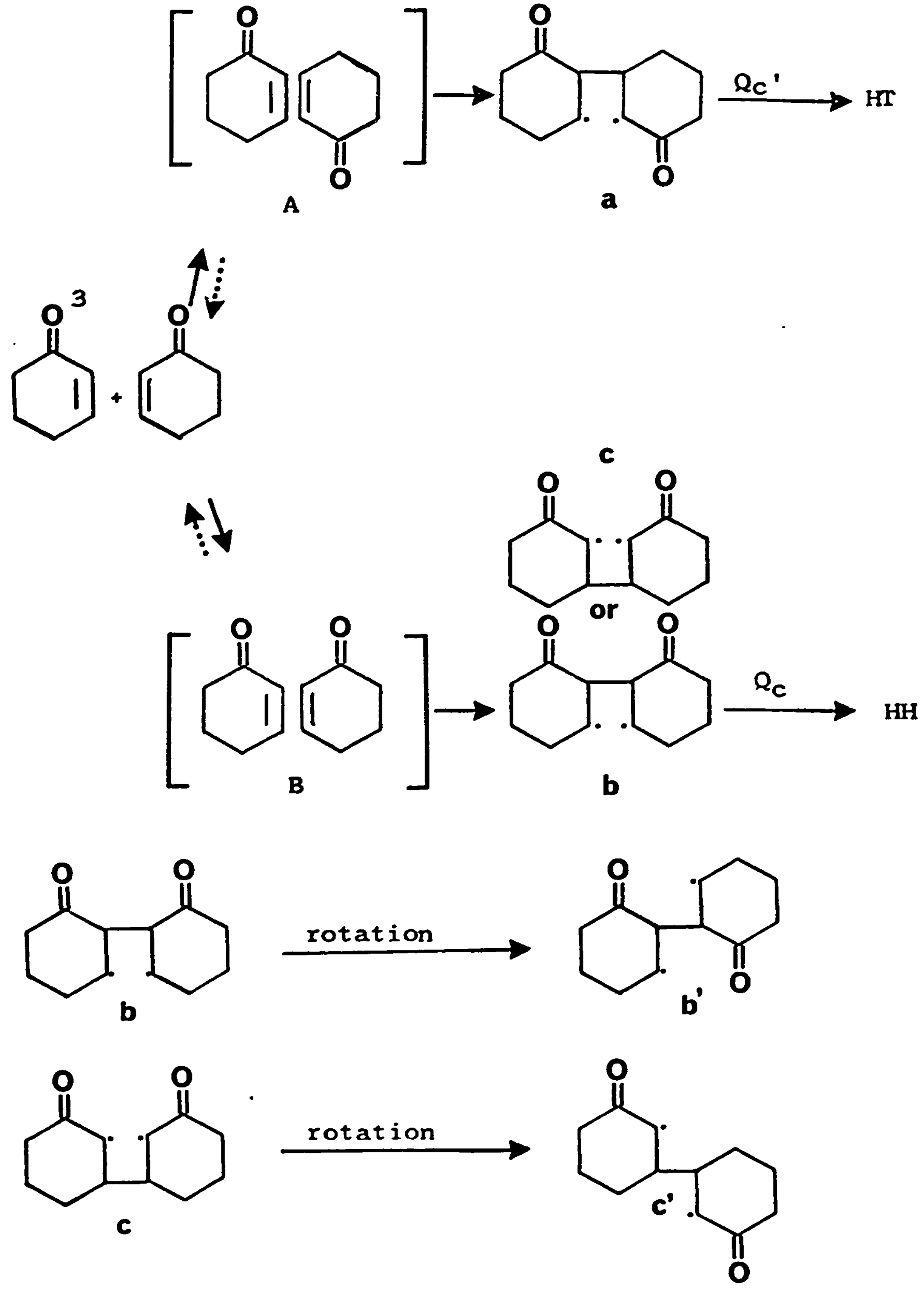
Therefore,

$$1/Q_{dim} = 1/(Q_c + Q'_c)Q_{isc} + k_3/(k_4 + k'_4)(Q_c + Q'_c)Q_{isc} \cdot 1/(Is)$$

The isophorone triplet can attack a ground state molecule to form metastable intermediate A, a precursor to the head-to-head dimer, and B, a precursor to the head-to-tail dimers (Scheme 9). The maximum quantum yield for formation of head-to-head dimer ($Q_{max} = 0.29$ in acetic acid (24)) is interpreted as a measurement of $Q_{isc} \cdot Q_c$ (Q_c is the efficiency with which A goes to head-to-head dimer). The same applies for Q_{max} for the formation of the head-to-tail dimer ($Q_{max} = 0.04$ in acetic acid (24)). The Q_{isc} has not been measured by an independent method. However, it was found that Q_{isc} for cyclopentenone, and cyclohexenone was unity (92). There is no reason why Q_{isc} for isophorone cannot be unity or very close to unity; however, this must be confirmed.

The dimer ratios are dependent on the ratios k_5/k'_4 and Q_c/Q'_c. Thus if one triplet is formed, k_4 does not have to be equal to k'_4, because two different compounds are being

Scheme 10

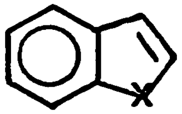


formed from the same intermediate. The fact that k_4 is not necessarily equal to k'_4 also accounts for the different slopes of the I/Q versus 1/(Is) plots for the HH and HT photodimerization.

The solvent effect observed for cyclic enones can be attributed to differences in the dipole moments of the collision complexes A and B. A head-to-tail alignment (complex B) would be favoured over a head-to-head alignment (complex A) in a non-polar solvent. This situation is reversed as the polarity of the solvent increases.

The above mechanism (Scheme 10) and rationale was first proposed by Wagner and Buchek (92) as an explanation of the results obtained for the photodimerization of cyclopentenone and cyclohexenone in acetonitrile. The Q_{isc} for both cyclic ketones were found to be unity, but the limiting quantum yield for dimerization of cyclopentenone and cyclohexenone were found to be 0.36 and 0.74 respectively. Hence. there is a finite value for Q_c and Q'_c. In addition to the above explanation, Wagner and Buchek (92) explained the solvent effects in terms of the conformation of diradicals a and b. In non-polar solvents diradicals b and c could rotate to a conformer with a lower dipole moment (b' and c') and would have their radical sites too far apart for coupling to form the cyclobutane ring. Polar solvents would maintain the polar conformations of b and c allowing a higher probability for coupling to the cyclobutane ring.

Since the Wagner-Buchek treatment rationalizes the work of Chapman as well as their own, this approach may well be useful in elucidating the mechanism of the other alkene photodimerizations.

The mode of photodimerization for systems of the indene type 

(π — π^* excitation) have not been studied extensively. Indene (113), 1,1-dimethylindene (115), coumarone (117) and thianaphthene 1,1-dioxide (136) differ only in the function of the 1 position (X = CH_2, 113; $C(CH_3)_2$, 115; O, 117; SO_2, 136).

It would be interesting and informative to compare the structure of the photodimers, solvent effects, if any, mechanistic and kinetic data as a function of X. Hopefully such mechanistic data will be useful in interpreting the effect that X may have on the excited state since in the ground state the electronegativity of the X group can have a significant effect on the reactivity of the olefinic bond conjugated to the benzene ring.

The photodimerization of 113, 115, 117 and thianaphthene-1,1-dioxide (136) have all been observed, however, the structure of the dimer(s) of 136, is not known. The purpose of this work is to elucidate the structure of the photoproduct(s) of thianaphthene 1,1-dioxide and to investigate in detail its other photochemical properties.

CHAPTER II

THE PHOTODIMERIZATION OF THIANAPHTHENE-1,1-DIOXIDE

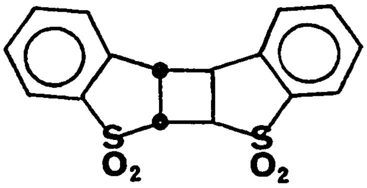
STRUCTURE ELUCIDATION

Historical

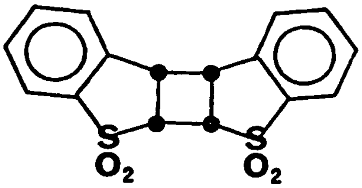
The photodimerization of thianaphthene-1,1-dioxide, 136, was observed by Davies and James (94) and Mustafa (95). Attempts at structure elucidation have led only to the conclusion that photodimerization leads to one product (mp 329-330° (dec)) in which two molecules of thianaphthene-1,1-dioxide are coupled by a cyclobutane ring according to structures A to H (Chart 2).

One path of chemical degradation which could give unambiguous evidence toward determining the structure would be reductive removal of the SO_2 group. This might be achieved in a two step process by removal of the sulphur atoms to give diphenylcyclobutane. Attempts at desulphonation with Raney nickel in acetone gave only poor yields of ethylbenzene (94). Reduction of the sulphone group with $LiAlH_4$ in tetrahydrofuran did not occur (94, 95).

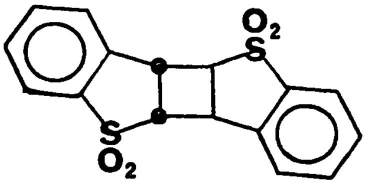
Chart 2



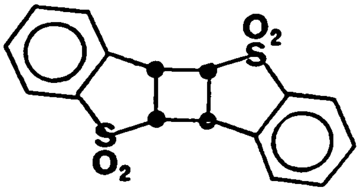
A



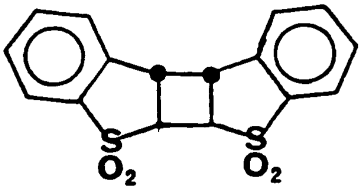
B



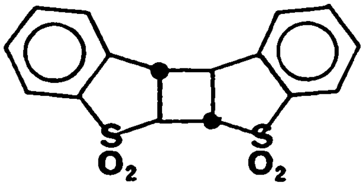
C



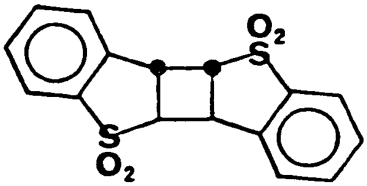
D



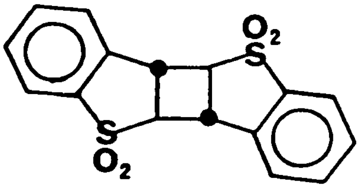
E



F



G



H

Results and Discussion

Photodimerization Reaction*

In a typical run, a benzene solution of 136 (4.0g/1), previously flushed with dry nitrogen, was irradiated with a Hanovia mercury vapor lamp (type L 450 watt filtered by pyrex) for 20 hours at room temperature. A white precipitate crystallized on the walls of the reaction flask. Examination of the solid as well as the residue from the benzene solution by tlc and glpc revealed that two photoproducts had formed; one 137 being a major constituent of the insoluble material and the other 138 being the major constituent of the benzene solution. This is in contrast to the results of earlier workers (94, 95), who observed only one photoproduct. Work-up (see experimental) of the insoluble material and the residue from benzene solution gives pure 137 (mp 329-330° dec.) and pure 138 (mp 334-335° dec.) respectively. The total yield of the two photoproducts was 75% (21% of starting material was recovered). The ratio of compound 137 to 138 was 2.7 (73:27 glpc).

Structure Elucidation - Chemical Degradation

Elemental analysis and exact mass measurement of the

---

*David N. Harpp and Cyril Heitner, J. Org. Chem. 35, 3256 (1970).

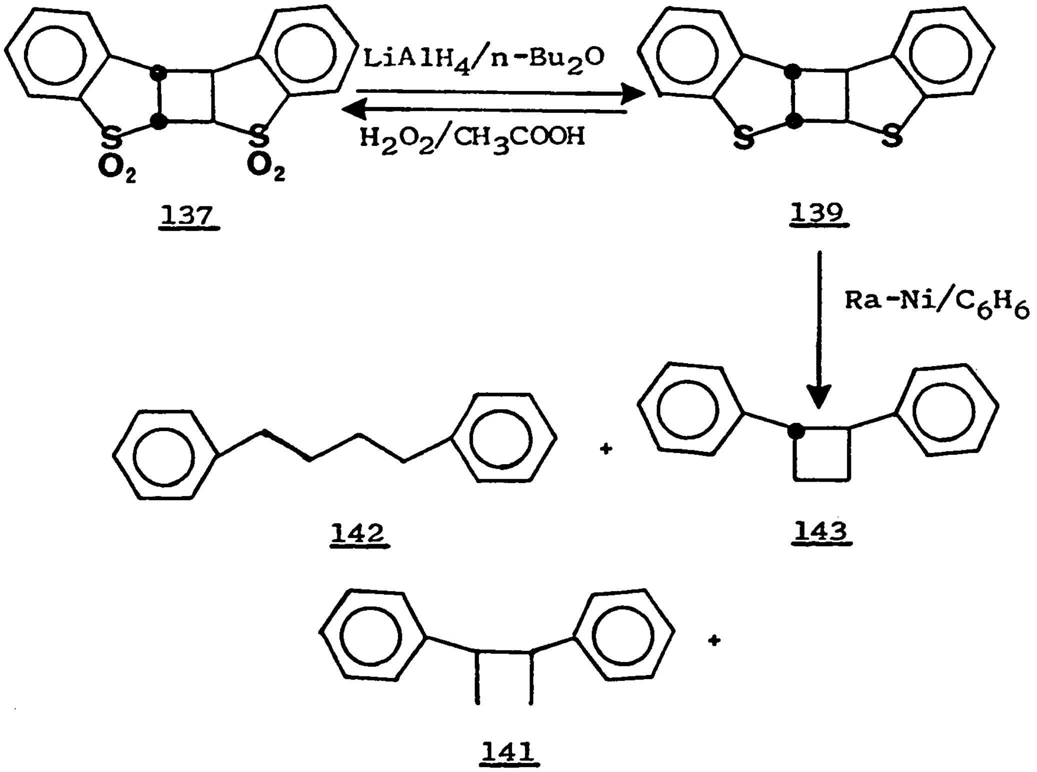
molecular ion of both 137 (332.0192) and 138 (332.0179) agreed with the formula $C_{16}H_{12}S_2O_4$ (m/e, M^+ required 332.0177). This indicates the formation of two isomeric dimers. The infrared spectra of 137 and 138 showed marked differences in the 850 cm^{-1} and 450 cm^{-1} regions. The nmr signal for non aromatic protons show an AA'BB' pattern confirming the cyclobutane structure proposed by Davies and James (94) and Mustafa (95) (Chart 2).

Structures E,F,G, and H are highly strained and would be expected to epimerize readily on treatment with base (96). When 137 and 138 were refluxed with sodium methoxide in methanol, no change in the dimers was observed, thus ruling out E-H as structures for 137 and 138.

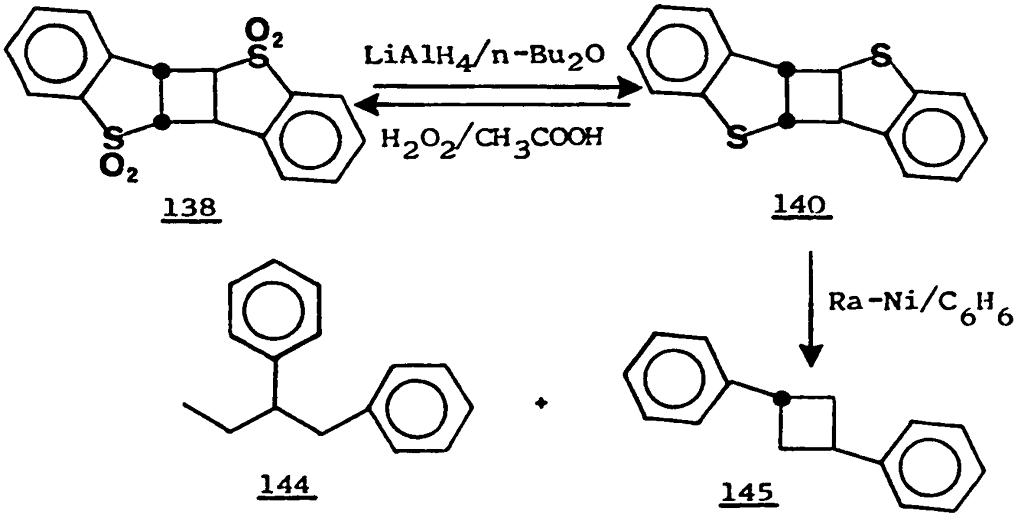
Evidence for the structure of 137 and 138 have been obtained (Schemes 11 and 12) by converting the sulphone to the corresponding sulphide followed by Raney nickel desulphurization to various diphenylcyclobutanes.

Compounds 137 and 138 were reduced by $LiAlH_4$ in n-butyl ether to give sulphide 139 and 140 respectively. These compounds (139 and 140) were oxidized (35% H_2O_2/HOAc) in over 90% yield to compounds 137 and 138 respectively (ir and mixed mp were identical to those of the original photodimers). Hence, no rearrangement occurred during reduction of the photodimers with $LiAlH_4$.

Scheme 11



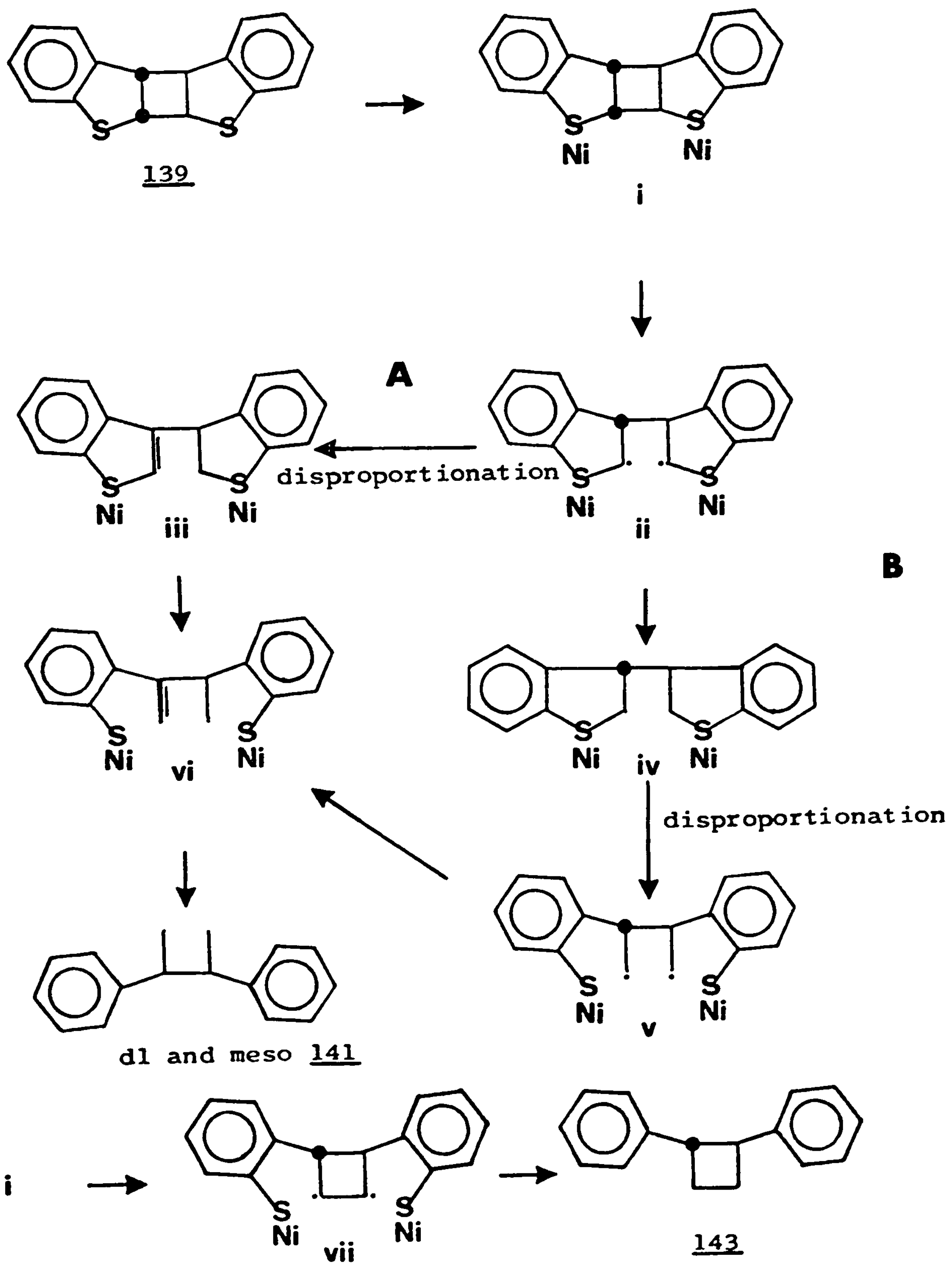
Scheme 12



Compound 139 was treated with RaNi W2 and afforded a mixture of dl and meso-2,3-diphenylbutane (141) (27%), 1,4-diphenylbutane (142) (11%) and trans-1,2-diphenylcyclobutane (143) (62%). The identity of the components of this mixture was verified with three different glpc columns (see experimental). In addition, trans-1,2-diphenylcyclobutane (143) was collected and the nmr spectrum was found to be identical with that of an authentic sample (97). In order to exclude the possibility of isomerization of cis to trans-1,2-diphenylcyclobutane during desulphurization, the cis isomer (97) was refluxed in the presence of Raney nickel, under conditions more extreme than that of compound 139. Only a small amount of 1,4-diphenylbutane (142) was produced (no dl or meso-2,3-diphenylbutane (141) was formed) and no isomerization to trans-1,2-diphenylcyclobutane (143) was observed. Also, when trans-1,2-diphenylcyclobutane (143) was refluxed with RaNi W2 in benzene only a small amount of 142 was produced.

The formation of meso-2,3-diphenylbutane was unexpected. If the photodimer 137 had head-to-head, syn structure (structure B), then not only meso 141 but cis-1,2-diphenylcyclobutane would be expected from the desulphurization reaction. Results from refluxing compound 143 with RaNi W2 has shown that meso and dl 141 were produced from a different route (Scheme 13) than via 143. Since there is ample evidence

Scheme 13


139
i
A
disproportionation
iii
ii
B
vi
iv
disproportionation
v
dl and meso 141
i
vii
143
S
Ni

that racemization (98 - 102) or isomerization of cis trans centres (103 - 107) α to the sulphur atoms are not observed, dl and meso 141 must arise from fragmentation processes on the catalyst surface. Snyder and Cannon (108) first observed such C-C bond fragmentation during the desulphurization of ethanedithioethers (compound 144), whereby not only ethane but substantial amounts of methane were produced from the central carbon atoms.

$R\text{-}S\text{-}CH_2\text{-}CH_2\text{-}S\text{-}R$

144

a) R = phenyl
b) R = ethyl

At least two routes for the formation of dl and meso-2,3-diphenylbutane that have literature precedent are possible (Scheme 13). Both pathways involve initial cleavage of the C-C bond α to the sulphur atom to form a 1,4-diradical, ii (103). Disproportionation of ii can yield iii (Scheme 13) and desulphurization of iii can give vi (103, 108) (Route A in Scheme 13). Also, reduction of ii can produce iv and desulphurization of iv can give the 1,4-diradical v (103), which on disproportionation can then give vi (103, 108) (Route B in Scheme 13). Hydrogenation of vi gives the observed dl and meso 141.

The important facts are that 143 and dl and meso 141 are produced by two different routes, and cis-1,2-diphenylcyclobutane does not isomerize under conditions which were even more extreme than desulphurization. Therefore, based upon the above results and considerations, structure A is assigned to compound 137 (head-to-head, anti).

Similarly, compound 140 when treated with RaNi W2 gave 1,3-diphenylbutane (144) (38%) and trans-1,3-diphenylcyclobutane (145) (62%). Trans-1,3-diphenylcyclobutane was isolated by preparative glpc. The nmr spectrum of 145 (aromatic, τ = 2.82, 10H, singlet; methine, 6.56, 2H, pentuplet, J = 8.0 Hz; methylene, 7.60, 4H, triplet, J = 8.0 Hz) in $CDCl_3$ is indicative of trans stereochemistry. Changing solvents to acetone - d_6 or benzene-d_6 did not change the multiplicity or symmetry of the nmr signals. In trans 145 the methylene protons would be symmetrically equivalent, hence, a triplet methylene nmr signal would be expected. The methylene protons of the cis isomer are not equivalent, thus causing more complex nmr patterns.

Similar arguments have been used in assigning the stereochemistry of trans and cis-1,3-dihalocyclobutanes (109), trans and cis-1,3-dihalo-1,3-dimethylcyclobutanes (110, 111) trans and cis-2,4-diphenylthietane (112), trans and cis-2,4-dimethylthietane (113) and trans-1,3-dimethyl-cyclobutane (110).

As in the case of the desulphurization of compound 139, the desulphurization of compound 140 with RaNi W2 is not accompanied by the isomerization of the centres α to the sulphur atom (103-107). Thus, structure C can be assigned to compound 138 (head-to-tail, anti).

Structure Elucidation - Spectroscopic Methods

Further evidence as to the structure of 138 was obtained by examination of the Raman and infrared spectra of 139 and 140. Compound 140 (with head-to-tail, anti structure), if planar, has a centre of symmetry (Ci symmetry). It has been established that molecules possessing Ci symmetry gave fewer coincident vibrational bands (Raman vs infrared) than do non-centrosymmetric photodimers (Chapter I page 29) (86).

Raman and infrared comparisons were made for compounds 139[*] and 140[*] scanning from 250-3200cm^{-1} (Table VI and VII). Transitions within ± 10cm^{-1}[#] for these comparisons were considered coincidences (Table VII). The observation of 14 fewer coincident bands (25 vs 39 Table VII) for 140 versus 139, strongly indicates that 140 is centrosymmetric, hence confirming the assignment of head-to-tail, anti structure

---

[*] In spite of meticulous purification, Raman spectra for compounds 137 and 138 were of poor quality due to fluorescence.

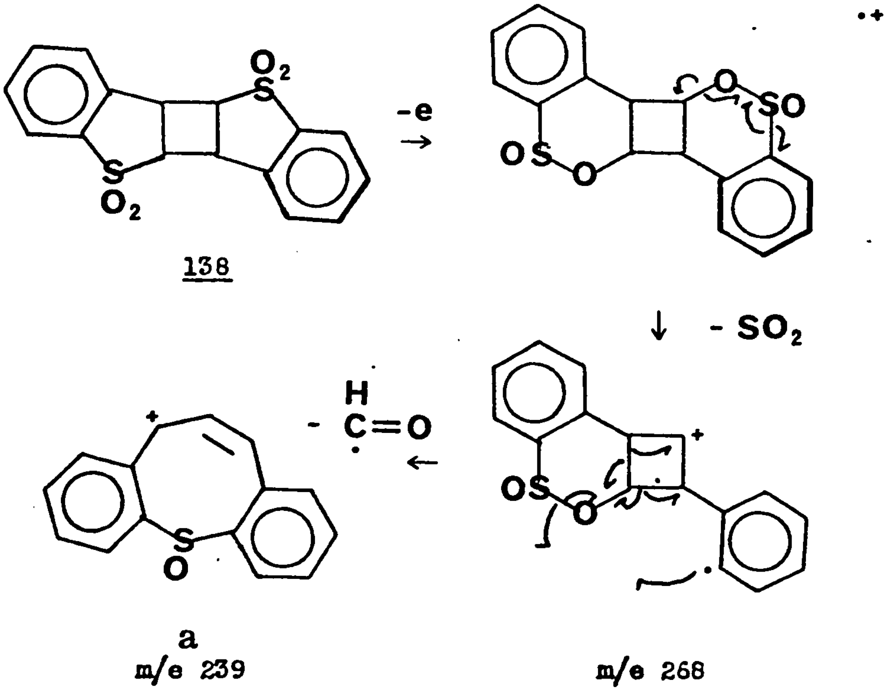
[#] This is 5 cm^{-1} outside the range utilized by previous workers (86), and should easily allow for crystal perturbations.

(structure C) for compound 138.

Examination of the aromatic region of the nmr spectra of compound 137 and 138 and compound 139 versus 140 (see Appendix A) shows that the aromatic signal for each above compound occurs between $\tau = 1.83$ to 2.15. This is consistent with anti stereochemistry for compound 137 and 138 (Chapter I page 33).

The mass spectra of 137 and 138 were examined (Appendix A). These were essentially identical except that compound 138 showed a relatively large peak (35% of base peak) at m/e = 239. Exact mass measurement gave $C_5H_{11}SO$ as the formula. Also, a metastable peak at m/e = 213 was found, indicating that m/e = 239 was the result of a fragmentation of the ion with m/e = 268. The following is consistent with the above data. A sulphinate due to SO migration has been postulated as the intermediate in fragmentation patterns of sulphones like 138 and 137 (117). A loss of CHO from the head-to-tail dimer seems much more likely than from the head-to-head dimer, since fragment a(benzylic stabilized cation) would result from the former (Scheme 14) and an unlikely fragment b from the latter (Scheme 15). This is additional evidence for the head-to-tail structure assignment for compound 138.

Scheme 14



Scheme 15

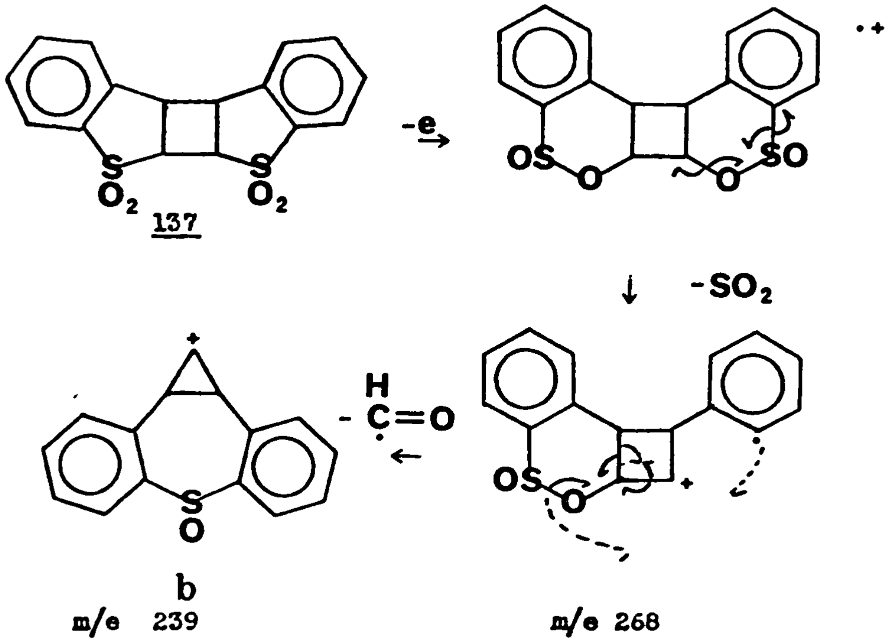


Table VI

COMPARISON OF THE RAMAN DISPLACEMENTS AND INFRARED FREQUENCIES FOR THE BENZOTHIOPHENE-1,1-DIOXIDE PHOTODIMERS

140				139			
head-to-tail				head-to-head			
Infrared		Raman		Infrared		Raman	
cm^{-1}		cm^{-1}		cm^{-1}		cm^{-1}	
252	1100	252			979	232	
292	1122		1115	252^{a}	992	252	992
		330	1130	265	1020		
363	1148			275^{a}	1025^{a}		1028
	1150	410	1155	282	1055^{a}	288	
430^{a}	1160				1060	340	1060
432	1181			368	1070	370	1070
445	1190	440	1190	415		415	1035
481	1205	475				430	1048
488			1230	448	1152	450	1155
528		528	1248	470	1188^{a}	478	1188
605	1260	605		495	1190	495	1190
692		690	1270	510	1198^{a}		1198
711	1282	710	1280	525	1240	520	1240
745		740	1310	535	1248	540	
750	1440			575	1262		1260
768	1458	760	1460	620	1275	621	1282
	1568	785	1565	694	1360	694	
	1580	841	1580	718	1320	720	1320
863		860	2925	728	1400		
871	2950		2950	745	1420^{a}	743	
902	2989		2980	753	1460	753	
	3010	928	3010	770^{a}	1462^{a}	770	
938		942	3020	800	1570		1570
960	3050		3050	833	1579^{a}	832	
971	3060	970		855	1582		1582
990		990	3130	862	2932		2930
1022		1020	3160		2960^{a}		2955
1055		1055		904	2980	904	2975
				935	3000	930	
				970	3040		3038
					3060		3060

a denotes shoulder

Table VII

COMPARISON OF THE RAMAN AND INFRARED FREQUENCY COINCIDENCES[a]

	Head-to-tail photodimer				Head-to-head photodimer		
Compound	ir	R	C[a]	Compound	ir	R	C
140	42	39	25[b]	139	60	42	39[b]
	42	39	19[c]		60	42	29[c]

[a] ir, R and C denote infrared peaks, Raman peaks and coincidences respectively.

[b] coincidences within 10 cm^{-1}. [c] coincidences within 5 cm^{-1}.

Experimental Section

Materials and apparatus: Benzene (Fisher Certified reagent) was used as photodimerization solvent. Melting points were taken on a Gallenkamp apparatus and are not corrected. The glpc data were obtained on a Hewlett-Packard F&M series 5670 research chromatograph using three columns (A, B, C). Column A was a 1/8" x 6' 20% Apiezon L on chromosorb W, AW-DMCS (acid-washed, dimethyldichlorosilane treated): column B was a 1/8" x 6' 10% UC-W98 (silicone gum rubber) on diatoport S and column C was 1/8" x 6' 10% LAC-728 on chromosorb W AW-DMCS treated. Infrared were measured on a Perkin-Elmer 225 and 337 spectrometers, nmr spectra were obtained from Varian Associates A-60 and T-60 spectrometers, mass spectra were recorded on an AEI MS 902 spectrometer, and Raman spectra were recorded as solid samples (several milligrams) on a Jarrel-Ash 25-300 Raman spectrometer.

Thianaphthene-1,1-dioxide (136). Sulphone 136 was obtained by the oxidation of thianaphthene with H_2O_2 in glacial acetic acid according to the method of Davies and James (94). This sulphone was further purified by recrystallization from ethanol/activated charcoal (m.p. 142.5-143°; lit:(94) mp 142°) yield 76%.

The Photodimerization of Thianaphthene-1,1-dioxide. Two liters of a benzene solution of 136 (8.0 g, 2.4×10^{-2} M), previously purged with dry nitrogen for 45 minutes, were irradiated with a Hanovia mercury vapor lamp (type L 450 watt) in the usual quartz water colled immersion apparatus with pyrex filter, for 20 hours at room temperature. A white precipitate (3.0 g) crystallized on the walls of the reaction flask; in addition, 4.7 g of material was recovered from the benzene solution. Examination by tlc (silica gel eluted with $CHCl_3$:acetone = 85:15) and glpc on column A, of the precipitate and the benzene solution revealed the presence of two compounds, compound <u>137</u>, being a major constituent of the insoluble material and compound <u>138</u>, being a major constituent of the benzene solution. In a typical run the residue from the benzene solution was combined with the precipitate and the total mixture analyzed with glpc on column A. The ratio of <u>137</u> to <u>138</u> was found to be 73:27. The total yield of the dimers was 6.0 g (75% yield).

Recrystallization of the fraction precipitating from benzene with DMSO gave 2.6 g of <u>137</u> (mp 329-330° dec); ir: $\bar{\nu}$, 1320 cm^{-1} and 1160 cm^{-1} (SO_2 stretching); nmr; τ, 1.83-2.15 (8H multiplet); 5.20-5.80 (4H AA'BB').

Anal. Calcd for $C_{16}H_{12}S_2O_4$: C, 57.83; H, 3.62; S, 19.27. Found: C, 57.80; H, 3.70; S, 19.18. Exact mass of molecular ion; Calcd for $C_{16}H_{12}S_2O_4$: 332.0177. Found: 332.0192.

The residue obtained by evaporation of the benzene was extracted with boiling water until <u>136</u> no longer crystallized from the water, (1.7 g, 21%, of 136 was recovered). The resulting mixture was recrystallized twice from DMSO (crystallizing mixture allowed to stand overnight), resulting in 1.1 g of 138 (mp 334-335°) dec.);ir:$\bar{\nu}$,1320 cm^{-1} and 1160 cm^{-1} (SO_2 stretching), nmr; τ , 1.85-2.15 (8H multiplet), 4.90-5.80 (4H AA'BB').

Anal. Calcd for $C_{16}H_{12}S_2O_4$: C, 57.83; H, 3.62; S, 19.27. Found: C, 58.22; H, 3.92; S, 19.06. Exact mass measurement of molecular ion: Calcd for $C_{16}H_{12}S_2O_4$, 332.0177. Found: 332.0179.

Reduction of Photodimers 137 and 138. Compound 137 (4.0 g, 0.012 mol) was refluxed with $LiAlH_4$ (2.8 g, 0.073 mol) in 200 ml of n-butyl ether (previously refluxed over sodium) for 5 hours. The excess $LiAlH_4$ was decomposed by carefully adding 3 ml of water, 3 ml of 15% NaOH and 6 ml of water in succession. After filtration and evaporation of the solvent, the crude product was chromatographed over 50 g of neutral alumina with petroleum ether (30-60°) and hexane to give 2.1 g of white crystals, 139 mp 217-218° (66% yield). Infrared analysis showed the absence of the two SO_2 stretching absorptions.

Anal. Calcd for $C_{16}H_{12}S_2$: C, 71.64; H, 4.47; S, 23.84. Found: C, 71.55; H, 4.61; S, 23.89.

Compound 138 was treated similarly except that the product 140 was purified by crystallization from $CHCl_3$ ethanol; 1.8 g (56%) mp 180-180.5° was obtained. Infrared analysis showed the absence of the SO_2 stretching bands.

A variety of other reductions were attempted ($LiAlH_4$ in tetrahydrofuran and n-butyl ethyl ether), and no identifiable products were obtained.

Anal. Calcd for $C_{16}H_{12}S_2$: C, 71.64; H, 4.47; S, 23.84. Found: C, 71.69; H, 4.16; S, 23.89.

Oxidation of bis-sulfides 139 and 140. After compound 139 (80 mg, 0.03 mmole) was dissolved in 10 ml of glacial acetic acid, 10 ml of 35% H_2O_2 was added and the resulting mixture heated on a steam bath for one hour. The solution was cooled and poured into 50 ml of cold water. The suspension was filtered and dried under vacuum. Compound 137 (75 mg, 73% mp 329-330° dec.) resulted. A mixture melting point with photoproduct 137 was not depressed. In addition, the ir spectrum was identical to that of photoproduct 137.

Similarly, 100 mg of 140 was oxidized to 80 mg (63% yield) of 138 (mp 334-335° dec.). A mixture melting point with photoproduct 138 was not depressed and the ir spectrum was identical to that of photoproduct 138. The mixture melting point of 137 and 138 was 285-290°.

Meso and dl-2,3-Diphenylbutane (141). These compounds were prepared from 37 g (0.2 mol) of 1-phenylethyl bromide according to the method of Conant and Blatt (114). Recrystallization of the mixture in ethanol gave 10 g (25% yield) of meso-2,3-diphenylbutane (mp 126-128°; lit: (114) mp 124-126°. The mother liquor was evaporated and the residue distilled under vacuum to give 5 g (13% yield) of dl-2,3-diphenylbutane (bp 100-102° /1 mm; lit (115); bp 103-104° /1 mm; n^{20} = 1.5552; lit (115); n_D^{20} = 1.55516;).

1,2-Dibenzoylethane. 1,2-Dibenzoylethane was prepared in 95% yield by the method of Shaefer (116).

Bisethylenedithioketal of Dibenzoylethane. This material was prepared by mixing 2.6 g (0.011 mol) of dibenzoylethane with 12 ml of ethylenedithiol and 2 ml of boron trifluoride etherate at room temperature for one hour. After recrystallization from dioxane, 3.6 g (85% yield) of white crystals mp 197-198° resulted.

Anal. Calcd for $C_{20}H_{22}S_4$: C, 61.28; H, 5.64. Found: C, 61.45; H, 5.65.

1,4-Diphenylbutane (142). The above bisethylenedithioketal (3 g, 0.0079 mol) was refluxed in ethanol with about 3 g of Raney nickel W2 for 15 hours, affording 1.5 g (89% yield) of 1,4-diphenylbutane (mp 48-49°, lit (97): mp 50.5-51.5°).

1,2-Diphenylcyclobutene. This material was prepared in 40% yield as previously reported (97).

cis-1,2-Diphenylcyclobutane. This material was prepared by hydrogenation of 1,2-diphenylcyclobutene over a platinum catalyst in a 95% yield (97); nmr ($CDCl_3$) τ, 3.05 (10H singlet); 5.88-6.20 (2H multiplet): 7.45-7.55 (4H multiplet).

Trans-1,2-Diphenylcyclobutane (143). The cis isomer (0.2 g, 0.96 mmol) was mixed with 0.2 g of potassium t-butoxide in anhydrous DMSO at 70° for 22 hours. The solution was added to water, extracted with benzene and chromatographed over silica gel with petroleum ether. The trans isomer (143) (0.18 g, 90% yield) was isolated: nmr ($CDCl_3$) τ, 2.81 (10H singlet); 6.27-6.61 (2H multiplet) and 7.52-8.05 (4H multiplet).

Desulphurization of compound 139. Compound 139 (1.7 g, 0.0063 mol) was refluxed with about 4 g of RaNi W2 slurry in benzene for 4 hours. After filtration and evaporation of the benzene, 1.1 g of an oil was isolated. Analysis by glpc on columns A, B and C, using internal standards showed that the mixture contained trans-1,2-diphenylcyclobutane 143, dl and meso-2,3-diphenylbutane (141) and 1,4-diphenylbutane (142) in 62%, 27% and 11% yield respectively. Using column C, trans-1,2-diphenylcyclobutane (143) was collected and the nmr spectrum obtained was identical to that of authentic material.

<u>1,3-Diphenyl-3-butanol</u>. This compound was prepared by adding 12 g (0.10 mol) of acetophenone to an ether solution of Grignard reagent made from 27.7 g (0.15 mol) of β-phenylethyl bromide and 5 g of magnesium. The reaction mixture was refluxed for two hours and worked up in the usual way. The crude alcohol was distilled at 136° /0.25 mm, giving on cooling an amorphous solid (12 g). The infrared spectrum showed the presence of an OH group and the absence of a carbonyl and bromide group. This material was used without further purification.

<u>1,3-Diphenylbutane</u> (<u>144</u>). 1,3-Diphenyl-3-butanol (7.6 g, 0.034 mol) in 150 ml of glacial acetic acid was mixed with 0.1 g of 10% Pd/C at 45 p.s.i. of hydrogen for 15 hours. After chromatography over silica gel with petroleum ether (30-60°): CCl_4 (1:1) graduated slowly to CCl_4, 1,3-diphenylbutane (<u>144</u>) (3.5 g, 50% yield) was obtained. The material was found to be glpc pure (column A, B & C); n^{20} = 1.5520; lit (115): n_D^{20} = 1.5525), and nmr $CDCl_3$: τ , 2.80-2.91 (10H m): 7.18-7.69 (3H m): 7.98-8.40 (2H m): and 8.80 (3H d).

Desulphurization of Compound 140. Compound 140 (1.0 g) was refluxed with 3 g of Raney nickel W2 in benzene for 15 hours. Filtration and evaporation gave 0.5 g (65%) of an oil and 0.3 g of 140.

Analysis by glpc showed that two compounds were present. The first fraction, 1,3-diphenylbutane (144) was identified on glpc by comparing the retention times with an authentic sample on column A, B and C. About 50 mg of the second fraction was collected from glpc column A and was identified by mass spectra (molecular ion m/e = 208) and nmr spectra ($CDCl_3$) τ , 2.82, (10H s); 6.56, (2H p), J = 8.0 Hz; 7.60 (4H t), J = 8.0 Hz, as trans-1,3-diphenylcyclobutane (145).

Anal. Calcd for $C_{16}H_{14}$: C, 92.26; H, 7.74. Found: C, 92.14; H, 7.55. Exact mass measurement of molecular ion: Calcd for $C_{16}H_{14}$; 208.1245. Found: 208.1252.

Attempted Epimerization of Dimers 137 and 138. Compounds 137 and 138 (150 mg) were each refluxed 12 hours with 1.2 g of sodium methoxide in 25 ml of methanol. Dimers 137 and 138 were recovered unchanged (glpc, col. A; mp and mixed melting point).

CHAPTER III

MECHANISM OF THE PHOTODIMERIZATION OF THIANAPHTHENE-1,1-DIOXIDE (136)

Results

Multiplicity of Excited State

In order to investigate the multiplicity of the excited state of thianaphthene-1,1-dioxide (136) responsible for photodimerization, attempts were made to quench (i.e. inhibit) the dimerization with a triplet quencher, trans α-methylstilbene (148). This quencher has a triplet energy level at about 50 Kcal/mole (118), and does not absorb at the irradiating wavelength of 313 nm (λ max for trans α-methylstilbene is 276 nm). When thianaphthene-1,1-dioxide (136) (0.05M) was irradiated in the presence of 148 (0.05M), the production of photodimers was negligible. The simultaneous irradiation of the same concentration of 136 without quencher resulted in a 70% production of photodimers. Also, some isomerization of the quencher sensitized by the triplet excited state of 136, was observed (Table IX). Therefore, the triplet excited state of 136 was quenched.

Thianaphthene-1,1-dioxide (136) was irradiated at 366 nm in the presence of a variety of triplet sensitizers (Table VIII). At this wave length compound 136 does not absorb any light; in all cases, greater than 98% of the light is absorbed by the sensitizers. Benzene solutions of 136 (0.024M) and sensitizer (0.0241 M) were irradiated for 24 hours. Dimer production for each sensitized reaction is summarized in Table VIII.

Table VIII

Sensitized Photodimerization of Thianaphthene-1,1-dioxide.

Triplet sensitizer	Triplet energy (119) Kcal/mole	Intersystem crossing efficiency (Ω_{isc})	Dimer yield %	HH/HT
Benzophenone	69	1.0	82	2.70
Chrysene	57	0.67	65	2.75
Benzil	54	0.92	85	2.70
Fluorene-9-one	53	0.93	47	2.69
Pyrene	49	-	0	-
No sensitizer	-	-	0	-

The ratio of HH and HT photodimers did not vary significantly with the triplet energy of the sensitizer.

Experiments of the type described above have been used to support a mechanism proceeding wholly via the triplet excited state (18). In the case of the photodimerization of thianaphthene-1,1-dioxide, the fact that trans α-methylstilbene quenches the production of both HH and HT photodimers and that these dimers are produced upon the irradiation of several triplet sensitizers in the presence of the monomer <u>136</u> is consistent with a triplet excited state as an intermediate.

<u>Thianaphthene-1,1-dioxide Triplet Energy</u>

Attempts made to observe the phosphorescence from thianaphthene-1,1-dioxide (<u>136</u>) in an ethanol glass at 77° K, met with failure. Therefore, measurements of the triplet energy of thianaphthene-1,1-dioxide was made by two indirect methods. The first involved the use of several sensitizers of decreasing triplet energy. The results summarized in Table VIII indicate that $E_{triplet}$ lies between 53 and 49 Kcal/mole. The second method is more precise and involves the use of thianaphthene-1,1-dioxide as a sensitizer to establish a photostationary state of the α-methylstilbenes. The composition of the photostationary state of α-methylstilbene has been determined as a function of the triplet energy level of the sensitizer (118).

Three tubes each containing a benzene solution of 0.05 M of trans α-methylstilbene and sensitizer (benzoquinone, pyrene, and thianaphthene-1,1-dioxide) were irradiated with light at wavelength 313 nm. The composition of the photostationary states produced by each sensitizer was determined on glpc (see experimental). The results are summarized in Table IX and indicate a triplet energy for thianaphthene-1,1-dioxide of 50 ± 1 Kcal/mole. This value is consistent with the results obtained in the sensitization experiment (Table VIII).

Table IX

Photostationary State of α-Methylstilbene

Sensitizer	Triplet Energy Kcal/mole (118)	cis/trans
Benzoquinone	50	0.88
Pyrene	48.5	2.38
		2.38
Thianaphthene-1,1-dioxide	50	0.83
		0.85

Quantum Yield of the Photodimerization of Thianaphthene-1,1-dioxide (136)

Quantum yields of the photodimerization of compound 136 were determined in benzene as a function of concentration. Each quantum yield was determined by parallel irradiation of four degassed samples with uranyl oxalate actinometer at 313 nm.

Dimer yields were based upon the disappearance of <u>136</u> as monitored by uv analysis assuming that for every mole of dimer found, two moles of compound <u>136</u> were consumed; $1/\Omega_{DIM} = 2/\Omega_{TND}$ vs $1/C_{TND}$ was plotted and found to be linear (correlation coefficient = 1.00). A least squares calculation gave a limiting quantum yield of 0.18.

Table X

Dimerization of <u>136</u> at Various Concentrations

Concentration (C) Moles/liter x 10^{-2}	Ω_{TND}	σ	1/C	$1/\Omega_{DIM} = 2/\Omega_{TND}$
2.41	0.028		41.3	
	0.038			
	0.039			
	0.034			
	0.035*	± 0.001		57.1
3.61	0.050		27.3	
	0.050			
	0.047			
	0.056			
	0.051*	± 0.001		39.2
4.32	0.064		20.7	
	0.071			
	0.064			
	0.063*	± 0.001		31.7

*These values are weighted averages and average deviations.

The Photodimerization of Thianaphthene-1,1-dioxide

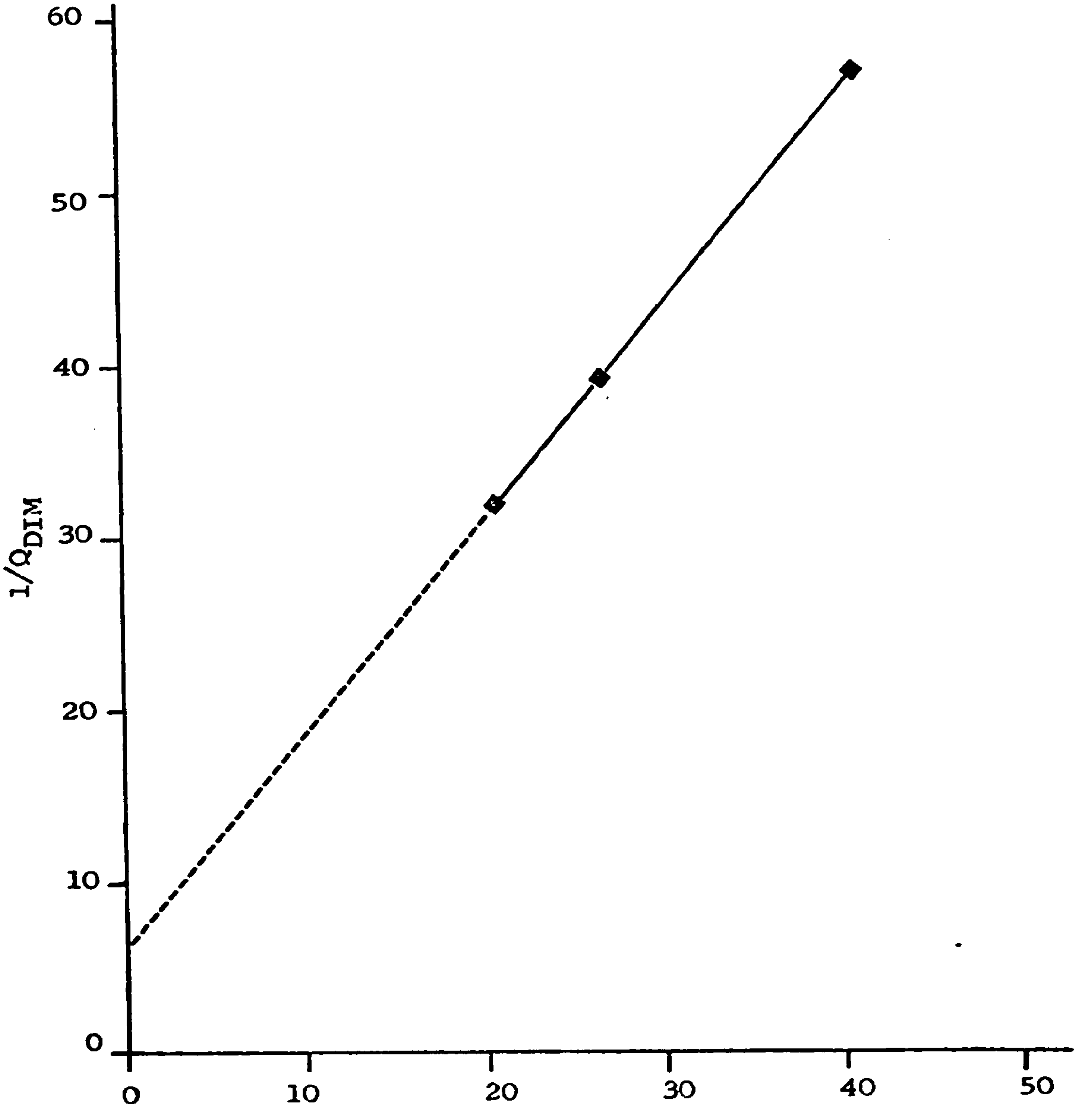


Figure 2

Solvent Effect

The product distribution as a function of solvent polarity was studied. The ratio of the head-to-head to head-to-tail dimer (HH/HT) was found to increase with the polarity of the solvents. Quantitative glpc was used to determine dimer ratios. The plot of log HH/HT versus the Kirkwood-Onsager parameter, $(D - 1)/(2D + 1) \cdot \rho/M$, was found to be linear, with a correlation coefficient of 0.895 (P = 0.02, i.e. there is only a 1 in 50 chance that the points are random. This exceeds the generally accepted value of P = 0.05 (120)) (Fig. 3). In the Kirkwood-Onsager parameter, D is the dielectric constant, ρ is the density and M is the molecular weight of the solvent (Table XI). This result has been found to be consistent with preferential solvation of the head-to-head transition state. The above (Figure 3)

Table XI

Solvent Effects for the Dimerization of Thianaphthene-1,1-dioxide

Solvent	Dielectric constant (D)	Density	$\frac{(D-1)\rho}{(2D-1)\ M}$	$\frac{HH}{HT}$	Log $\frac{HH}{HT}$	Yield %
Benzene	2.27	0.8786	0.00229	2.70	0.4317	83
Chloroform	4.70	0.4832	0.00496	5.89	0.7701	85
Ethyl acetate	6.03	0.9003	0.00383	5.74	0.7589	77
1,2-Dichloroethane	10.37	1.2564	0.00573	6.50	0.8129	73
Acetic acid	6.15	1.0492	0.00675	7.35	0.8663	66
Dichloromethane	8.90	1.3266	0.00663	7.36	0.8669	82

Solvent Effect

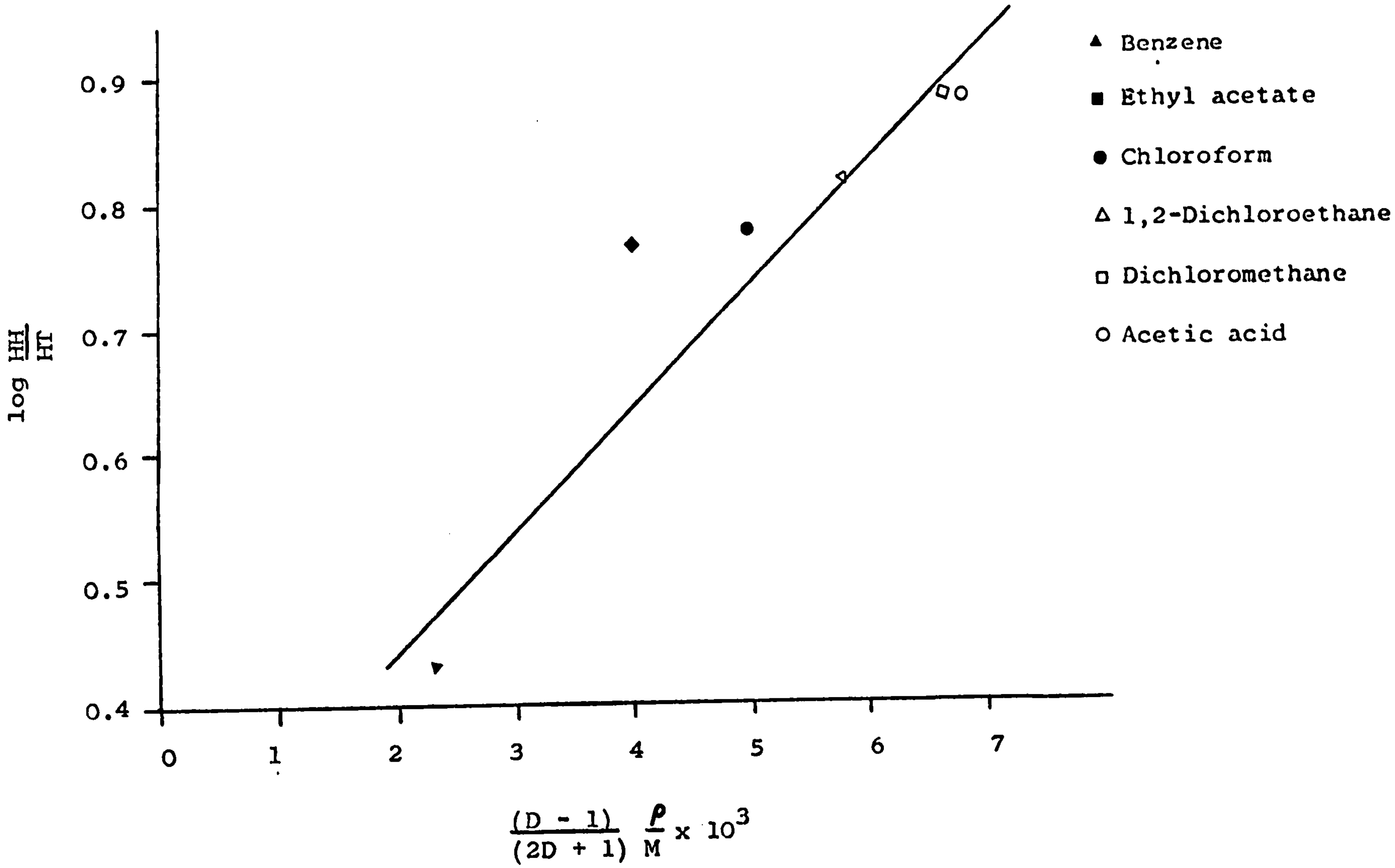


Figure 3

correlation of the HH/HT ratios has been used as evidence for polarity differences in the transition states leading to the endo and exo adducts of cyclopentadiene, to methyl acrylate and methyl trans-crotonate (121).

Quantum Yield of the Sensitized Photodimerization of Compound 136.

In order to determine the yield of photodimers from the triplet state ($Q_t \cdot Q_c$ in Scheme 16), the quantum yields of dimerization of 136, sensitized by benzophenone, were determined in benzene as a function of concentration. If the hypothesis of Wagner and Buchek (92) (Chapter I) is applied to this photosensitized dimerization of compound 136, the following mechanism results:

Scheme 16

	Rate
$B \xrightarrow{h\nu} {}^1B$	I
${}^1B \xrightarrow{k_1} {}^3B$	$k_1({}^1B)$
${}^1B \xrightarrow{k_2} B$	$k_2({}^1B)$
${}^3B \xrightarrow{k_3} B$	$k_3({}^3B)$
$TND + {}^3B \xrightarrow{k_4} {}^3TND + B$	$k_4({}^3B)(TND)$
${}^3TND \xrightarrow{k_5} TND$	$k_5({}^3TND)$
${}^3TND + TND \xrightarrow{k_6} H{-}{-}{-}H$	$k_6({}^3TND)(TND)$

$\text{H---H} \xrightarrow{k_7} \text{TND}$	$k_7(\text{H---H})$
$\text{H---H} \xrightarrow{k_8} \text{HH dimer}$	$k_8(\text{H---H})$
${}^3\text{TND} + \text{TND} \xrightarrow{k_6'} \text{H---T}$	$k_{6'}({}^3\text{TND})(\text{TND})$
$\text{H---T} \xrightarrow{k_7'} \text{TND}$	$k_{7'}(\text{H---T})$
$\text{H---T} \xrightarrow{k_8'} \text{HT dimer}$	$k_{8'}(\text{H---T})$

B is benzophenone.
TND is thianaphthene-1,1-dioxide.
H---H and H---T are the metastable intermediates to the head-to-head photodimer <u>137</u> and head-to-tail photodimer 138, respectively.

$$Q_{HH} = k_8\frac{(\text{H---H})}{I}$$

Q_{HH} is the quantum yield for the formation of head-to-head dimer.

For the stationary state of the production of H---H,

$$\frac{d(\text{H---H})}{dt} = k_6({}^3\text{TND})(\text{TND}) - k_7(\text{H---H}) - k_8(\text{H----H}) = 0$$

$$(\text{H---H}) = k_6/(k_7 + k_8)({}^3\text{TND})(\text{TND})$$

$$Q_{HH} = \frac{k_8k_6}{(k_7 + k_8)}\,\frac{({}^3\text{TND})(\text{TND})}{I}$$

$$Q_c = \frac{k_8}{k_7 + k_8}$$

Q_c is the fraction of HH dimer formed from its metastable intermediate.

Therefore,

$$Q_{HH} = \frac{Q_c k_6({}^3\text{TND})(\text{TND})}{I}$$

For the steady state of the formation of ^{3}TND,

$$\frac{d({}^3\text{TND})}{dt} = k_4({}^3\text{B})(\text{TND}) - k_5({}^3\text{TND}) - k_6({}^3\text{TND})(\text{TND}) = 0$$

$$({}^3\mathrm{TND}) = \frac{k_4({}^3\mathrm{B})(\mathrm{TND})}{k_5 + k_6(\mathrm{TND})}$$

For the stationary state of the production of $^3\mathrm{B}$,

$$\frac{d({}^3\mathrm{B})}{dt} = k_1({}^1\mathrm{B}) - k_3({}^3\mathrm{B}) - k_4({}^3\mathrm{B})(\mathrm{TND}) = 0$$

$$({}^3\mathrm{B}) = \frac{k_1({}^1\mathrm{B})}{k_3 + k_4(\mathrm{TND})}$$

For the steady state of the production of $^1\mathrm{B}$,

$$\frac{d({}^1\mathrm{B})}{dt} = I - k_1({}^1\mathrm{B}) - k_2({}^1\mathrm{B}) = 0$$

$$({}^1\mathrm{B}) = \frac{I}{k_1 + k_2}$$

$$({}^3\mathrm{B}) = \frac{Ik_1}{(k_1 + k_2)(k_3 + k_4)(\mathrm{TND})}$$

$$Q_{isc} = \frac{k_1}{k_1 + k_2}$$

Q_{isc} is the inter-system crossing of benzophenone singlet to benzophenone triplet.

$$({}^3\mathrm{TND}) = \frac{k_4(\mathrm{TND})}{k_5 + k_6(\mathrm{TND})} \cdot \frac{Q_{isc}I}{k_3 + k_4(\mathrm{TND})}$$

$$Q_{HH} = Q_c\, Q_{isc}\, \frac{k_6(\mathrm{TND})}{k_5 + k_6(\mathrm{TND})}\, \frac{k_4(\mathrm{TND})}{k_3 + k_4(\mathrm{TND})}$$

$$Q_t = \frac{k_6(\mathrm{TND})}{k_5 + k_6(\mathrm{TND})}$$

Q_t is the fraction of triplets attacking the ground state to form a metastable intermediate (H---H).

$$Q_{HH} = Q_c\, Q_{isc}\, Q_t\, \frac{k_4(\mathrm{TND})}{k_3 + k_4(\mathrm{TND})}$$

$$\frac{1}{Q_{HH}} = \frac{k_3 + k_4(\mathrm{TND})}{Q_c\, Q_{isc}\, Q_t\, k_4(\mathrm{TND})} = \frac{1}{Q_c\, Q_{isc}\, Q_t} + \frac{k_3}{Q_c\, Q_{isc}\, Q_t\, k_4(\mathrm{TND})}$$

Lifetime (τ) of benzophenone triplet $= \frac{1}{k_3}$

$$\frac{1}{Q_{HH}} = \frac{1}{Q_c\, Q_{isc}\, Q_t} + \frac{1}{Q_c\, Q_{isc}\, Q_t\, \tau\, k_4(\mathrm{TND})}$$

$$\frac{1}{Q_{HT}} = \frac{1}{Q_{c'}\, Q_{isc}\, Q_{t'}} + \frac{1}{Q_{c'}\, Q_{isc}\, Q_{t'}\, \tau\, k_4(\mathrm{TND})}$$

$Q_{c'}$ is the fraction of HT dimer formed from its metastable intermediate H---T.

$$\frac{1}{Q_{DIMER}} = \frac{1}{(Q_c + Q_{c'})(Q_t + Q_{t'})\ Q_{isc}} + \frac{1}{(Q_c + Q_{c'})(Q_t + Q_{t'})\ Q_{isc}\ \tau\ k_4(TND)} \qquad (3)$$

$Q_{t'}$ is the fraction of triplets attacking the ground state to form a metastable intermediate (H---T).

The intercept of the plot $1/Q_{DIM}$ versus $1/C_{TND}$ should give $1/(Q_c + Q_{c'})(Q_t + Q_{t'})\ Q_{isc}$. The Q_{isc} for benzophenone has been shown to be equal to 1.0 (119); $Q_t + Q_{t'}$ can be shown to be unity if the thianaphthene-1,1-dioxide triplet state is relatively long lived and attack on the ground state molecule by the triplet state is diffusion controlled (i.e. $k_6 + k_6 = 10^9$ mole liter^{-1} sec^{-1} and $k_5 = 10^5$ sec^{-1}). These assumptions are reasonable because the formation of the metastable intermediate should occur upon collision and the rate of encounters of triplet with ground state molecules has been assumed to be 10^9 to 10^{10} mole liter^{-1} sec^{-1} (119). The results obtained below confirm the above assumptions made for compound <u>136</u>.

$$(Q_t + Q_{t'}) = \frac{(k_6 + k_{6'})(^3TND)(TND)}{k_5(^3TND) + (k_6 + k_{6'})(^3TND)(TND)}$$

$$= \frac{(k_6 + k_{6'})(TND)}{k_5 + (k_6 + k_{6'})(TND)} \qquad (TND) = 10^{-2}$$

$$= \frac{(10^9)(10^{-2})\ 1}{10^5 + (10^9)(10^{-2})} = \frac{100 \times 10^5}{(1 + 100) \times 10^5}$$

$$= \frac{100}{101} \sim 1.00$$

Table XII

The Dimerization of Thianaphthene-1,1-dioxide (136) Sensitized by Benzophenone.#

Concentration (C) Moles/liter x 10^{-2}	Ω_{TND}	σ	$1/C_{TND}$	$1/\Omega_{DIM} = 2/\Omega_{TND}$
2.41	0.82		41.3	
	0.82			
	0.75			
	0.75			
	0.78*	± 0.01		2.56
3.61	1.03		27.3	
	1.03			
	1.08			
	1.03			
	1.03*	± 0.01		1.94
4.82	1.22		20.7	
	1.22			
	1.22			
	1.22			
	1.22*	± 0.00		1.64

#Benzophenone concentration is equal to 1.99 x 10^{-2} M.

*Weighted mean and weighted average deviation.

The Photodimerization of Thianaphthene-1,1-dioxide Sensitized by Benzophenone

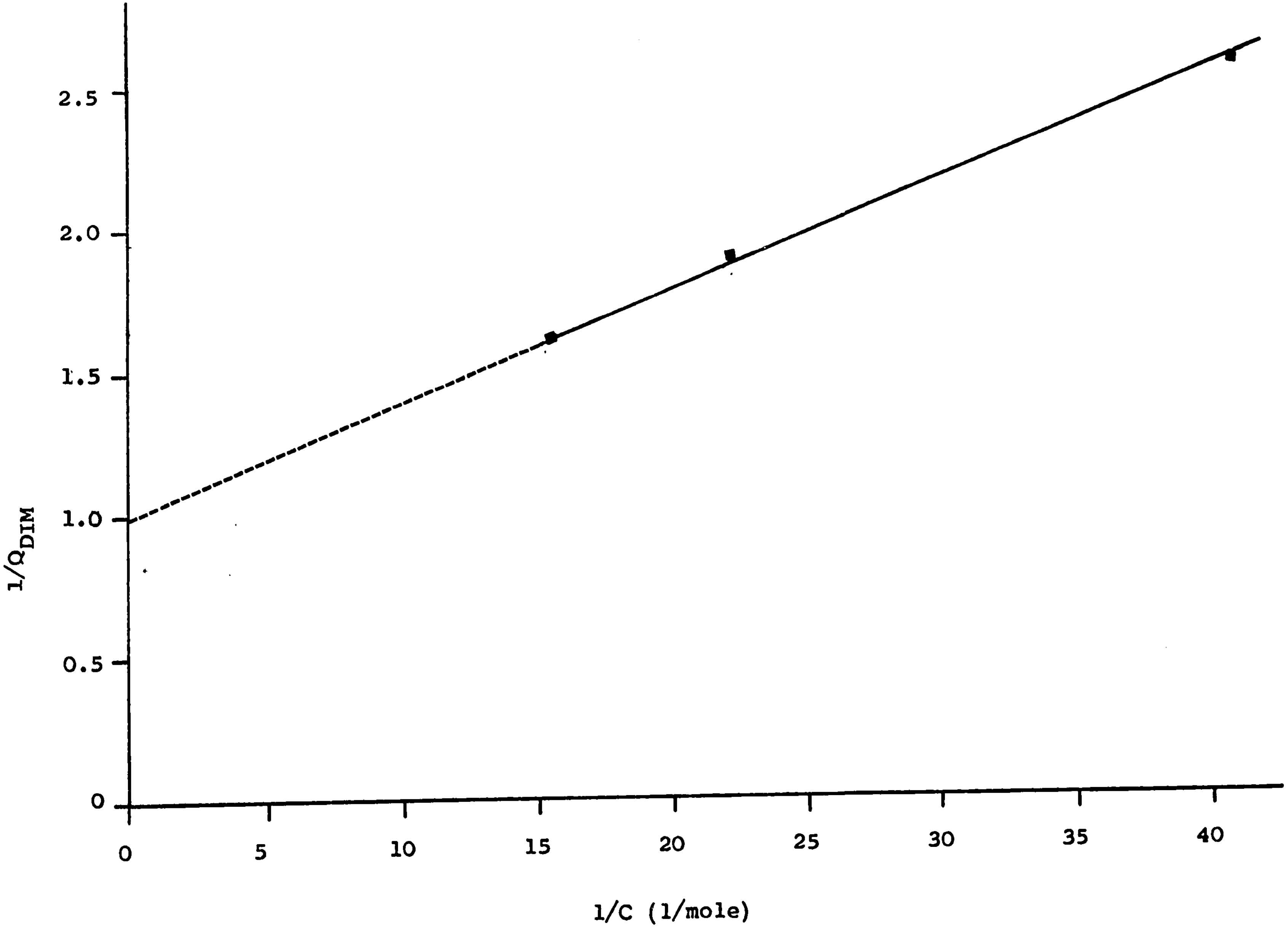


Figure 4

Therefore, $Q_c + Q_{c'}$ can be calculated from $1/Q_{isc}\,(Q_c + Q_{c'})$ $(Q_t + Q_{t'})$ (equation 3).

If the relationship between Q_{DIM} and monomer concentration for the non-sensitized photodimerization was utilized, Q_{isc} for thianaphthene-1,1-dioxide (136) could be calculated (equation 4).

$$1/Q_{DIM} = \frac{1}{Q_{isc}\,(Q_c + Q_{c'})} + \frac{k_3}{Q_{isc}\,(Q_c + Q_{c'})(k_4 + k_{4'})(TND)} \qquad (4)$$

Each quantum yield at a given concentration of 136 and a constant concentration of benzophenone, was determined by parallel irradiation of four degassed samples with benzophenone-benzhydrol actinometer at 366 nm (Q = 0.69 (122)). Dimer yields were determined using the same methods as that for the determination of quantum yields of the unsensitized dimerization. These results are tabulated in Table XII.

A plot of $1/Q_{DIM}$ versus $1/C_{TND}$ is linear with an intercept of 0.98 (fig. 4). This is indicative of $Q_c + Q_{c'}$ and $Q_t + Q_{t'}$ being unity. Therefore, using equation 4, Q_{isc} for thianaphthene-1,1-dioxide (136) is 0.18.

Discussion

The above results are consistent for the photodimerization which involves attack on the ground state molecule by the triplet excited state as illustrated by the mechanism in Scheme 17.

Scheme 17

	Rate
$\mathrm{TND} \xrightarrow{h\nu} {}^{1}\mathrm{TND}$	I
${}^{1}\mathrm{TND} \xrightarrow{k_1} \mathrm{TND}$	$k_1({}^{1}\mathrm{TND})$
${}^{1}\mathrm{TND} \xrightarrow{k_2} {}^{3}\mathrm{TND}$	$k_2({}^{1}\mathrm{TND})$
${}^{3}\mathrm{TND} \xrightarrow{k_3} \mathrm{TND}$	$k_3({}^{3}\mathrm{TND})$
$\mathrm{TND} + {}^{3}\mathrm{TND} \xrightarrow{k_4} \mathrm{H{-}{-}{-}H}$	$k_4({}^{3}\mathrm{TND})(\mathrm{TND})$
$\mathrm{TND} + {}^{3}\mathrm{TND} \xrightarrow{k_{4'}} \mathrm{H{-}{-}{-}T}$	$k_{4'}({}^{3}\mathrm{TND})(\mathrm{TND})$
$\mathrm{H{-}{-}{-}H} \xrightarrow{k_5} \mathrm{TND}$	$k_5(\mathrm{H{-}{-}{-}H})$
$\mathrm{H{-}{-}{-}T} \xrightarrow{k_{5'}} \mathrm{TND}$	$k_{5'}(\mathrm{H{-}{-}{-}T})$
$\mathrm{H{-}{-}{-}H} \xrightarrow{k_6} \mathrm{HH\ dimer}$	$k_6(\mathrm{H{-}{-}{-}H})$
$\mathrm{H{-}{-}{-}T} \xrightarrow{k_{6'}} \mathrm{HT\ dimer}$	$k_{6'}(\mathrm{H{-}{-}{-}T})$

From the above mechanism the relationship between Q_{DIM} and concentration of thianaphthene-1,1-dioxide (136) (equation 4) is derived.

The formation of head-to-head and head-to-tail dimers from two triplet states is not supported by observations of constant HH/HT ratios with decreasing triplet energy level of the sensitizer (Table VIII). *If two triplet states were

---

*It has been observed (123) that the rate constant for energy transfer decreases as the triplet energy level of the donor approaches that of the acceptor. Therefore, the rate of energy transfer to the substrate triplet of higher energy would decrease at a faster rate with decreasing sensitizer triplet energy level, than that of the triplet with a lower energy level, thus favouring the formation of one dimer over the other.

intermediates of this photodimerization reaction, the HH/HT ratio would be expected to change as the triplet energy level of the sensitizer approaches that of thianaphthene-1,1-dioxide (123).

The observation of a limiting quantum yield of unity for the dimerization of 136 sensitized by benzophenone implies that the formation of dimers from a metastable intermediate of the type proposed by Wagner and Buchek (92) was 100% efficient (i.e. $Q_t = 1.0$). Therefore, the increase of HH over HT dimers with an increase in solvent polarity was due to the selective formation of these intermediates rather than their selective decomposition.

The electrostatic free energy change, when a dipole is transferred from a vacuum to a solvent is given by:

$$G_{solvent} - G_{vac.} = \Delta G = \frac{u^2(D - 1)}{a^3(2D + 1)} \quad (121).$$

The free energy difference for two different dipoles (HH and HT transition states) is then:

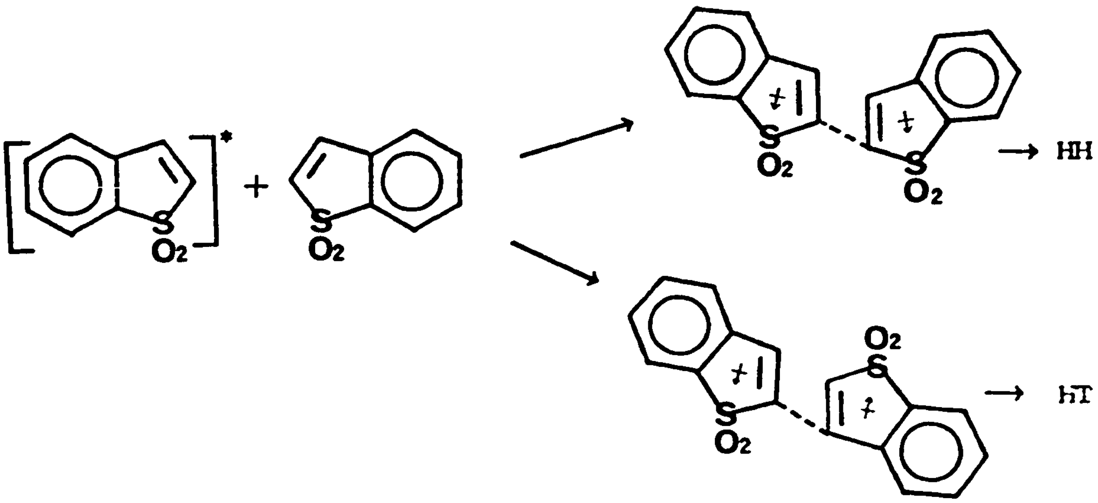
$$\Delta G_{HH} - \Delta G_{HT} = \frac{u^2_{HH} - u^2_{HT}}{a^3} \cdot \frac{(D - 1)}{(2D + 1)} \qquad (121).$$

A good correlation between ΔG and solvent polarity is obtained when "a" the "cavity radius" is identified with the molar volume (M/ρ) of the solvent (121). Since the photodimerization of thianaphthene-1,1-dioxide (136) does not involve an equilibrium between the products and starting material, the reaction is kinetically controlled. Therefore, the following relationship holds:

$$\log HH/HT = \log k_{HH}/k_{HT} = 2.303(\Delta G_{HH} - \Delta G_{HT})/RT.$$

A linear plot of log HH/HT vs $(D - 1)/(2D + 1) \cdot \rho/M$ can be taken as evidence that an increase in log HH/HT with increasing solvent polarity corresponds to an increase in the difference of free energies of activation, $\Delta G_{HH} - \Delta G_{HT}$. This result is easily accepted if it is assumed that the total dipole moment of the head-to-head transition state is greater than that of the head-to-tail transition state (Scheme 17). This assumption is quite reasonable if the transition state is imagined to consist of an aggregate of two thianaphthene-1,1-dioxide molecules lying in roughly parallel planes (Scheme 18). In the head-to-head transition state, the component dipoles point in the same direction and the net moment

Scheme 18



would be expected to be greater than that of the head-to-tail transition state where the component dipoles lie in opposite directions. Therefore, the solvent effect is due to the polarity difference in the transition state leading to the head-to-head and head-to-tail dimers rather than the polarity differences in the metastable intermediate proposed by Wagner and Buchek (92).

Summary

The results stated above indicate that the photodimerization of thianaphthene-1,1-dioxide occurs via an attack on the ground state molecule by a triplet excited state molecule (E $\simeq$ 50 Kcal/mole) according to the mechanism written in Scheme 17. The intersystem crossing efficiency (Ω_{isc}) from singlet to triplet excited state was found to be equal to 0.18 and the efficiency of dimerization from metastable intermediate, Ω_c + Ω'_c was found to be unity. Therefore, the solvent effect is not likely due to a selective decomposition of the metastable intermediate as proposed by Wagner and Buchek (92), rather, there is evidence that the solvent dependency of HH/HT is due to a preferential solvation of the more polar transition state leading to head-to-head dimer.

A solvent dependency (Kirkwood-Onsager) of the photodimerization of cyclopentenone (31) similar to that of the photodimerization of thianaphthene-1,1-dioxide (136) has been reported (124). It is suggested that other similar solvent effects, observed by Eaton (17), Hammond (19) and Chapman (22-24) for the dimerizations of cyclopentenone (31) cyclohexenone (34) and isophorone (42) respectively may well be attributed to the polarity differences in the transition states leading to head-to-head and head-to-tail dimers. Berson and coworkers (121) have observed that the logarithms of the ratio of the stereoisomers in the kinetically controlled Diels-Alder addition to methyl methacrylate and methyl trans-crotonate are linearly related to the Kirkwood-Onsager parameter and have attributed this effect to a difference of the polarity in the transition state, thus lending credence to the above proposals.

Experimental Section

Solvents. Spectrograde benzene, ethyl acetate, methylene chloride, and reagent grade 1,2-dichloroethane were fractionally distilled twice through a 100 cm Vigreux column in which the middle 50% was collected. Spectrograde chloroform was washed twice with distilled water to remove ethanol, dried over anhydrous calcium chloride, fractionally distilled twice and used immediately. Acetic anhydride (10 ml) was added to one liter of reagent grade glacial acetic acid and the mixture was fractionally distilled collecting the middle 50%.

<u>Substrate</u>. Thianaphthene-1,1-dioxide was prepared according to the method in Chapter II, page 65. It was recrystallized three times in absolute ethanol and dried in vacuum at 50° (mp 142.5-143°).

<u>Sensitizers</u>. Benzophenone, chrysene, benzil, fluorene-9-one, and pyrene (Baker sensitizer grade reagents) were all recrystallized from absolute ethanol and dried in vacuo.

<u>Quenchers</u>. Trans α-methylstilbene (Aldrich Chemicals) was recrystallized from petroleum ether (bp 60-90°) and dried in vacuo.

<u>Solvent Effect</u>. Two hundred and fifty ml of a solution of thianaphthene-1,1-dioxide (1.0 g, 2.4×10^{-2} M), previously purged with dry nitrogen for 45 minutes, was irradiated with a Hanovia mercury vapour lamp (type L 450 watt) in the usual water cooled quartz immersion apparatus with a pyrex filter for

two hours at room temperature. After solvent evaporation, starting material (136) was removed by extraction with boiling water. The mixture of dimers (0.400 g) was dissolved in 25.0 ml reagent grade DMSO. The dimer ratios were determined via glpc on a Hewlett-Packard F&M 5750 flame ionization instrument equipped with a calibrated 1/8" x 6' column of 10% Apiezon L on chromosorb W. The column temperature was 300°.

Calibration of Apiezon L column. Mixtures of dimers (0.40 g) of HH/HT ratios 0.165, 0.997, 1.65, 2.99 and 6.28 were dissolved in 25.0 ml of reagent grade DMSO. The ratios of the areas were found to be 0.208, 0.313, 0.583, 1.01 and 2.10 respectively. Therefore, the calibration constant K = $(HH/HT)_{weight}/(HH/HT)_{area}$ was found to be equal to 2.98 ± 0.06.

Sensitized Dimerization of Thianaphthene-1,1-dioxide. A series of benzene solutions of thianaphthene-1,1-dioxide (0.100 g, 2.40×10^{-2} M), each with one of benzophenone, chrysene, benzil, fluoren -9-one, or pyrene (2.41×10^{-2} M) were pipetted into pyrex test tubes (25 x 150 mm) which were constricted to facilitate sealing. One sample contained no sensitizer, only a solution of thianaphthene-1,1-dioxide (2.40×10^{-2} M). This was used as a blank. These were then degassed using three freeze-thaw cycles and sealing under pressures of the order of 2×10^{-2} torr. These tubes were put on the "quantum yield merry-go-round apparatus" and irradiated for 24 hours at 366 nm using the Hanovia medium pressure lamp (type L, 450 watt) and the alizarin red, aluminum sulphate, calcium chloride filter (125). After the sample tubes were opened and the reaction mixture freed from benzene, the reaction mixtures were filtered from boiling cyclohexane to remove the sensitizer and then from boiling water to remove starting material (<u>136</u>). The dimer ratios were determined by glpc using the same methods and apparatus as that for HH/HT ratios for solvent effects.

<u>Thianaphthene-1,1-dioxide</u> (<u>136</u>) <u>as a Sensitizer.</u> Benzene solutions (25.0 ml) of trans α-methylstilbene (0.05 M), thianaphthene-1,1-dioxide (<u>136</u>) (0.05 M); trans α-methylstilbene (0.05 M), benzoquinone (purified by sublimation) (0.05 M) and trans α-methylstilbene (0.05 M), pyrene (0.05 M) were pipetted into pyrex test tubes (constricted on top to facilitate sealing)(two to each acceptor-donor pair). These samples were degassed by four freeze-thaw cycles and sealed under a pressure of 2 x 10^{-2} torr. These solutions were then irradiated on the merry-go-round apparatus with the ultra-violet lamp used previously at 313 nm using the K_2CrO_4-K_2CO_3 filter (92). The isomerization of trans α-methylstilbene was followed by glpc on a 1/8" x 6' column of 10% LAC 728 on chromosorb W until cis/trans ratios were constant (60 hours irradiation).

<u>The Quantum Yield of Photodimerization of Thianaphthene-1,1-dioxide</u> (<u>136</u>). The sample tubes were 25 x 150 mm pyrex test tubes attached to 19/24 ground glass female joints provided with a constriction for sealing. Benzene solutions (25.0 ml at concentrations of 2.41×10^{-2} M, 3.62×10^{-2} M, and 4.82×10^{-2} M) were degassed (four freeze-degas-thaw cycles) and sealed at a pressure of 2×10^{-2} torr. Four sample tubes with solutions at one concentration were placed on the merry-go-round apparatus in the presence of four tubes with uranyl oxalate actinometer solution and irradiated with the lamp previously used at 313 nm. The amount of thianaphthene-1,1-dioxide reacted was determined by quantitative uv spectrophotometric analysis using an extinction coefficient, ϵ (304 nm) of 2.32 ± 0.06 l mole^{-1} cm^{-1}. Tubes containing 0.05 M uranyl oxalate (made from 0.05 M uranyl sulphate and 0.05 M of oxalic acid) in distilled water were irradiated simultaneously with solutions of compound <u>136</u> during the determination of quantum yields of all non-sensitized dimerizations. The amount of oxalate reacted was determined by titrating an acidified solution of actinometer solution with standardized $KMnO_4$ solution (0.06 N) at 50°. The quantum yield for oxalate decomposition was taken at 0.56 at 313 nm (124). Total periods of irradiation (1.75 hours) were adjusted so that 35-40% of actinometer and 9-11% of thianaphthene-1,1-dioxide reacted.

The Determination of the Molar Extinction Coefficient of Thianaphthene-1,1-dioxide (136). Benzene solutions of compound 136 at concentrations of 6.566×10^{-4} M, 5.253×10^{-4} M, 3.940×10^{-4} M, 2.626×10^{-4} M and 1.313×10^{-4} M were prepared. The absorbance, A, of these solutions were measured in 1 cm cells on a Unicam SP 800 uv spectrophotometer at 304 nm. The molar extinction coefficient of $2.32 \pm 0.06 \times 10^3$ l mole^{-1} cm^{-1} was calculated by the Beer-Lambert equation using the method of least squares.

The Quantum Yield of the Sensitized Dimerization of Thianaphthene-1,1-dioxide (136). The sample cells used in this procedure were identical to those used in the determination of the quantum yields of the non-sensitized reaction. Benzene solutions (25.0 ml at concentrations of 2.41×10^{-2} M, 3.62×10^{-2} M and 4.82×10^{-2}M of thianaphthene-1,1-dioxide and 1.99×10^{-2} M of benzophenone in all three samples) were degassed (four freeze-degas-thaw cycles) and sealed at a pressure of 2×10^{-2} torr. Four samples at one concentration of 136 were placed on the merry-go-round apparatus and irradiated in the presence of four samples of benzophenone-benzhydrol actinometer at 366 nm. The amount of 136 reacted was determined in the presence of sensitizer by uv spectrophotometric measurements at a wavelength of 310 nm in which compound 136 has a molar extinction coefficient of $2.28 \pm 0.06 \times 10^3$ l mole^{-1}

cm^{-1}. This extinction coefficient was determined in the same way as previously described. For a concentration of 0.1 M of benzhydrol and 0.1 M of benzophenone, the quantum yield for the photoreduction of benzophenone has been found to be 0.69 (122). The amount of benzophenone reacted was determined by uv spectrophotometry using extinction coefficient at 344 nm equal to 1.36×10^2 l $mole^{-1}$ cm^{-1} (122). Total periods of irradiation were adjusted so that 50% of actinometer and 5% of thianaphthene-1,1-dioxide reacted.

Filter Solutions for the Isolation of the 313 nm and 366 nm bands. In both cases (wavelength = 313 nm and 366 nm) the emission from a Hanovia medium pressure lamp (type L, 450 watt), positioned in the center of the turntable, was filtered by a pyrex sleeve. When uv light of wavelength = 313 nm was needed, an aqueous solution of 0.2 g of potassium chromate and 10 g of potassium carbonate per litre of solution was put in the pyrex sleeve (92). When a wavelength of 366 nm was needed, an aqueous solution of 0.37 g of alizarin red, 0.015 g of aluminum sulphate.18 H_2O, and 0.25 g of calcium chloride per litre of solution was used. A pH of 4.64 was maintained with acetic acid-sodium acetate buffer (0.1 N acetic acid and 0.1 N sodium acetate) (125).

CHAPTER IV

THE PHOTOCYCLOADDITION OF THIANAPHTHENE-1,1-DIOXIDE TO OLEFINS

Introduction

Consideration of the most plausible mechanism for the photodimerization of olefins has led to Scheme 17 (Chapter III, page 88). The basic consideration is the addition of a triplet excited state of the olefin to the ground state of the same olefin. The ground state partner of the two merely provides an olefin substrate for attack by the excited molecule. Therefore, it should be possible to replace the ground state molecule with any olefin that cannot become excited at the wavelength at which the attacking olefin becomes excited. Table XIII summarizes typical photocycloadditions of a variety of olefin pairs.

Table XIII illustrates the high orientational selectivity observed by unsymmetrical olefins in their various cycloaddition reactions (addition of cyclopentenone to trichloroethylene is an exception (126)). Also, identical products for cycloaddition involving cis or trans disubstituted olefins were noted.

These results have been explained using a mechanism first proposed by Corey (96) (Scheme 19).

Table XIII

Photocycloaddition Reactions

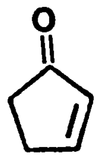
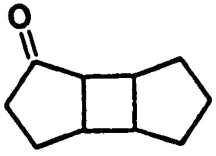
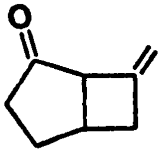
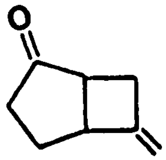
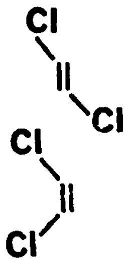
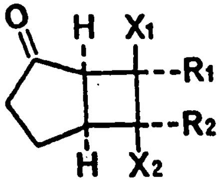
No.	Olefin	Olefin Substrate	Conditions	Products	Ref.
1	 31		hν	 149	16
2	31	 $CH_2=C=CH_2$	hν	 150  151	16
3	31		hν	 152a $X_1 = X_2 = H$; $R_1 = R_2 = Cl$. 152b $R_1 = X_2 = H$; $R_2 = X_1 = Cl$. 152c $X_1 = R_2 = H$; $X_2 = R_1 = Cl$.	126

Table XIII

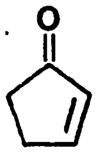
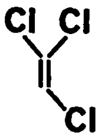
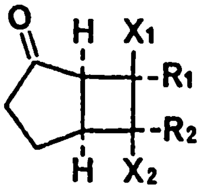
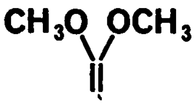
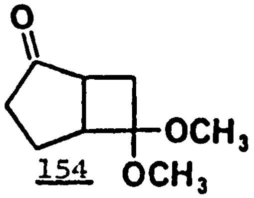
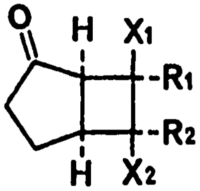
No.	Olefin	Olefin Substrate	Conditions	Products	Ref.
4	 31		hν	 153a R_1 = H; X_1 = X_2 = R_2 = Cl. 153b X_1 = H; X_2 = R_1 = R_2 = Cl. 153c R_2 = H; X_1 = X_2 = R_1 = Cl. 153d X_2 = H; X_1 = R_1 = R_2 = Cl.	126
5	31		hν	 154	96
6	31		hν	 155a X_1 = X_2 = R_1 = H; R_2 = CH_3. 155b X_1 = R_1 = R_2 = H; X_2 = CH_3. 155c X_1 = X_2 = R_2 = H; R_1 = CH_3. 155d X_2 = R_1 = R_2 = H; X_1 = CH_3.	127

Table XIII

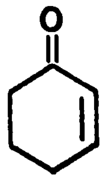
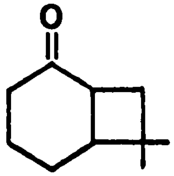
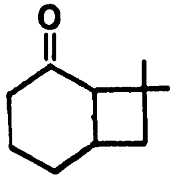
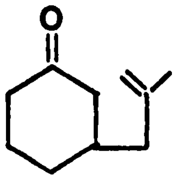
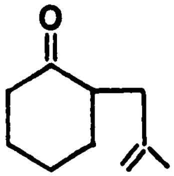
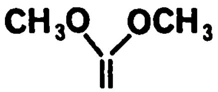
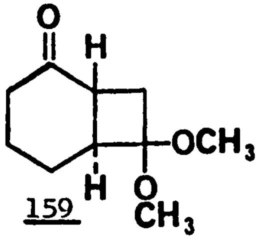
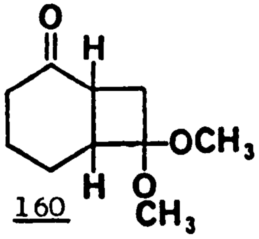
No.	Olefin	Olefin Substrate	Conditions	Products	Ref.
7	 34		hν	 156a  156b	96
				 157  158	
8	34		hν	 159  160	96

Table XIII

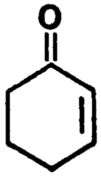
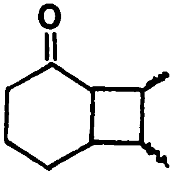
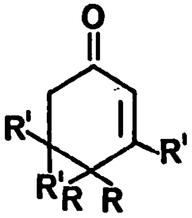
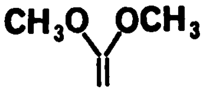
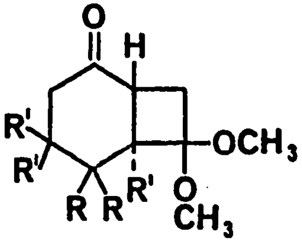
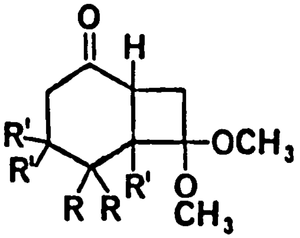
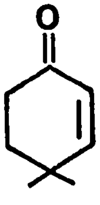
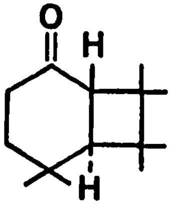
No.	Olefin	Olefin Substrate	Conditions	Products	Ref.
9	 34		hν	 161, 162, 163	96
10	 42 R' = CH_3, R = H. 164 R' = H, R = CH_3.		hν	  165a R = H; R' = CH_3. 165c R = H;R' = CH_3 165b R = CH_3; R' = H. 165d R = CH_3;R' = H	12
11	 164		hν	 166 Paterno Buchi and straight chain adducts.	129

Table XIII

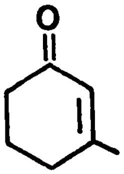
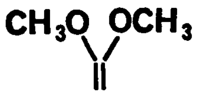
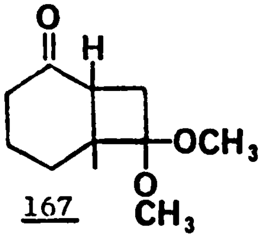
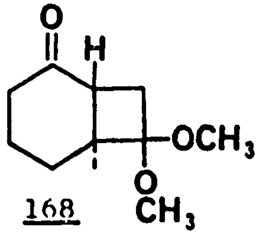
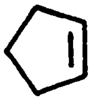
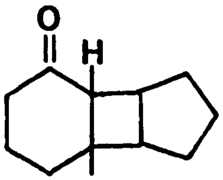
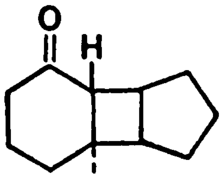
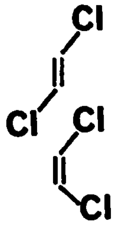
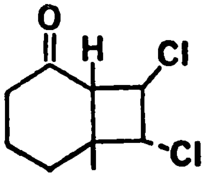
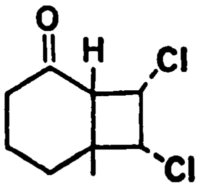
No.	Olefin	Olefin Substrate	Conditions	Products	Ref.
12	 37		hν	 167  168	130
13	37		hν	 169  170	130
14	37		hν	 171  172	130

Table XIII

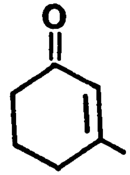
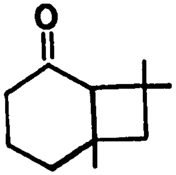
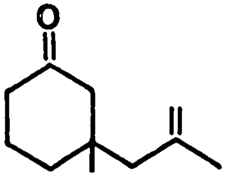
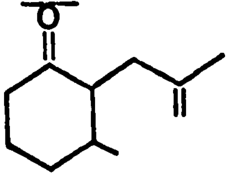
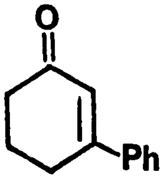
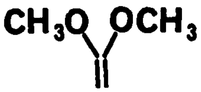
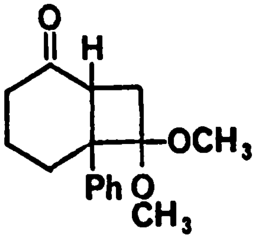
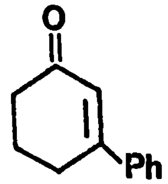
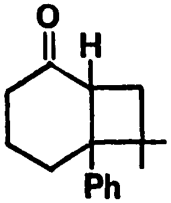
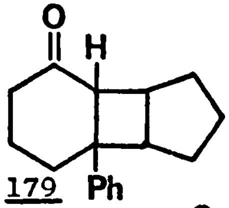
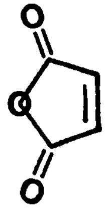
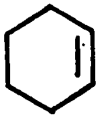
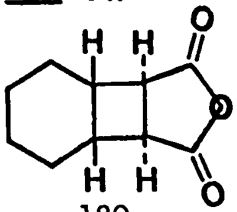
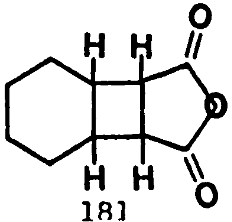
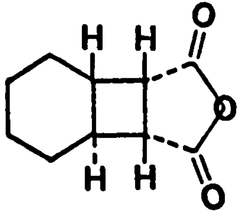
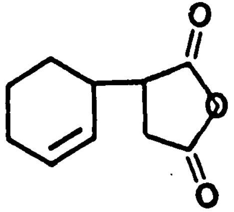
No.	Olefin	Olefin Substrate	Conditions	Products	Ref.
15	 37		hυ	 173  174  175	96,131
16	 176		hυ	 177	130

Table XIII

No.	Olefin	Olefin Substrate	Conditions	Products	Ref.
17	 176		hν	 178	130
18	176		hν	 179	130
19	 104a		hν	 180  181  182  183	131

Table

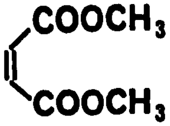
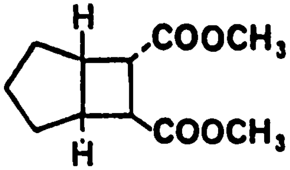
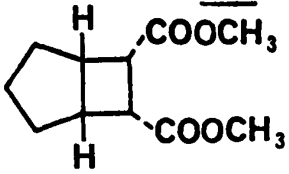
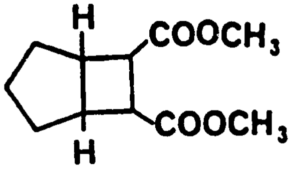
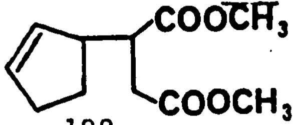
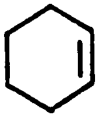
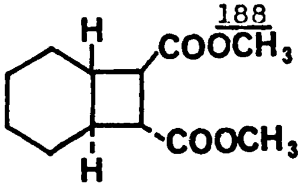
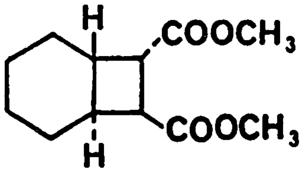
No.	Olefin	Olefin Substrate	Conditions	Products	Ref.
20	 184		$h\nu$	 185  186  187  188	132
21	184		$h\nu$	 189  190	132

Table XIII

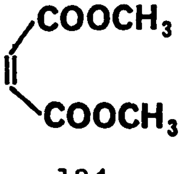
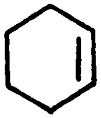
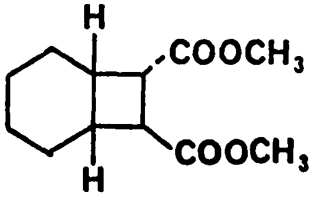
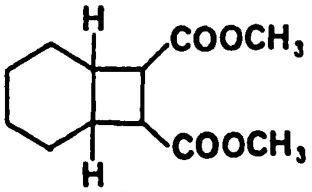
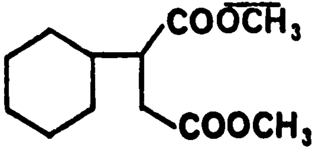
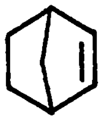
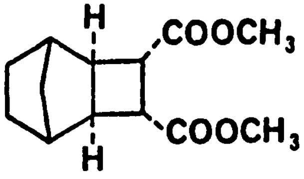
No.	Olefin	Olefin Substrate	Conditions	Products	Ref.
21	 184		hυ	 191  192  193	132
22	184		hυ	 194	133

Table XIII

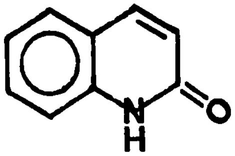
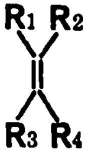
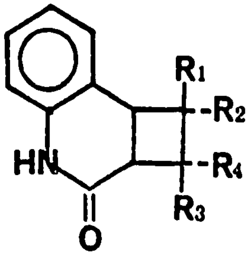
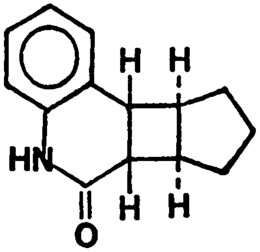
No.	Olefin	Olefin Substrate	Conditions	Products	Ref.
23	 92a	 a) $R_1 = R_2 = R_3 = R_4 = CH_3$. b) $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$. c) $R_1 = R_2 = C_2H_5$; $R_3 = R_4 = H$. d) $R_1 = R_2 = OCH_3$; $R_3 = R_4 = H$. e) $R_1 = OCH_3$; $R_2 = R_3 = R_4 = H$. f) $R_1 = CN$; $R_2 = R_3 = R_4 = H$. g) $R_1 = R_2 = R_3 = R_4 = Cl$.	hν	 195a 195b 195c 195d 195e 195f 195g	134
24	92a		hν	 196	134

Table XIII

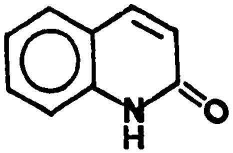
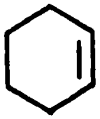
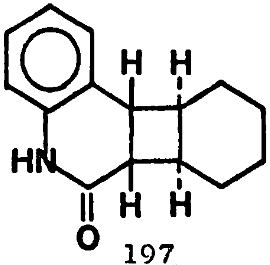
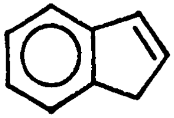
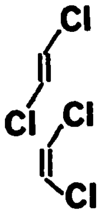
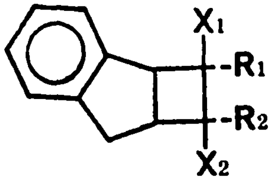
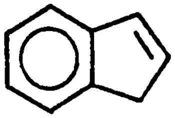
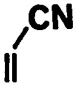
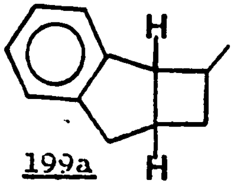
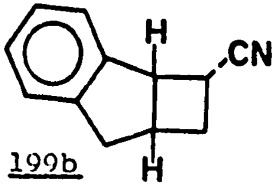
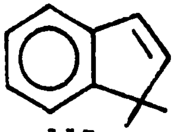
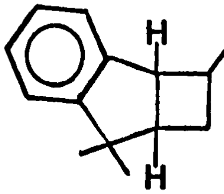
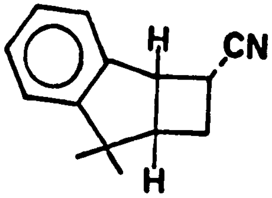
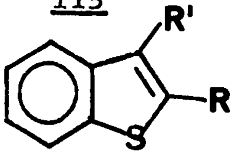
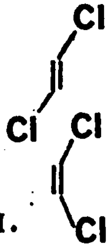
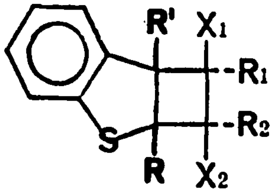
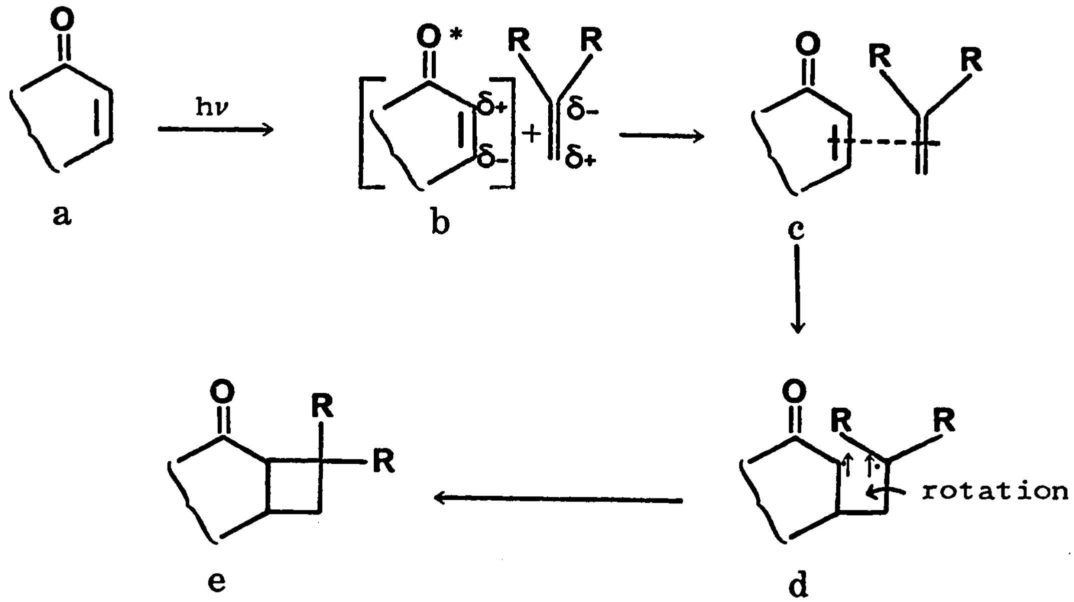
No.	Olefin	Olefin Substrate	Conditions	Products	Ref.
25	 92a		hν	 197	134
26	 113		hν acetophenone sensitizer	 198a $X_1 = X_2 = Cl$; $R_1 = R_2 = H$. 198b $X_2 = R_1 = Cl$; $X_1 = R_2 = H$. 198c $X_1 = R_2 = Cl$; $X_2 = R_1 = H$. 198d $R_1 = R_2 = Cl$; $X_1 = X_2 = H$.	135

Table XIII

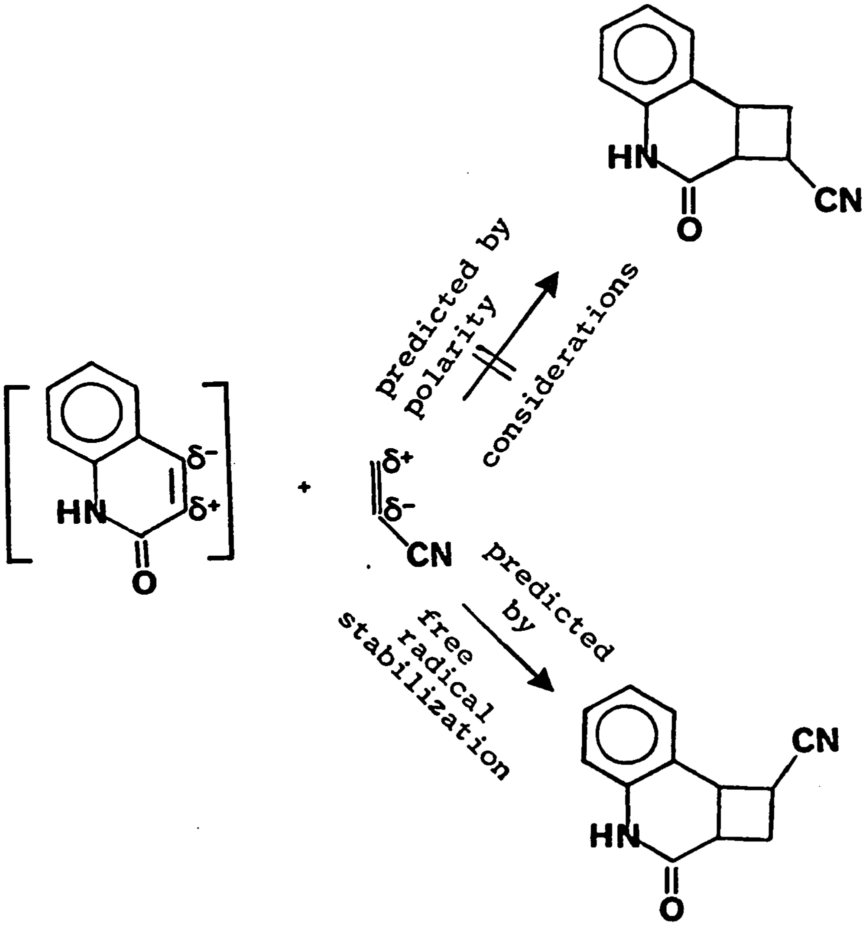
No.	Olefin	Olefin Substrate	Conditions	Products	Ref.
27	 113		hν acetophenone sensitizer	 199a  199b	136
28	 115		hν acetophenone sensitizer	 200c  200b	136
29	 201a R=H;R'=H. 201b R=CH_3;R'=H. 201c R=CH_3;R'=CH_3		hν acetophenone and benzophenone sensitizers	 202 $X_1 = X_2$ = Cl; $R_1 = R_2$ = H. 203 $X_2 = R_1$ = Cl; $X_1 = R_2$ = H. 204 $X_1 = R_2$ = Cl; $X_2 = R_1$ = H. 205 $R_1 = R_2$ = Cl; $X_1 = X_2$ = H.	137

Scheme 19



The above mechanism depicts attack by the excited state of the olefin on the substrate to form a metastable intermediate (or π complex) similar to that proposed by Wagner and Buchek (92). Collapse of this intermediate to a 1,4-diradical by bond formation between the excited state olefin and the substrate then occurs. Before ring formation, there is time for rotation of the C-C bond of the substrate moiety (Scheme 19; structure d); the cyclobutane ring then forms. The mechanism generally accounts for the orientational selectivity of cycloadditions between unsymmetrical olefins and the lack of stereospecificity of addition to cis and trans alkenes.

Scheme 20

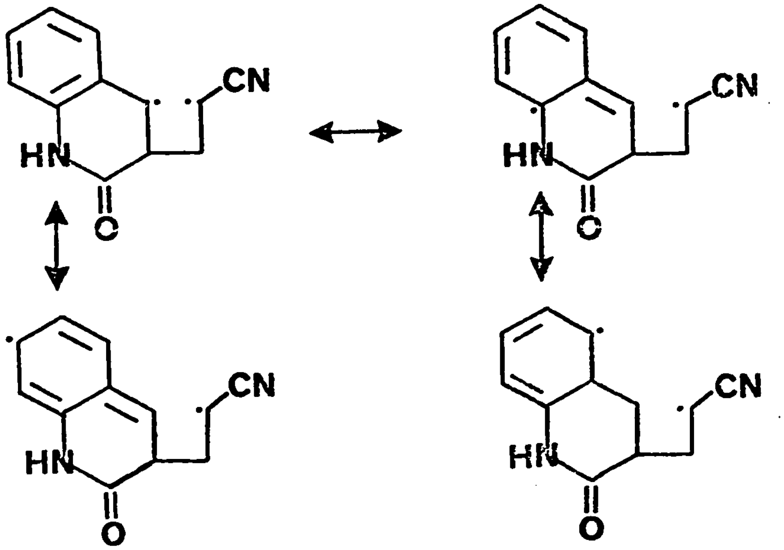


HN
O
δ-
δ+
+
δ+
δ-
CN
predicted by polarity considerations
predicted by free radical stabilization
HN
O
CN
HN
O
CN

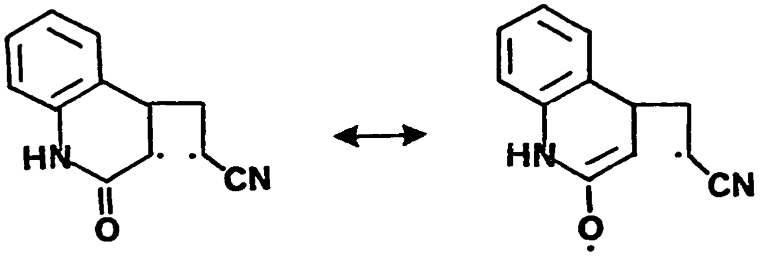
However, the mechanism postulated by Corey (96) does not account for the orientation of the cycloadducts of carbostyril (No. 23, compound <u>195f</u>, Table XIII (134), indene (No. 27, Table XIII) and 1,1-dimethylindene (No. 28, Table XIII) to acrylonitrile. All other olefins add to the excited state of the above alkenes in the orientation predicted by the mechanism illustrated in Scheme 19 (No. 23, 26, Table XIII). Acrylonitrile adds in an opposite orientation to that predicted by Corey's mechanism (Scheme 20). It has been well established that a change in polarity occurs in an $n-\pi^*$ transition (for cyclic enones) while no such change has been observed for a $\pi - \pi^*$ transition (carbostyril, indene, 1,1-dimethylindene) (148). These results (carbostyril, indene, 1,1-dimethylindene) can be best explained by considering the stabilization of the resulting 1,4-diradical intermediate. The 1,4-diradical A, with a resonance stabilized benzylic free radical, would be expected to be more stable than diradical B (with a less stabilized free radical conjugated to the amide group, Chart 3). This hypothesis also accounts for the observations of Corey (96).

Photo-induced cycloaddition reactions forming cyclobutane derivatives have been used as key steps in the synthesis of a variety of complex natural products. The following reaction schemes are typical examples of such syntheses.

Chart 3

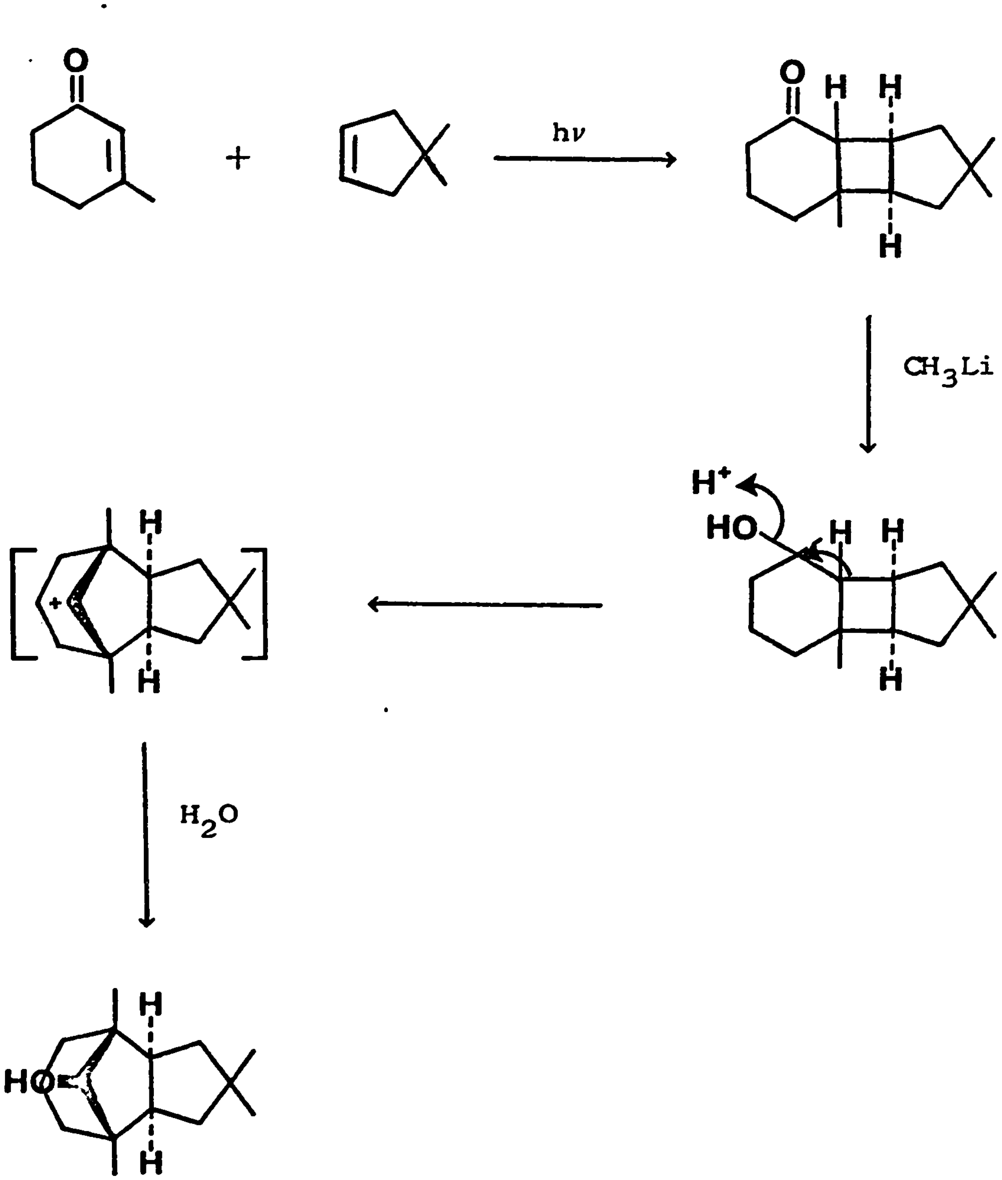


A



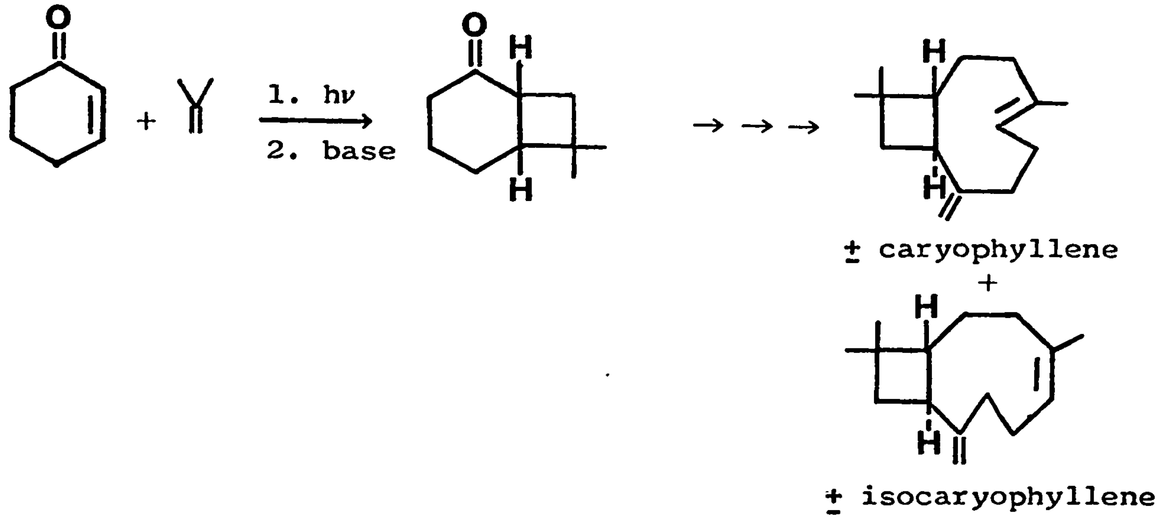
B

Scheme 21 (138)

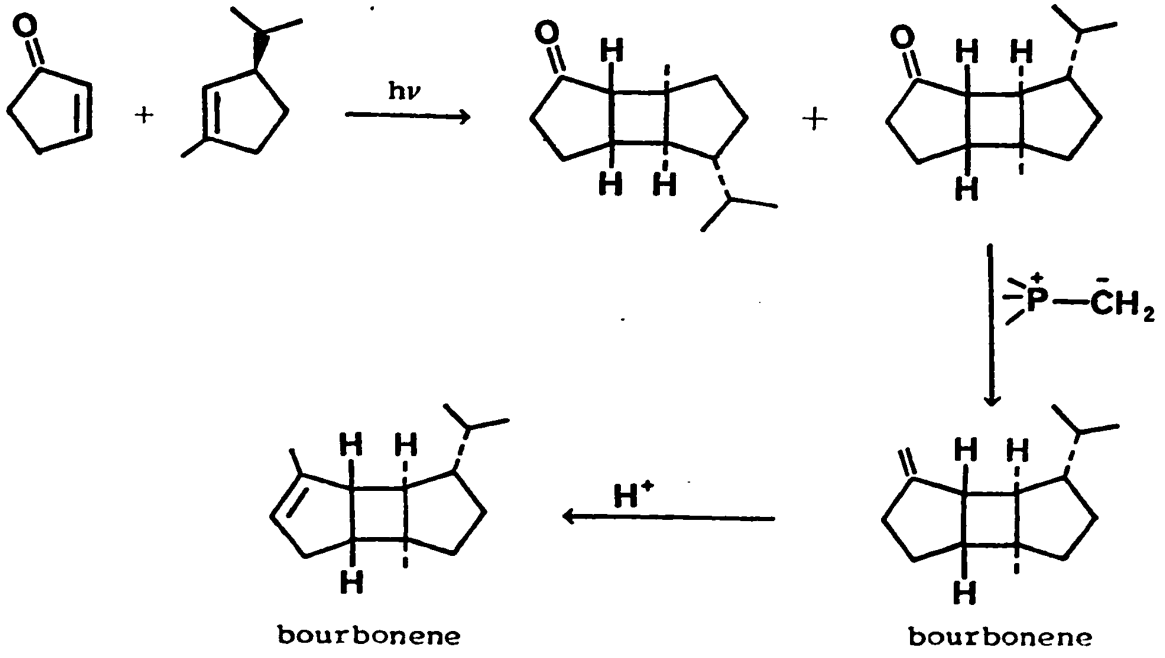


α-caryophyllene alcohol

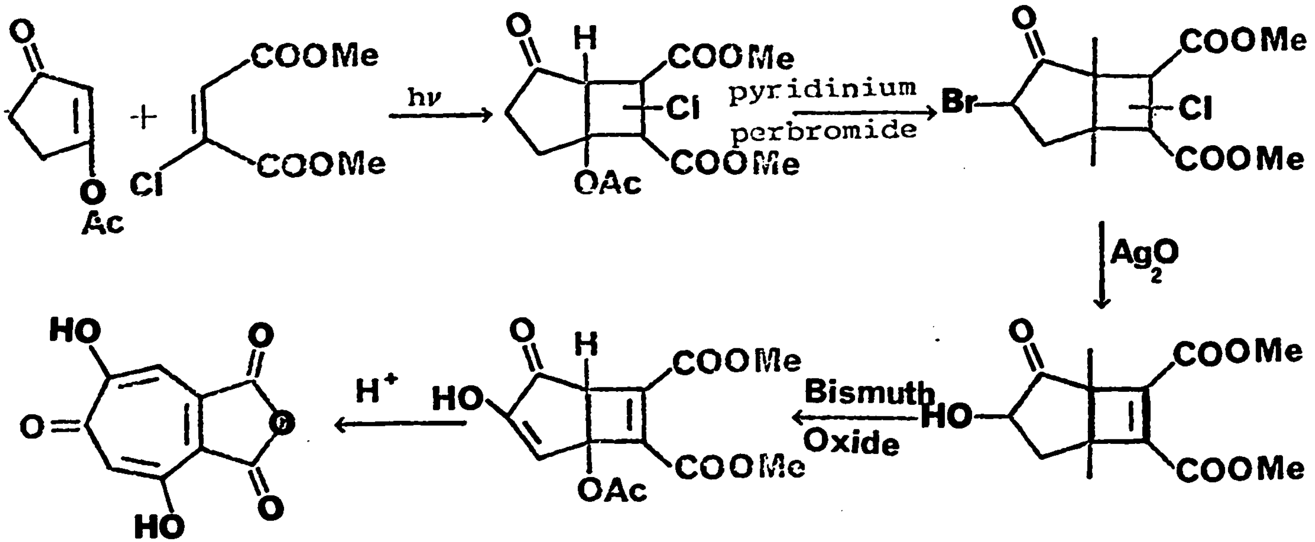
Scheme 22 (139)



Scheme 23 (140)

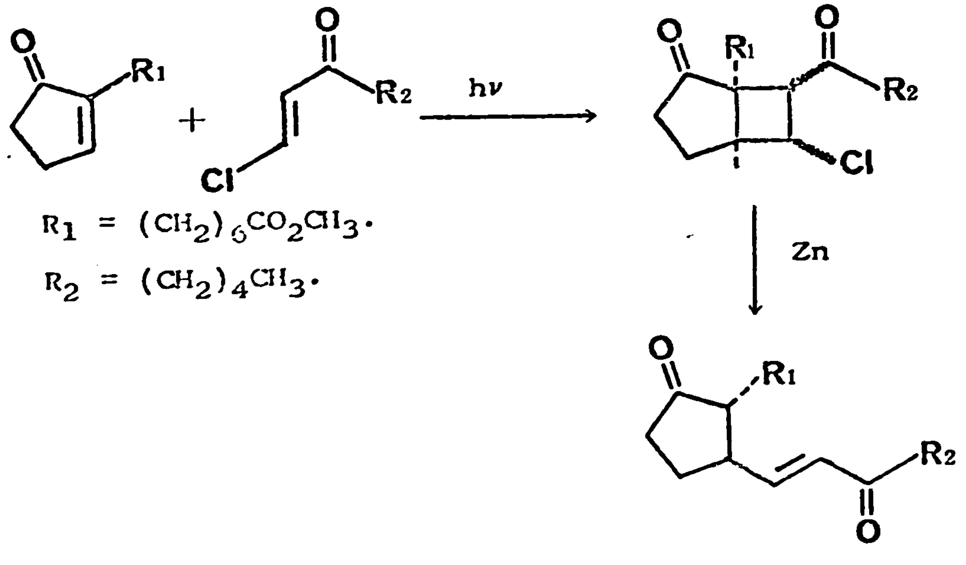


Scheme 24 (141)



stipitatonic acid

Scheme 25 (142)

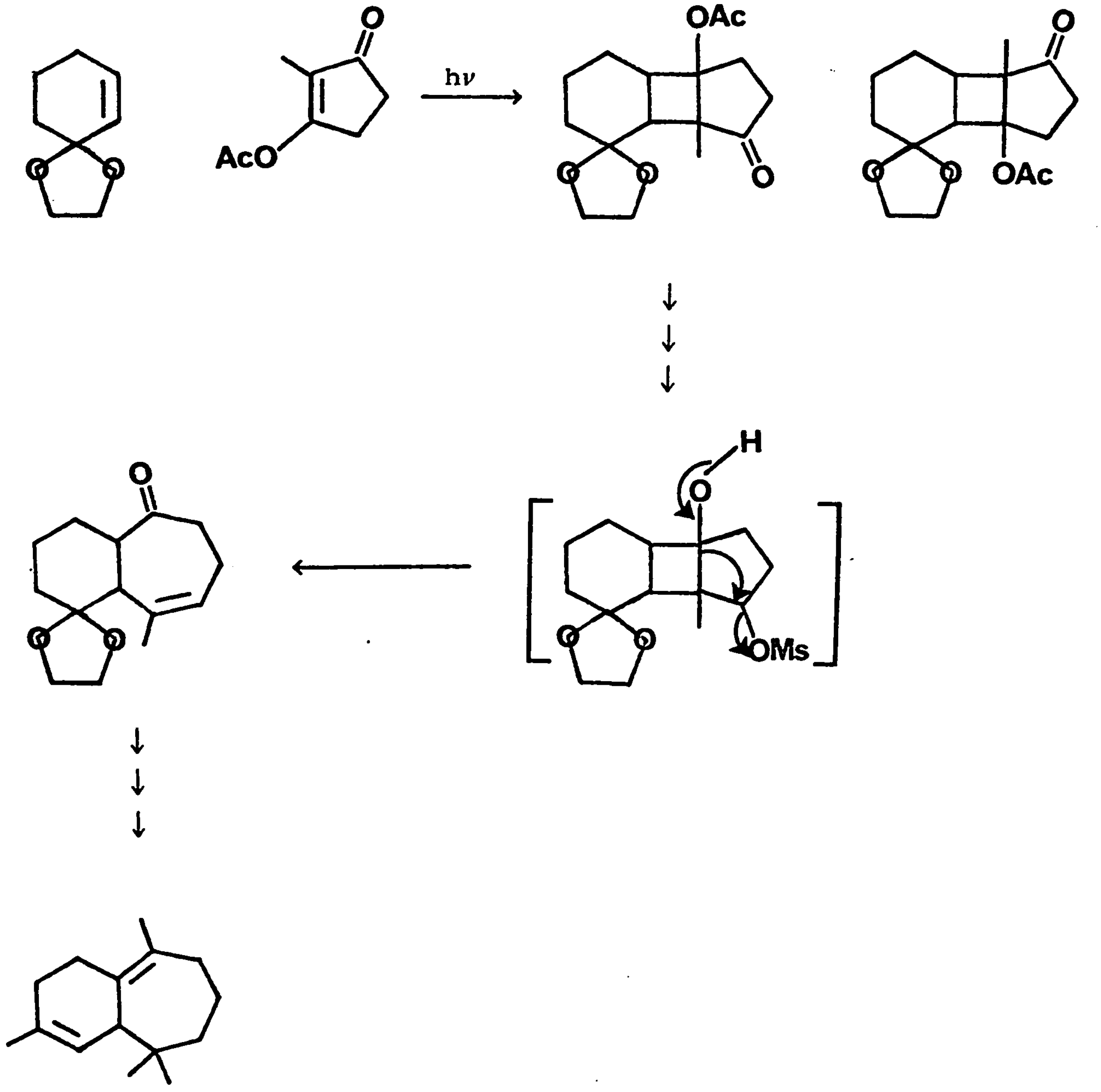


$R_1 = (CH_2)_6CO_2CH_3$.

$R_2 = (CH_2)_4CH_3$.

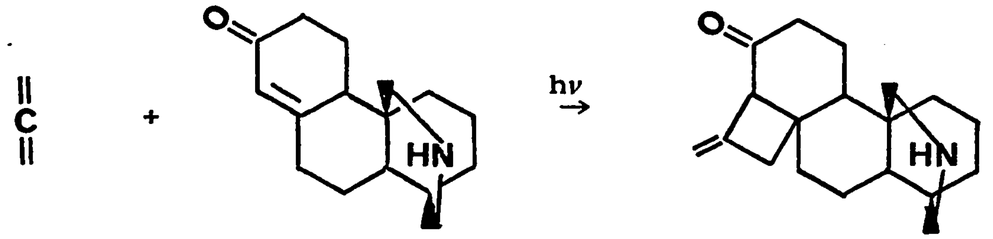
prostanoic acids

Scheme 26 (143)



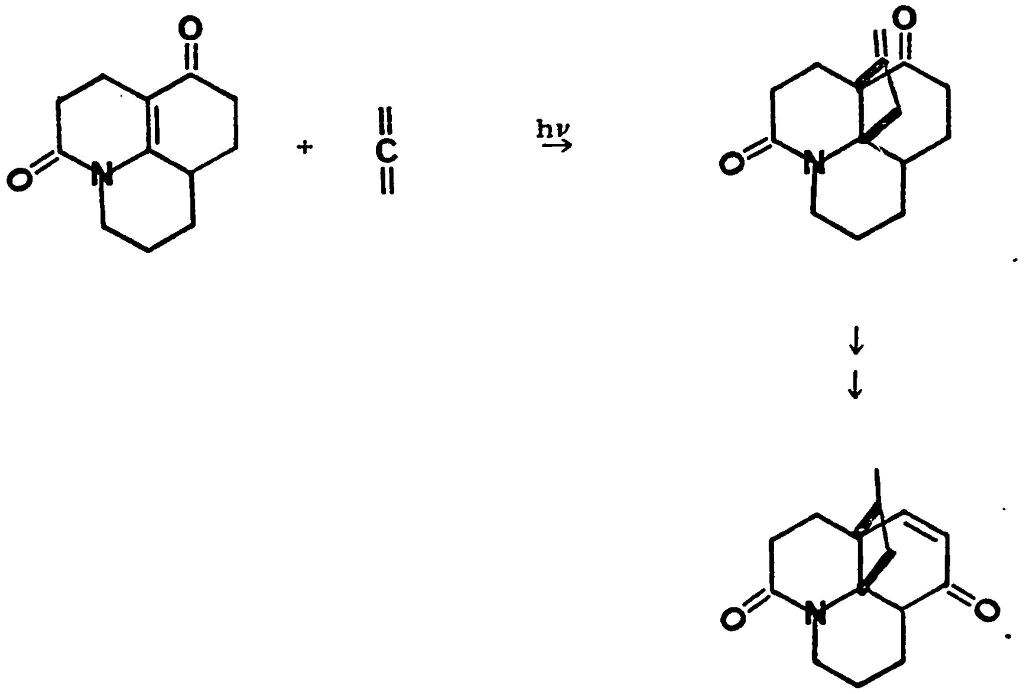
β-himachalene

Scheme 27 (144)



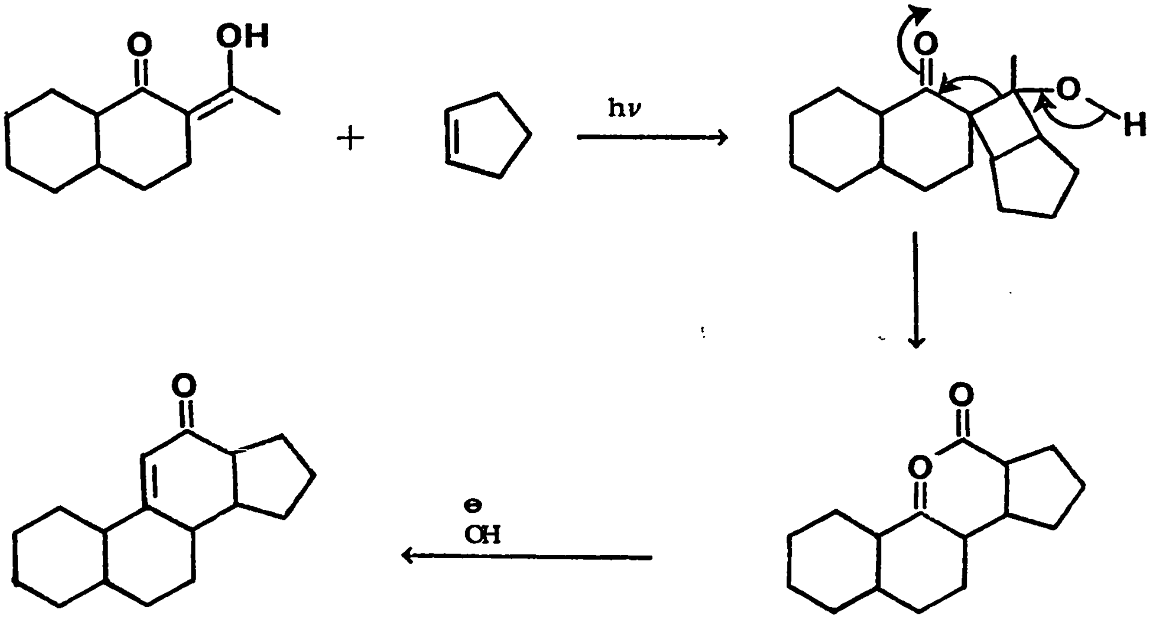
precursor to atisine
and veatchine

Scheme 28 (145)



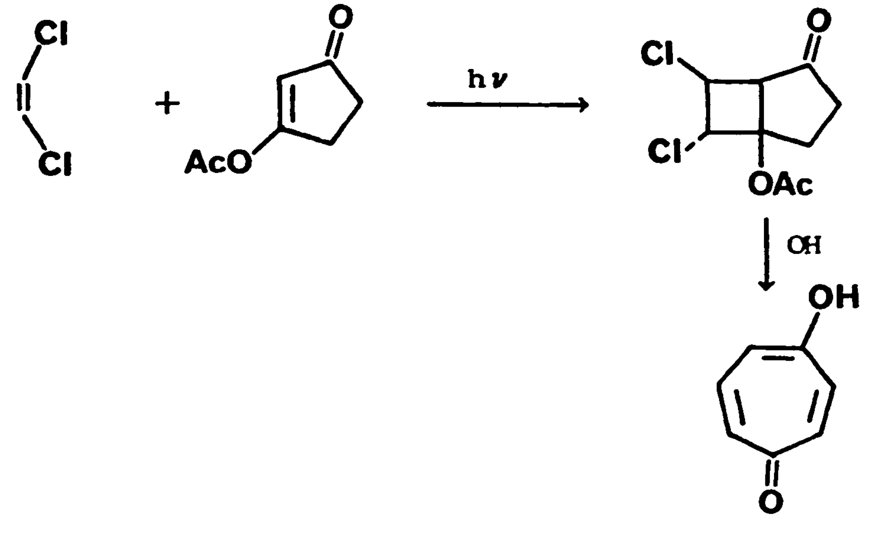
annatonine

Scheme 29 (146)



steroid skeleton

Scheme 30 (147)



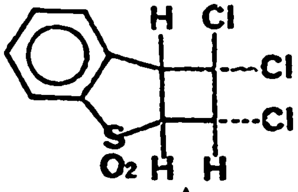
γ-tropolone

Results

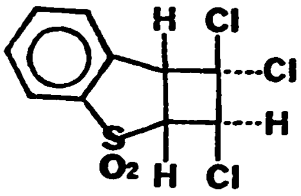
All photochemical reactions of thianaphthene-1,1-dioxide (136a) with olefins were conducted with a Hanovia medium pressure mercury vapour lamp (type L, 450 watt) in a water cooled pyrex immersion well which the reaction mixture surrounded. Hence, reaction solutions were irradiated with light of wavelength 300 nm and greater. Thianaphthene-1,1-dioxide (136a) absorbs 99% of the emitted radiation while the olefins absorb no more than 1%.

Cycloaddition to Trichloroethylene. Thianaphthene-1,1-dioxide (136a) was dissolved in trichloroethylene, purged with dry nitrogen for 45 minutes and irradiated for 3 hours. The products were isolated by allowing the oily residue to crystallize from benzene. Fractional crystallization from benzene gave adduct 206a (52% yield) and photodimers 137 and

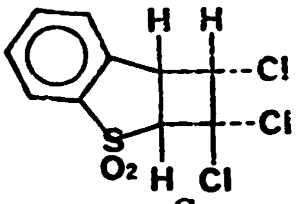
Chart 4



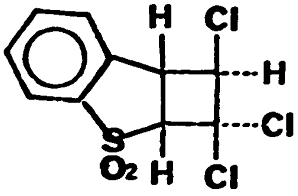
A



B



C



D

138 (48% yield). Analysis of the mass spectrum (m/e = 296 for the parent peak) and ir spectrum (ir maxima at 1320 cm^{-1} and 1160 cm^{-1} attributed to SO_2 stretching and 670 cm^{-1} due to C-Cl stretching) indicated a 1:1 adduct 206a with the possible structures listed in Chart 4. Photo adducts with trans stereochemistry at the junction of the five and four membered ring are very unlikely. Aside from considerable ring strain, trans five-four ring junctions are even less likely considering the two step process proposed by Corey (96). Tests similar to those done in Chapter II (page 54) for this stereochemistry cannot be performed because of rapid hydrohalide elimination from the substrate.

The structure and stereochemistry of 206a were determined by a comparison analysis of cycloadducts 206a and 206b.

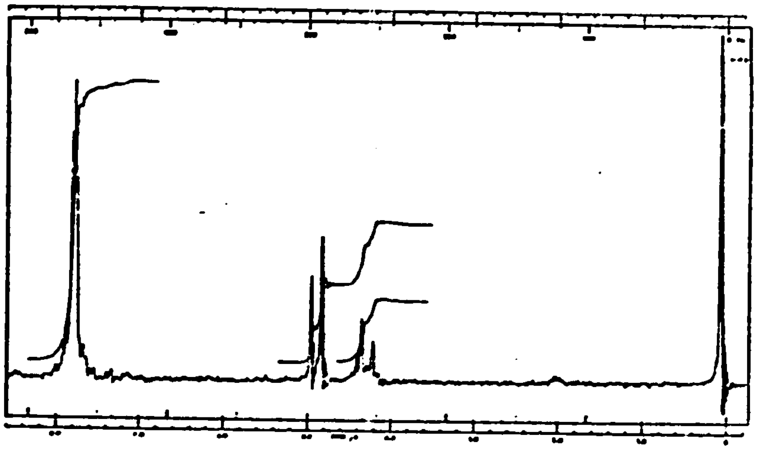


Figure 5

Nuclear Magnetic Resonance of Compound 206b.

The latter was formed by using 3-deuterothianaphthene-1,1-dioxide (136b). Resonances appeared in the nmr spectrum of 206b, (Fig. 5), τ, 2.18 (4H, multiplet) aromatic; 5.18 (1H, doublet, $J = 8.0$ Hz) methine; 5.69 (1H, doublet, $J = 8.0$ Hz) methine. This spectrum is consistent with structure A or B in Chart 4. If structure C or D were invoked, the coupling between the chloro proton (A) and the sulphonyl proton (X) would be expected to be in the order of 0-2.5 Hz instead of 8.0 Hz (cross ring coupling constants higher than 2.5 Hz have been recorded only for rigid bicyclobutane derivatives (87)). The nmr spectrum of compound 206a (Fig. 6) consists of a multiplet at $\tau = 2.18$ (4H, multiplet) aromatic and an ABX multiplet in which the AB portion is centered at $\tau = 5.18$ (2H) and the X part centered at $\tau = 5.69$ (1H). Examination of the ABX signals only gave $J_{AB} = 1.5$ Hz and $J_{AX} + J_{BX} = 15.5$ Hz. Because the AB section of the ABX spectrum has only six recognizable peaks, it was not possible to determine values for D+, D- and $1/2(J_{AX} + J_{BX})$ (149). Hence, J_{AB} and $J_{AX} - J_{BX}$ could not be calculated. However, from $(J_{AX} + J_{BX})$ and J_{AX} (determined from nmr spectrum of deuterated adduct 206b) a value of J_{BX}(7.5 Hz) was determined. The X section of the ABX spectrum contained four peaks, thus J_{AX} and J_{BX} have the same sign (149).

The nmr data obtained for compound 206a are consistent with structure A (Chart 4) rather than B. It has been observed

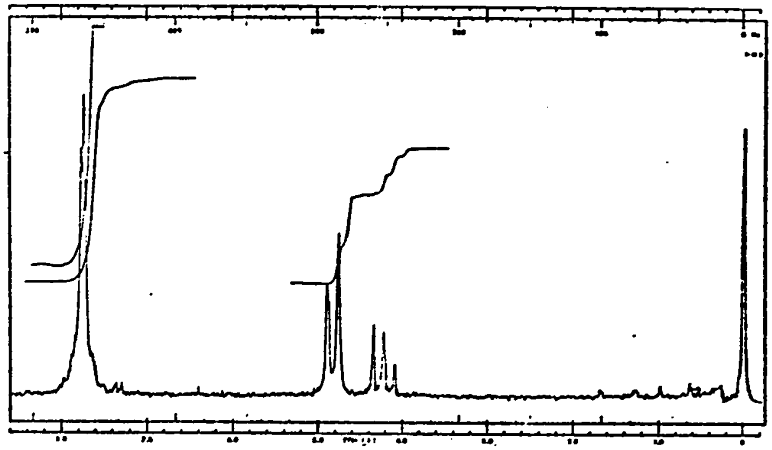


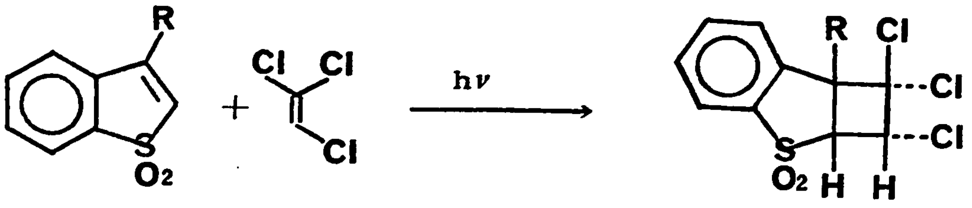
Figure 6
Nuclear Magnetic Resonance of Compound 206a.

(87) that $J_{cis}/J_{trans} > 1$. Hence, $J_{BX} = 7.5$ Hz for the vicinal cis benzylic and sulphonyl protons and $J_{AX} = 8.0$ Hz, $J_{BX(cis)}/J_{AX} < 1$, supports cis stereochemistry for proton A and X (Scheme 31). Since cross ring coupling constants for protons with 1,3 cis stereochemistry range from 0.9 Hz to 2.5 Hz for cyclobutane compounds and cross coupling constants for protons with trans stereochemistry are 0.5 Hz (87), the value for J_{AB} of 1.5 Hz provides further evidence that protons A, B, and X have cis stereochemistry.

Purging the trichloroethylene solution of compound 136a with O_2 inhibited cycloaddition, indicating a triplet excited state as intermediate.

The elemental analysis for compound 206a was not completely satisfactory. This is most likely due to slow decomposition (dehydrohalogenation) on standing. Characterization

Scheme 31

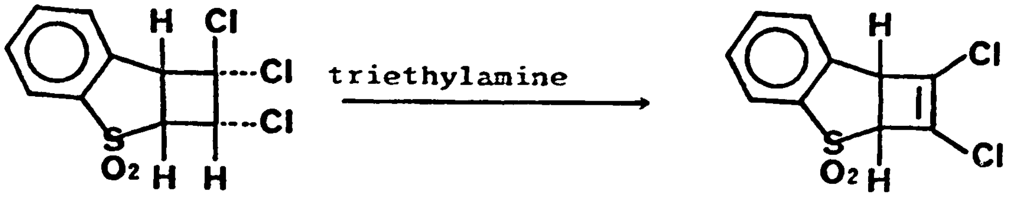


136a R = H;
136b R = D.

206a R = H;
206b R = D.

of a stable derivative was therefore advisable. Dehydrohalogenation of 206a in refluxing triethylamine gave compound 212 (mp 169-170°) nmr:(C_6 D_6) τ, 2.60-3.35. (4H, multiplet) aromatic, 6.35, (2H, AB quartet ($\Delta\nu$ = 20.1 Hz, J_{AB} = 4.0 Hz) methine; ir: $\bar{\nu}$, 1680 cm^{-1} (C-C stretching), 1320 cm^{-1} and 1150 cm^{-1} (SO_2 stretching), 650 cm^{-1} (C-Cl stretching). The above data is consistent with the loss of HCl to give compound 212 (Scheme 32).

Scheme 32



206a

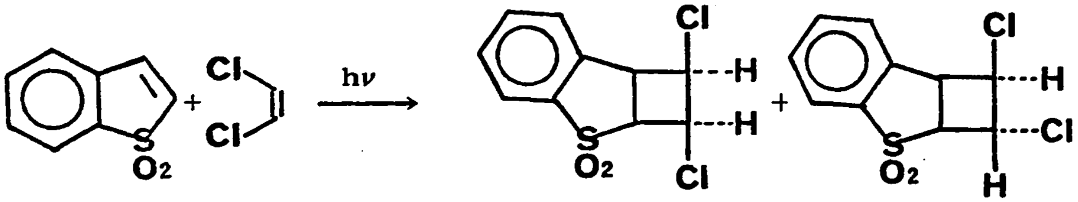
212

Cycloaddition to cis and trans-Dichloroethylene.

Thianaphthene-1,1-dioxide (136a) was dissolved in cis or trans dichloroethylene and irradiated under standard conditions. The solvent was then evaporated and the reaction mixture was crystallized (ethanol, cis dichloroethylene adduct; benzene, trans adduct). Examination of the crude reaction mixture by glpc, nmr and ir spectrophotometry revealed the same two products for each reaction.

The crystals obtained from photoaddition of thianaphthene-1,1-dioxide (136) to cis-dichloroethylene were fractionated on a column of silica gel with chloroform. The first fraction contained compound 207 (mp 145.5-146.5°), nmr: ($CDCl_3$), τ, 2.00-2.50 (4H, multiplet) aromatic; 4.94-5.15 (1H, multiplet) methine; 5.33-5.60 (3H, multiplet) methine; infrared: $\bar{\nu}$, 1320 cm^{-1} and 1170 cm^{-1} (SO_2); 665 cm^{-1} (C-Cl); mass spectra: m/e for molecular ion = 262, and the second fraction, a mixture of 207 and 208, was recrystallized from CCl_4); to give pure 208 (mp 169-170°); nmr: ($CDCl_3$) τ , 2.00-2.50 (4H, multiplet) aromatic; 5.03-5.60 (3H, multiplet) methine; 5.80-6.00 (1H, multiplet) methine; infrared: $\bar{\nu}$, 1320 cm^{-1} and 1170 cm^{-1} (SO_2), 640 cm^{-1} (C-Cl); mass spectra; m/e for molecular ion = 262 .

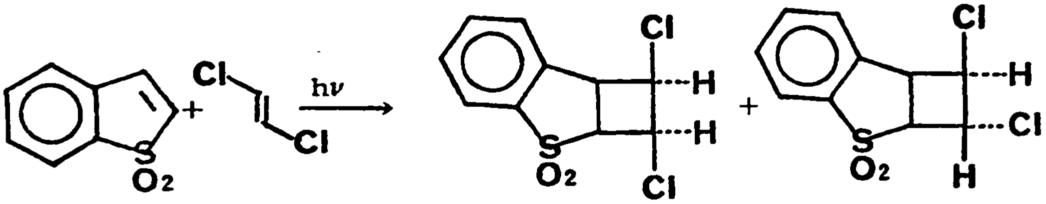
Scheme 33



136a 207 208

53% 47%

Scheme 34



136a 207 208

23% 77%

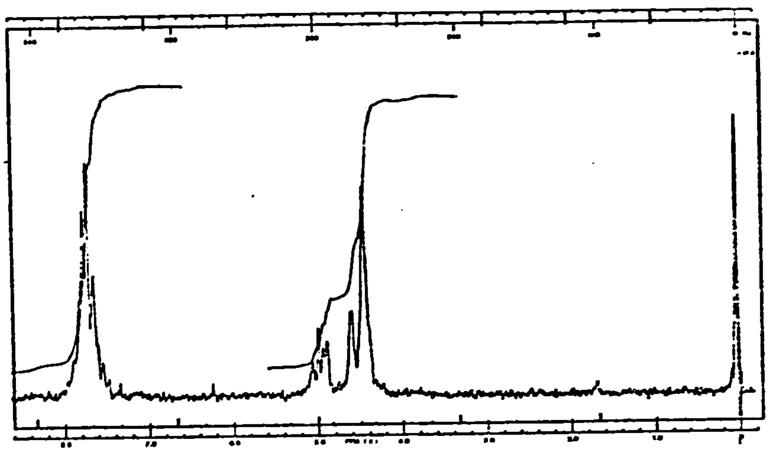


Figure 7

Nuclear Magnetic Resonance of Compound 207.

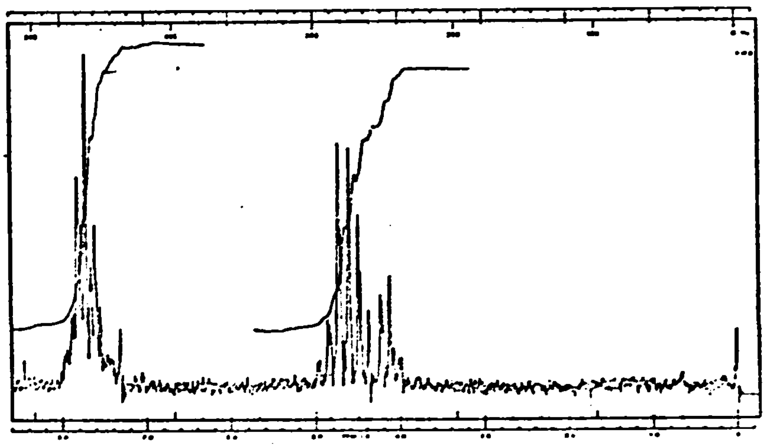


Figure 8

Nuclear Magnetic Resonance of Compound 208.

Consideration of the spectral data has led to structure assignments for 207 and 208 as shown in Schemes 33 and 34. It has been observed that halogen atoms shield protons that are cis to them (149). The lower field signals appear to move into the envelope while peaks have been shifted to high field from the envelope (in comparing cis 207, Fig. 7, with trans 208, Fig. 8). This would account for the observed spectra. Hence, a tentative structure as illustrated in scheme 32 and 33 can be proposed without defining the stereochemistry of the ring junction protons.

By comparing the integration for the nmr signal that is unique to each of 207 and 208 in the reaction mixtures, the ratios of 207:208 = 53:47 and 207:208 = 23:77 was estimated for cycloadditions of 136a to cis and trans-1,2-dichloroethylene respectively. It is of interest to note that in these cycloaddition reactions, only 2 of the 4 possible products were observed. The photocycloaddition of cis and trans 1,2-dichloroethylene to thianaphthene gave four products (137).

Cycloaddition to 1,1-Dichloroethylene. Thianaphthene-1,1-dioxide and 1,1-dichloroethylene were irradiated in benzene under standard conditions. Workup and recrystallization from ethanol gave 209a (mp 139.5-140.5^{o}); nmr: (Fig. 9) ($CDCl_3$) τ, 2.10-2.50 (4H, multiplet) aromatic; 5.20, (1H, quartet J_{AB} = 8.0 Hz,

J_{AC} = 2.5 Hz) methine, proton A; 5.73, (1H, quartet J = 8.0 Hz) methine, proton B; 6.25-7.00, (2H, multiplet methylene, proton C; ir: $\bar{\nu}$, 1310 cm^{-1} and 1160 cm^{-1} (SO_2); 615 cm^{-1} (C-Cl); mass spectra: m/e for the molecular ion = 262).

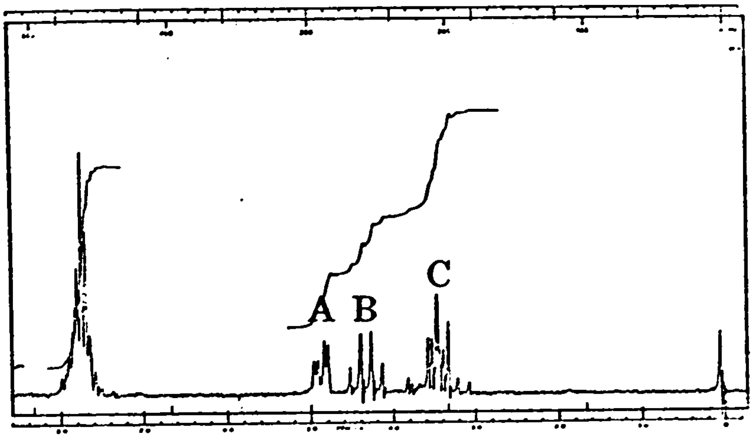
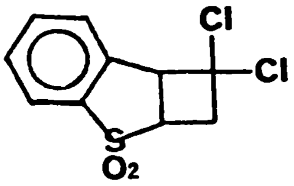


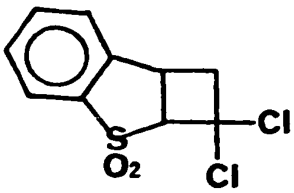
Figure 9
Nuclear Magnetic Resonance of Compound 209a.

Spectroscopic evidence indicates that compound 209a is a 1:1 adduct between thianaphthene-1,1-dioxide (136) and 1,1-dichloroethylene as represented by structure A and B (Chart 5).

Chart 5



A



B

Irradiation of the resonance at τ = 6.25-7.00 caused the quartet at τ = 5.20 (for proton A) to collapse to a doublet (J = 8.0 Hz). Also, the quartet at τ = 5.20 collapsed to a doublet (J = 2.5 Hz) and the multiplet at τ = 6.25-7.01 into a distorted quartet when the resonance at τ = 5.73 was irradiated.

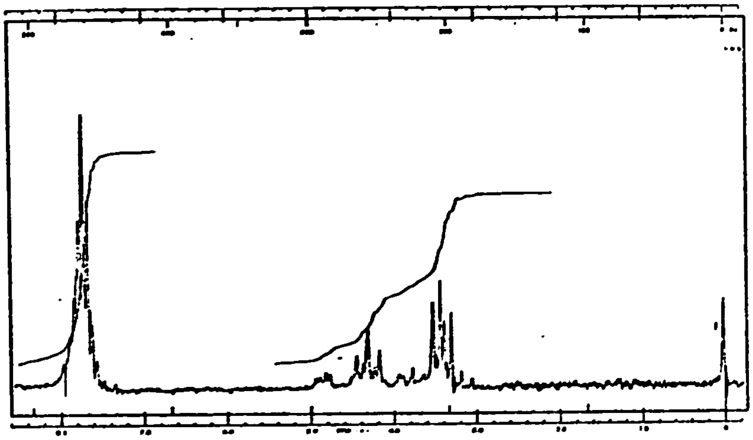


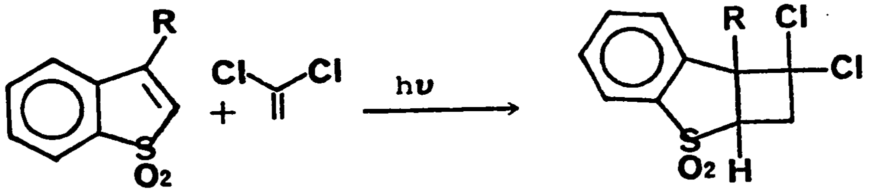
Figure 10

Nuclear Magnetic Resonance of Compound 209b.

This indicates that proton A is strongly coupled to proton B while B is strongly coupled to proton C. Proton A is weakly coupled to proton C. The assignments for proton A and B thus elucidate the structure of adduct 209a.

The irradiation of 3-deuterothianaphthene-1,1-dioxide (136b) in the presence of 1,1-dichloroethylene under the same conditions as for 136a gave compound 209b (identical mp as 209a). However, examination of the nmr spectrum revealed that the resonance at τ = 5.20 was not present and the resonances at τ = 5.73 had collapsed to a triplet (J = 8.0 Hz). (In addition, the signal at τ = 6.25-7.00 had appeared as a pair of doublets (τ = 6.53, J = 8.0 Hz) and τ = 6.61, J = 8.0 Hz)). Thus, A is the benzylic proton (5 position) and B is the sulphonyl proton (2 position). The above results are consistent with 209a having structure A.

Scheme 35



136a R = H;
136b R = D.

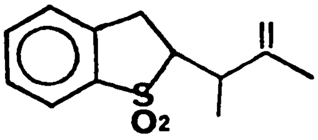
209a R = H;
209b R = D.

Cycloaddition of Thianaphthene-1,1-dioxide (136a) to Tetrachloroethylene. Thianaphthene-1,1-dioxide was irradiated in the presence of tetrachloroethylene. The only materials recovered after all of compound 136a was consumed, were photodimers 137 and 138. No 1:1 adduct was observed.

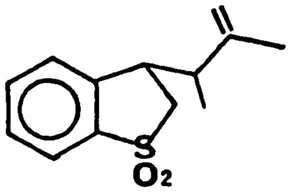
Cycloaddition of Thianaphthene-1,1-dioxide (136a) to 2-methyl-2-butene. Compound 136a was irradiated in the presence of 2-methyl-2-butene in benzene for one hour. Analysis of the reaction mixture by glpc and tlc indicated that there were two products formed. The components of the reaction mixture were separated by preparative tlc developed by cyclohexane:ethyl acetate = 8:2.

The first fraction, 210a, after recrystallization in ethanol, had mp 145.0-145.5°, nmr: $(CDCl_3)$ (Fig. 11) τ, 2.18-2.58 (4H, multiplet) aromatic; 5.08, (2H, broad singlet) vinylidene; 6.40-7.20, (3H, multiplet) methylene and methine; 8.23, (3H, doublet, $J = 1.0$ Hz) methyl; 8.55 (3H, doublet, $J = 6.2$ Hz) methyl; ir: $\bar{\nu}$, 1670 cm^{-1} (C=C); 1305 cm^{-1} and 1152 cm^{-1} (SO_2); mass spectra: m/e for the molecular ion = 236. The above data is consistent with a 1:1 adduct of compound 136a and 2-methyl-2-butene of structure A or B in Chart 6.

Chart 6



A



B

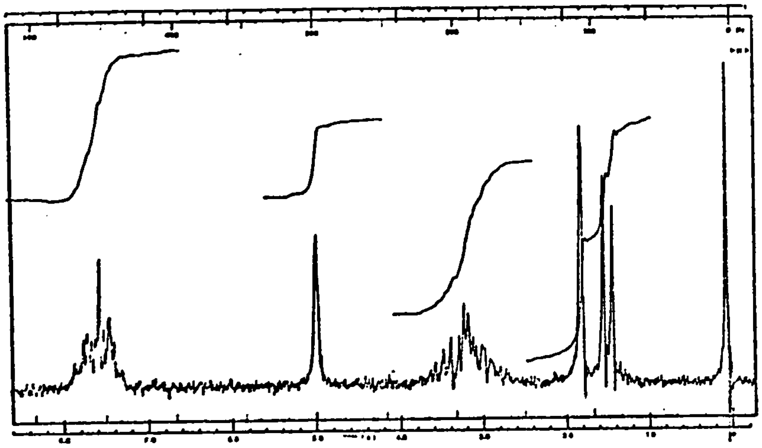
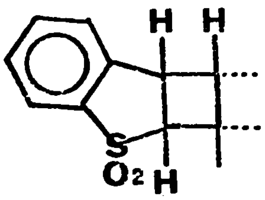


Figure 11
Nuclear Magnetic Resonance of Compound 210a.

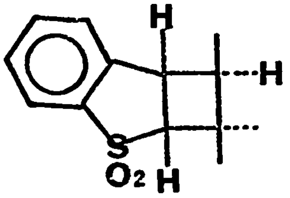
The second fraction 211a had mp 131.5-132°; nmr: (Fig. 12) ($CDCl_3$) τ, 2.11-2.75 (4H, multiplet) aromatic; 6.20-6.56 (2H, multiplet) methine; 7.58 (1H, quintet) methine; 8.70 (3H, singlet) methyl; 8.88 (3H, doublet, J = 7.5 Hz) methyl; 9.20 (3H, singlet) methyl; ir: $\bar{\nu}$, 1470 cm^{-1} molecular ion = 236. The structures that are consistent with the spectral properties listed above are 1:1 adducts A, B, C or D shown in Chart 7.

Chart 7

A B



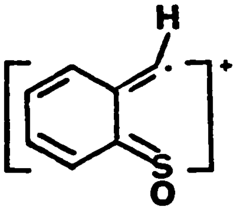
C



D

In order to facilitate mass spectral and nmr interpretation, 3-deuterothianaphthene-1,1-dioxide (136b) was used as a substrate for the previous photochemical reaction. The two 3-deutero products (210b and 211b) were separated as before.

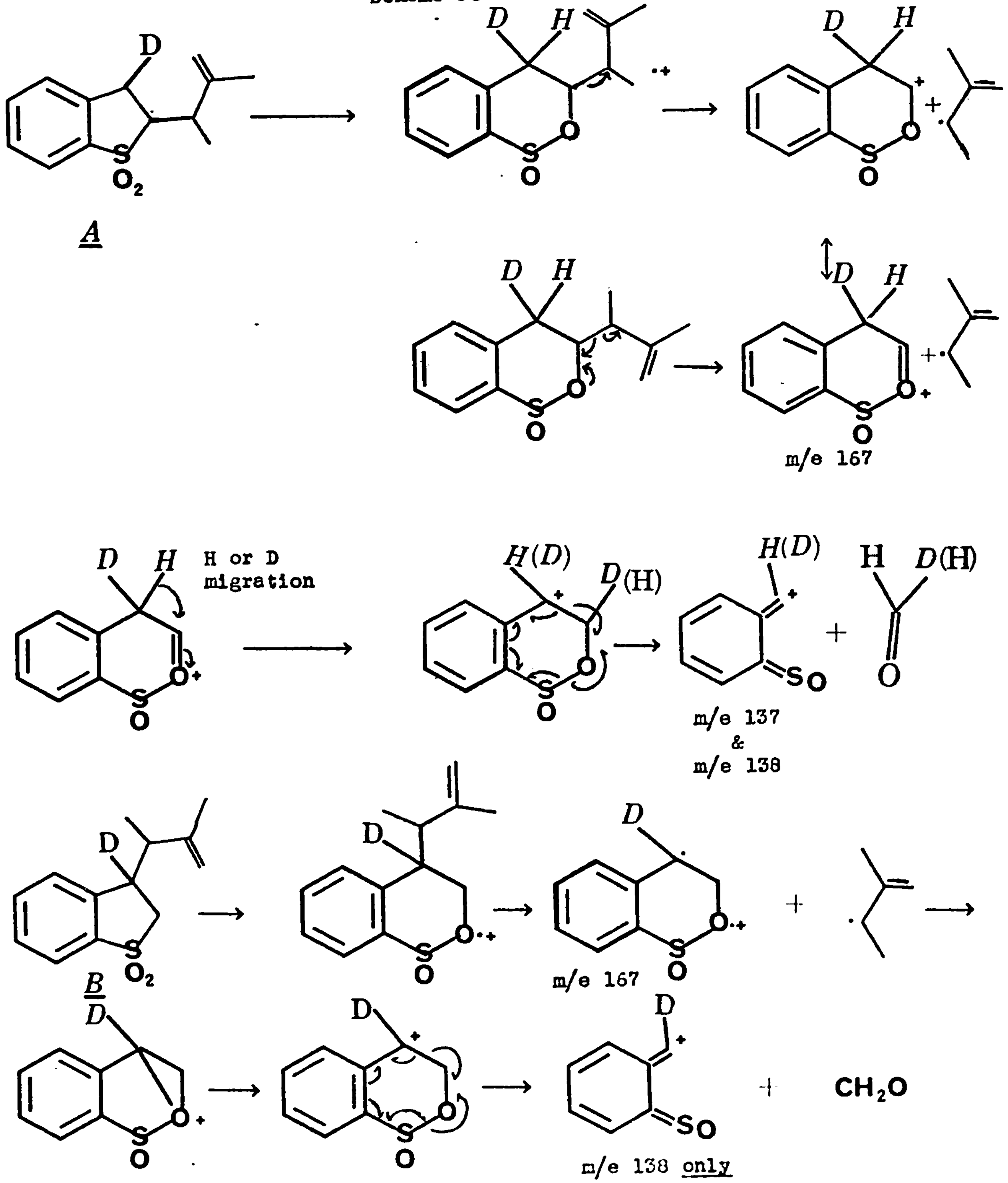
One of the consistently prominent peaks in the mass spectra of thianaphthene-1,1-dioxide (136a) and its derivatives (dimers 137 and 138, adducts 206a, 207, 208, 209a, 210a and 211a) occurs at m/e = 137.006 (corresponding to C_7H_5SO).



$\equiv C_7H_5SO$

This peak can be envisioned to arise from either A or B (Chart 6) via ions with m/e = 167 as illustrated in Scheme 36. Compound 210b (with deuterium in the benzylic position) has a mass spectrum in which peaks at m/e = 137 and 138 are prominent. This observation is consistent with 210a having

Scheme 36


A
D
H
S
O
O_2
H(D)
D(H)
H or D migration
m/e 167
m/e 137
&
m/e 138
B
CH₂O
m/e 138 only

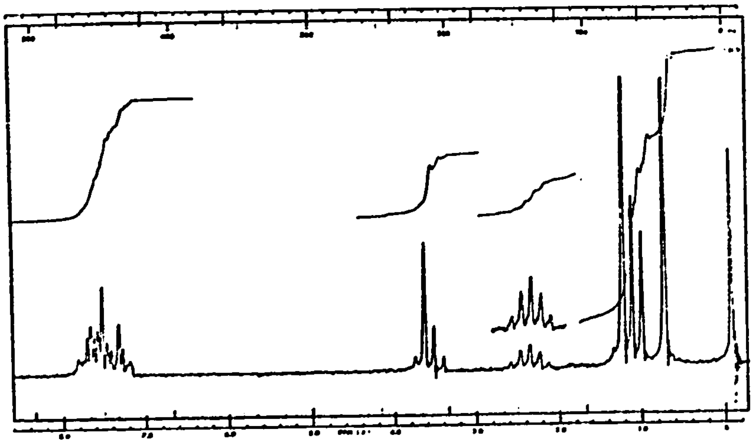


Figure 12
Nuclear Magnetic Resonance of Compound 211a.

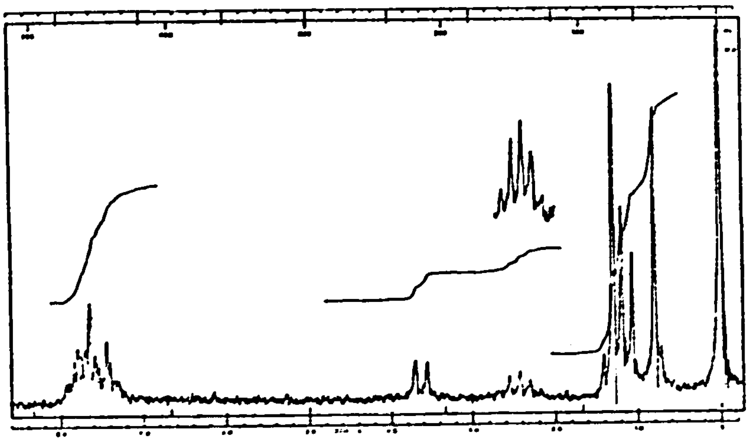


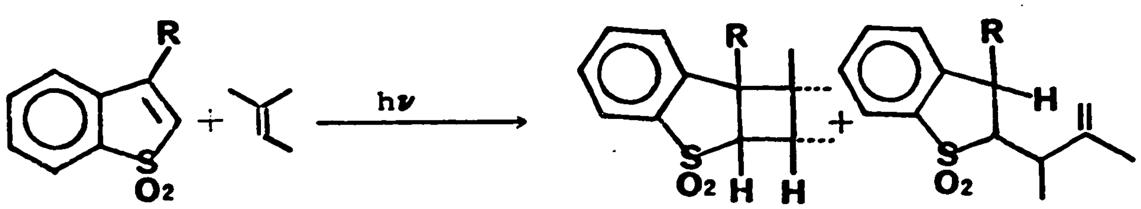
Figure 13

Nuclear Magnetic Resonance of Compound 211b.

structure A in Chart 6. If compound 210a had structure B, then one would expect to find a very small peak for m/e = 137 in the mass spectra of the 3-deutero derivative (210b) (Scheme 36).

The nmr of compound 211b (Fig. 13) (the 3-deutero derivative of compound 211a) was identical to that of compound 211a (Fig. 12) except that the resonance at $\tau = 6.20\text{-}6.56$ collapsed to a doublet at $\tau = 6.35$ ($J = 9.0$ Hz). This means that the α sulphonyl proton is vicinal to the α methyl proton, since the broad quintet at $\tau = 7.58$ did not collapse to a first order quartet. The vicinal coupling constant, $J = 9.0$ Hz, is consistent with all methine protons being cis (if one assumes that protons at the junction of five and four membered rings formed by a two step process are cis). Therefore, the data given are consistent with compound 211 having structure A in Chart 7. The reaction to produce compounds 210 and 211 is summarized in Scheme 37.

Scheme 37



136a R = H;
136b R = D.

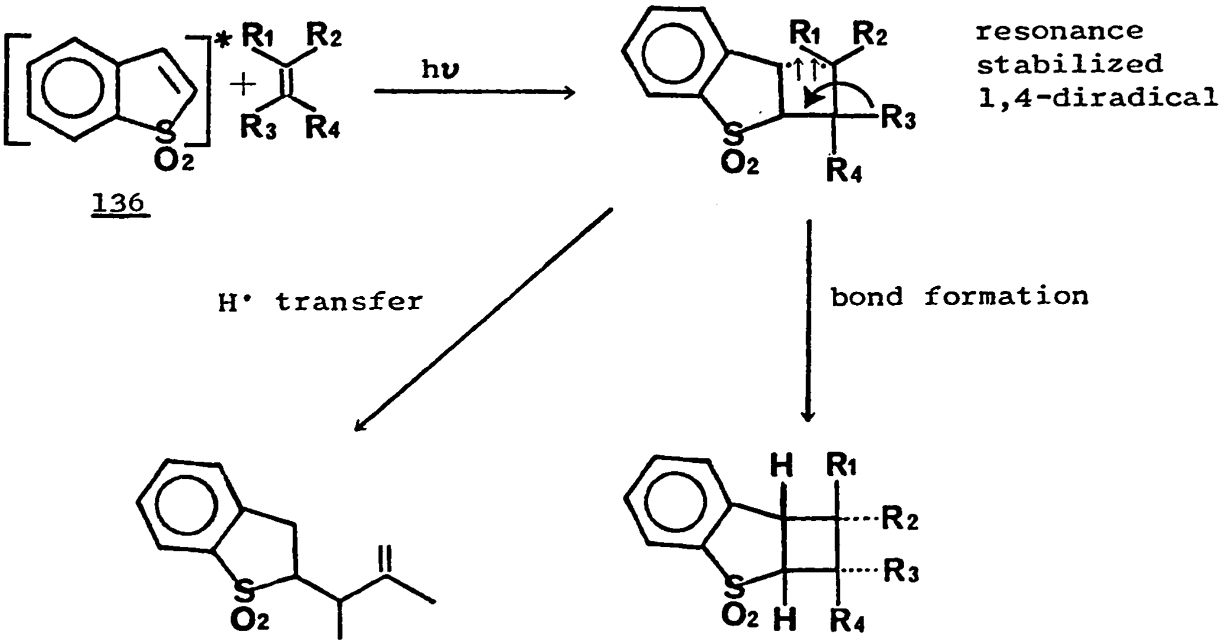
211a R = H;
211b R = D.

210a R = H;
210b R = D.

Discussion

The results obtained for the photocycloaddition of thianaphthene-1,1-dioxide (136a) to the various olefins in the previous section are consistent with a resonance stabilized 1,4-diradical intermediate. The initial addition appears to involve bond formation between the 2-position of compound

Scheme 38

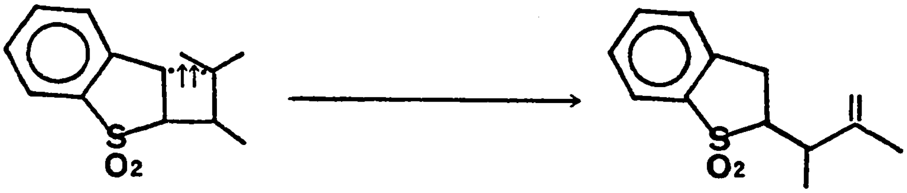


136 and the least substituted carbon atom of the olefins (analogous to free radical attack on an alkene (150)). The resulting intermediate thus is the most stabilized diradical (benzylic and tertiary). The hypothesis is borne out by the fact that photocycloaddition of 136 to trichloroethylene and 2-methyl-2-butene gives only one cyclobutane derivative. If attack occurred from the 3-position to the highly substituted carbon atom of the olefin (carbon atom with two chlorine or two methyl groups), then rotation around the C-C bond of the substrate moiety would cause two stereoisomers to form. The occurrence of this type of rotation during photocycloaddition was illustrated (page 127) in the case of cis and trans 1,2-dichloroethylene, where cycloaddition to both the cis and trans isomers resulted in a mixture of two adducts identical in structure except for the stereochemistry of the chlorine atoms. The products of cycloaddition of compound 136 to 1,1-dichloroethylene is also consistent with a free radical-like attack by the 2-position of the excited state 136 on the least substituted carbon atom.

The fact that tetrachloroethylene does not add to the excited state of thianaphthene-1,1-dioxide (136) can be attributed to steric hindrance by the 4 chlorine atoms to attack on the bond. This steric hindrance results in photodimerization being much faster than mixed cycloaddition.

The isolation of compound 210a and 210b from the reaction mixture of the photocycloaddition of 136a and 136b to 2-methyl-2-butene provides evidence for the existence of the 1,4-diradical intermediate b (Scheme 39). Compound 210 was likely formed by a hydrogen abstraction from the methyl group of the 2-methyl-2-butene moiety by the benzylic position.

Scheme 39



b

210

Thianaphthene-1,1-dioxide (136) reacts under similar conditions as cyclic enones (96, 128) and indenes (135, 136) to give comparable compounds (Table XIII). The photocycloaddition of cyclic enones to unsymmetrical olefins gives two cyclic products with each possible orientation in which one orientation predominates (96, 128), while indene (135), 1,1-dimethylindene (136) carbostryil (134) and thianaphthene-1,1-dioxide (136) give one product. These results can be explained by invoking resonance stabilized diradical intermediates for those olefins that are fused and conjugated to aromatic systems. Such intermediates are not involved in the case of cyclic enones.

Experimental Section

Apparatus. Infrared spectra of KBr pellets were measured with a Perkin-Elmer 337 spectrometer, nmr spectra were obtained from a Varian Associates T-60 and mass spectra were recorded on an AEI MS 902 spectrometer. Melting points were taken on a Gallenkamp apparatus and are not corrected. The glpc data were obtained on a Hewlett-Packard F&M series 5670 research chromatograph. A Hanovia medium pressure mercury vapour lamp (type L, 450 watt) in a pyrex water cooled immersion apparatus, surrounded by the reaction mixture, was used for all photocycloadditions.

Thianaphthene-1,1-dioxide (*136a*). This compound was prepared and purified as was described in the experimental section of Chapter II.

3-Bromothianaphthene. This material was synthesized according to the method of G. Komppa (151).

3-Deuterothianaphthene. This compound was synthesized by slowly adding 2.0 g of D_2O to thianaphthene-3-

magnesium bromide. The latter was formed by adding 6.4 g (0.032 mol) of 3-bromothianaphthene in 20 ml of tetrahydrofuran to 0.76 g (0.032 mol) of magnesium turnings in 20 ml of boiling tetrahydrofuran. Normal workup and fractional distillation at 78-80°/2 mm gave 2.5 g (0.018 mol, 62% yield) of 3-deuterothianaphthene (80% deuterated as determined by mass spectra).

3-Deuterothianaphthene-1,1-dioxide (136b). This compound was prepared in the same way as compound 136a (mp 142-142.5°, mp of 136a 142-142.5°).

The Photocycloaddition of Thianaphthene-1,1-dioxide (136a) to Trichloroethylene. Thianaphthene-1,1-dioxide (3.5 g, 0.021 mol) was dissolved in 500 ml of reagent grade trichloroethylene (distilled at 86-86.5°), the solution purged with dry nitrogen for 45 min and irradiated for three hours. After evaporating the solution and refluxing the resultant oil in CCl_4, 5.1 g of a white solid containing three compounds (tlc on silica gel developed by $CHCl_3$ and glpc on 1/8" x 6', 10% Apiezon L column of reaction mixture) was obtained. Fractional crystallization in 50 ml of benzene gave 1.7 g (0.005 mol, 48% yield) of compounds 137 and 138 and 3.4 g (0.013 mol, 52% yield) of compound 206a (mp 142-144°) ir: $\bar{\nu}$, 1320 cm^{-1} and 1160 cm^{-1} (SO_2 stretching); 670 cm^{-1} (C-Cl stretching); nmr: ($CDCl_3$) τ, 2.18 (4H, multiplet) aromatic; 5.18 (2H, AB part of ABX spectrum) methine; 5.69 (1H, quartet, X part of ABX spectrum) methine; mass spectrum: m/e for the molecular ion = 296.

Anal. Calcd. for $C_{10}H_7SO_2Cl_3$: C, 40.33; H, 2.43; S, 10.76; Cl, 35.80. Found: C, 41.01; H, 2.42; S, 10.93; Cl, 34.60.

The above reaction was repeated, after purging with O_2. No cycloaddition (including dimerization) occurred, indicating a triplet excited state as an intermediate.

The Dehydrochlorination of Compound 206a. Compound 206a (3.0 g, 0.009 mol) was dissolved in 50 ml of reagent grade triethylamine and refluxed for 20 hours. Evaporation of solvent and recrystallization from ethanol/activated charcoal gave 212 (2.0 g, 0.008 mol, 89% yield) (mp 169-170°); nmr: (C_6D_6) τ , 2.60-3.35 (4H, multiplet) aromatic; 6.35 (2H, AB quartet, $\Delta\nu$, 20.1 Hz, J_{AB}, 4.0 Hz) methine; ir: $\bar{\nu}$, 1680 cm^{-1} (C=C stretching); 1320 cm^{-1} and 1150 cm^{-1} (SO_2 stretching); 650 cm^{-1} (C-Cl stretching).

Anal. Calcd. for $C_{10}H_6SO_2Cl_2$: C, 45.98; H, 2.30; S, 12.25; Cl, 27.20. Found: C, 45.97; H, 2.34; S, 12.24; Cl, 27.21.

The Photocycloaddition of 3-Deuterothianaphthene-1,1-dioxide (136b) to Trichloroethylene. A 150 ml trichloroethylene solution of 3-deuterothianaphthene-1,1-dioxide (0.5 g, 0.003 mol) was irradiated for 30 min. The product was isolated and purified as above and resulted in compound 206b (0.5 g, 0.0014 mol, 47% yield); mp 142-144°; nmr: ($CDCl_3$) τ, 2.18 (4H, multiplet) aromatic; 5.18 (1H, doublet, J = 8.0 Hz) methine; 5.70 (1H, doublet, J = 8.0 Hz) methine; mass spectra: m/e for the molecular ion = 297.

The Photocycloaddition of Thianaphthene-1,1-dioxide (136a) to cis 1,2-Dichloroethylene. Thianaphthene-1,1-dioxide (1.75 g, 0.0105 mol) was dissolved in 350 ml of reagent grade (Eastman white label) cis 1,2-dichloroethylene and irradiated for 9 hours under nitrogen atmosphere. Dichloroethylene was removed by distillation and ethanol added to the oily residue, resulting in white crystals (2.0 g). The unreacted starting material (0.7 g) was separated from the products by filtering from boiling water. The resulting solid (1.3 g, 0.005 mol, 81% yield based on unreacted starting material) was examined by glpc (1/8" x 6', 10% Apiezon L on chromosorb W) and was found to contain two compounds, 207 and 208. This mixture was chromatographed over silica gel by $CHCl_3$ and partial separation was obtained. The first fraction contained 0.2 g (13% yield based on the amount of compound 136 consumed) of compound 207 (mp 144.5-146.5°); ir: $\bar{\nu}$, 1320 cm^{-1} and 1170 cm^{-1} (SO_2 stretching); 665 cm^{-1} (C-Cl stretching); nmr: ($CDCl_3$) τ, 2.00-2.50 (4H, multiplet) aromatic; 4.94-5.15 (1H, multiplet) methine; 5.33-5.60 (3H, multiplet) methine.

Anal. Calcd. for $C_{10}H_8SO_2Cl_2$: C, 45.63; H, 3.04; S, 12.17; Cl, 27.00. Found: C, 45.61; H, 3.09; S, 12.26; Cl, 26.97.

The second fraction contained a mixture of compounds 207 and 208. Fractional crystallization in absolute ethanol gave an additional 0.15 g of compound 207 (total yield of 207, 22%). Crystallization of the residue from the above filtrate gave 50 mg (3% yield) of compound 208 (mp 169-170°); ir: $\bar{\nu}$, 1320 cm^{-1} and 1170 cm^{-1} (SO_2 stretching); 640 cm^{-1} (C-Cl stretching); nmr: ($CDCl_3$) τ, 2.00-2.50 (4H, multiplet) aromatic; 5.03-5.60 (3H, multiplet) methine; 5.80-6.00 (1H, multiplet) methine.

Anal. Calcd for $C_{10}H_8SO_2Cl_2$: C, 45.63; H, 3.04; S, 12.17; Cl, 27.00. Found: C, 45.95; H, 3.20; S, 12.23; Cl, 26.26.

The ratio of compound 207 to compound 208 in the original mixture was estimated by comparing the integration of the resonances at $\tau = 4.94-5.15$ for compound 207 with that at $\tau = 5.80-6.00$ for compound 208. The ratio of 207 to 208 was found to be 53:47.

The Photocycloaddition of Thianaphthene-1,1-dioxide (136a) to trans 1,2-Dichloroethylene. A solution of thianaphthene-1,1-dioxide (0.134 g, 0.0008 mol) in 150 ml of trans 1,2-dichloroethylene was irradiated for 45 minutes. Distillation of the dichloroethylene and crystallization in ethanol: hexane

(4:1) gave 0.185 g (87% yield) of compounds 207 and 208. Fractional crystallization in ethanol gave 40 mg (20% yield) of compound 208 (mp 170-171°, mixed mp with 208 from photoaddition of cis 1,2-dichloroethylene was not depressed).

The ratio of compound 207 to 208 was found (by the same method as that for the products of the photoaddition of cis 1,2-dichloroethylene) to be 23:77.

The Photocycloaddition of Thianaphthene-1,1-dioxide (136a) to 1,1-Dichloroethylene. Thianaphthene-1,1-dioxide (0.5 g, 0.003 mol) and 1,1-dichloroethylene (12 g, 0.12 mol) in 150 ml of benzene were irradiated under standard conditions for 3 hours. The polymeric material that had formed was filtered, an additional 12 g of 1,1-dichloroethylene was added and the irradiation continued for 3 more hours. At this point glpc analysis (1/8" x 6', 10% UC-W98 on diatoport S) indicated complete reaction and together with tlc (silica gel developed by $CHCl_3$) indicated only one product. Recrystallization in ethanol gave compound 209a (mp 139.5-140.5°) (0.6 g, 0.0023 mol, 77% yield); ir: $\bar{\nu}$, 1310 cm^{-1} and 1160 cm^{-1} (SO_2 stretching); 615 cm^{-1} (C-Cl stretching); nmr: ($CDCl_3$) τ, 2.10-2.50 (4H, multiplet) aromatic; 5.20 (1H, quartet, $J_{2,3}$ = 8.0 Hz, $J_{3,5}$ = 2.5 Hz) methine; 5.73 (1H, quartet, J = 8.0 Hz) methine; 6.25-7.00 (2H, multiplet) methylene; mass spectra: m/e for the molecular ion, 262.

Anal. Calcd for $C_{10}H_8SO_2Cl_2$: C, 45.63; H, 3.04 S, 12.17; Cl, 27.00. Found: C,45.87; H, 3.05; S,12.42;Cl,26.18. Exact mass measurement of the molecular ion : Calcd for $C_{10}H_8SO_2Cl_2$, 261.9622. Found: 261.9631.

The Photocycloaddition of 3-Deuterothianaphthene-1,1-dioxide (136b) to 1,1-Dichloroethylene. This photoaddition was carried out in exactly the same way as above, except that 3-deuterothianaphthene-1,1-dioxide (136b) was used in place of compound 136a. Compound 209b was obtained (0.6 g, 77% yield, mp 139.5-140.5°); nmr: ($CDCl_3$) τ, 2.10-2.50 (4H, multiplet) aromatic; 5.73 (1H, triplet, J = 8.0 Hz) methine; 6.40-6.70 (2H, multiplet) methylene.

The Attempted Photocycloaddition of Thianaphthene-1,1-dioxide (136a) to Tetrachloroethylene. Thianaphthene-1,1-dioxide (1.7 g, 0.01 mol) and tetrachloroethylene (108 g, 0.8 mol) in 170 ml of benzene was irradiated until all of the starting material was consumed (6 hours). Evaporation of the benzene and tetrachloroethylene gave white crystals which tlc (silica gel developed by acetone) and glpc (1/8" x 6', 10% Apiezon L on chromosorb W) revealed to be dimers 137 and 138 (1.7 g, 100% yield). No mixed cycloadduct was observed.

The Photocycloaddition of Thianaphthene-1,1-dioxide (136a) to 2-Methyl-2-butene. Compound 136a (0.35 g, 0.0021 mol) and 2-methyl-2-butene (14 g, 0.2 mol) were irradiated in benzene for 1 hour under a nitrogen atmosphere. Evaporation of the solvent left 0.49 g of an oily material (theoretical yield for 100% cycloaddition is 0.46 g). Examination of the reaction mixture by tlc (silica gel developed by cyclohexane:ethyl acetate = 8:2) and glpc (1/8" x 6', 10% UC-W98 silicone rubber on diatoport S) showed that two products were formed. The reaction mixture was then chromatographed on preparative tlc plates (0.75 mm thick) of silica gel with cyclohexane:ethyl acetate = 8:2 (development was repeated until separation occurred). Fraction 1 gave (recrystallization with ethanol) compound <u>210a</u> (39 mg, 0.089 mmol, 9% yield, mp 145-145.5°); ir: $\bar{\nu}$, 1670 cm^{-1} (C=C stretching); 1305 cm^{-1} and 1152 cm^{-1} (SO_2 stretching); nmr: ($CDCl_3$) τ, 2.18-2.58 (4H, multiplet) aromatic; 5.08 (2H, broad singlet) vinylidene; 6.40-7.20 (3H, multiplet) methylene and methine; 8.23 (3H, doublet, J = 1.0 Hz) methyl; 8.55 (3H, doublet, J = 6.0 Hz) methyl; mass spectra: m/e for the molecular ion, 236.

Anal. Calcd for $C_{13}H_{16}SO_2$: C, 66.10, H, 6.78; S, 13.56; Found: C, 65.84; H, 6.83; S, 13.36.

Fraction 2 (recrystallization from ethanol) gave compound <u>211a</u> (115 mg, 0.5 mmol, 25% yield, mp 131.5-132°); ir: $\bar{\nu}$, 1470 cm^{-1} (C-CH_3 stretching); 1290 cm^{-1} and 1150 cm^{-1} (SO_2 stretching); nmr: ($CDCl_3$) τ, 2.11-2.75 (4H, multiplet) aromatic; 6.20-6.56 (2H, multiplet) methine; 7.58 (1H, quintet, J = 7.0 Hz) methine; 8.70 (3H, singlet) methyl; 8.88 (3H, doublet, J = 7.0 Hz) methyl; 9.20 (3H, singlet) methyl; mass spectra: m/e for the molecular ion, 236.

Anal. Calcd for $C_{13}H_{16}SO_2$: C, 66.10; H, 6.78; S, 13.56. Found: C, 66.03; H, 6.97; S, 13.41.

The Photocycloaddition of 3-Deuterothianaphthene-1,1-dioxide (136b) to 2-Methyl-2-butene. This experiment was executed in exactly the same way as was the cycloaddition of compound 136a to 2-methyl-2-butene. The resulting products were compound 210b (mp 145-145.5°); mass spectra: m/e for the molecular ion, 237; and compound 211b (mp 131.5-132°); nmr: ($CDCl_3$) τ, 2.11-2.75 (4H, multiplet) aromatic; 6.35 (1H, doublet, J = 9.0 Hz) methine; 7.58 (1H, quintet, J = 7.0 Hz) methine; 8.70 (3H, singlet) methyl; 8.88 (3H, doublet, J = 7.0 Hz) methyl; 9.20 (3H, singlet) methyl; mass spectra: m/e for the molecular ion, 237.

CHAPTER V

CONCLUSIONS AND CLAIMS TO ORIGINAL RESEARCH

The structures of the photodimers of thianapthene-1,1-dioxide have been elucidated by chemical degradation studies as head-to-head, anti and head-to-tail, anti.

Various aspects of the mechanism of the dimerization reaction were substantiated. A method has been devised to determine the Q_{isc} for the formation of a triplet excited state of energy less than 58 kcal/mole. The Q_{DIM} for the photodimerization was found to be 0.18; the Q_{DIM} for the benzophenone sensitized dimerization was 1.0. Thus, the Q_{isc} for the formation of the triplet excited state of thianaphthene-1,1-dioxide is 0.18.

A solvent effect on the ratio of head-to-head, anti to head-to-tail, anti was observed. The plot of log HH/HT versus the Kirkwood-Onsager parameter was found to be linear, indicating preferential solvation of the more polar transition state.

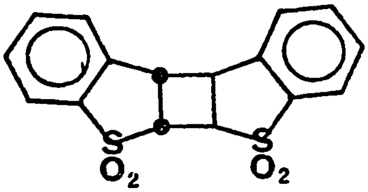
The photocycloaddition of thianaphthene-1,1-dioxide to various unsymmetrically substituted olefins gave products with orientational and stereochemical specificity. The mechanism appears to involve a resonance stabilized 1,4-diradical intermediate.

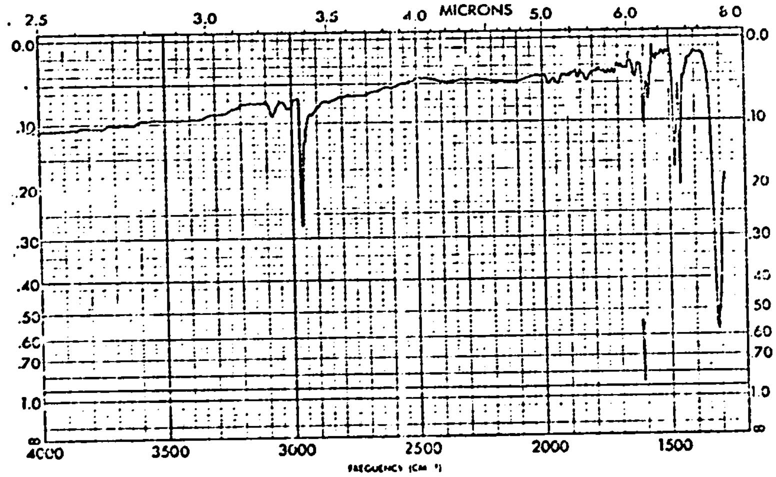
APPENDIX A

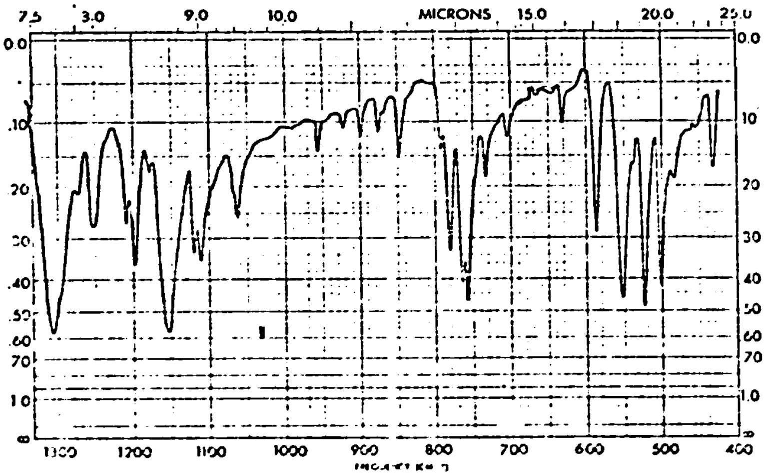
Absorption Spectra

Infrared Spectrum

5a, 5b, 10b, 10c-Tetrahydrocyclobuta-[1,2-b:4,3'-b']-bis-[1]-benzothiophene-5,5,6,6-tetraoxide (137)

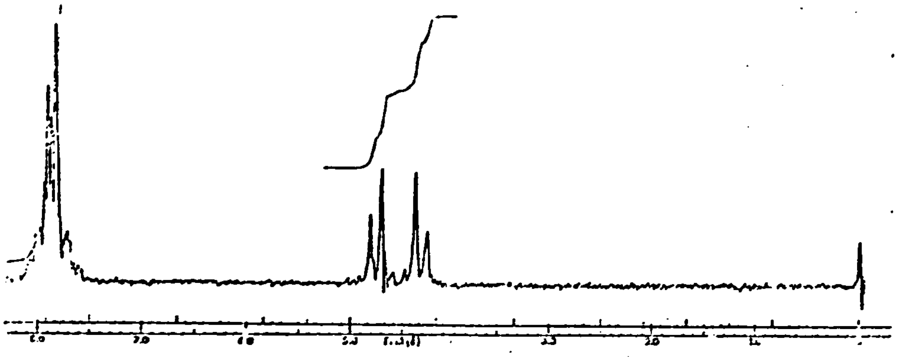






Nuclear Magnetic Resonance Spectrum

5a, 5b, 10b, 10c-Tetrahydrocyclobuta-[1,2-b:4,3-b']-bis-[1]-benzothiophene-5,5,6,6-tetraoxide (<u>137</u>)

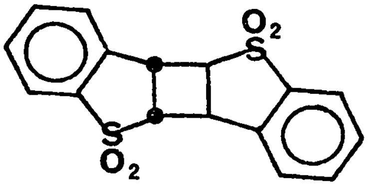


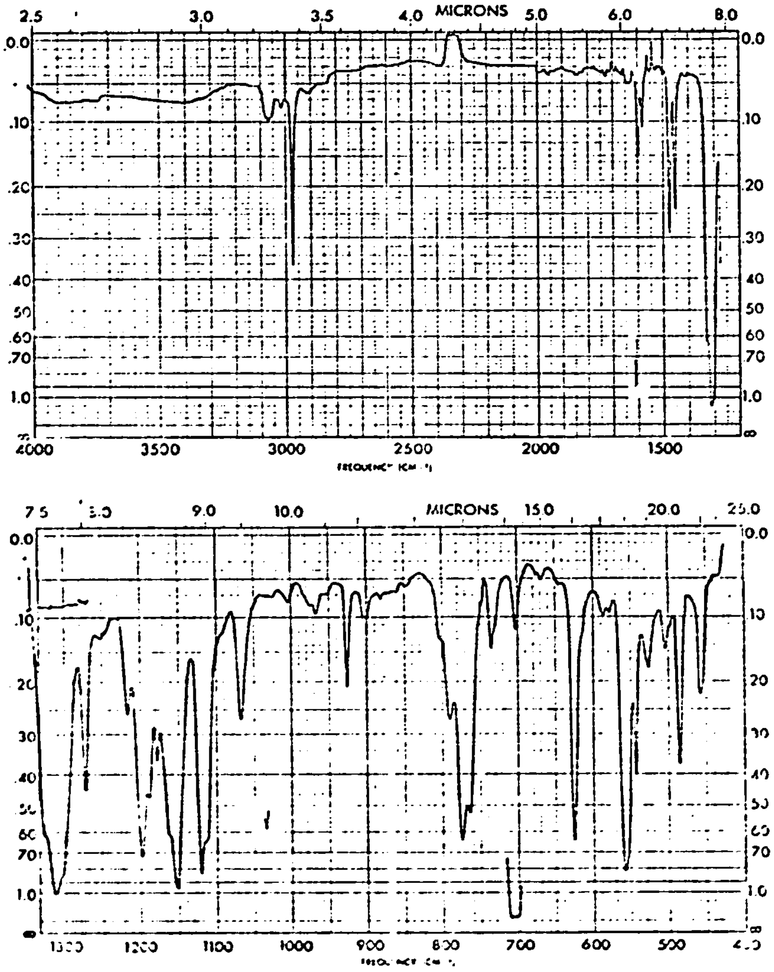
The Mass Spectrum of the Head-To-Head, Anti Photodimer, 137

m/e	% Abundance	m/e	% Abundance	m/e	% Abundance
50	4	109	18	189	4
51	7	110	2		
52	2			191	2
		118	10		
63	10	119	2	218	1
64	1			219	2
65	4	131	3	220	4
				221	2
69	1	134	3	222	2
74	4	137	100	233	1
75	6	138	10	234	2
76	12	139	7	235	1
77	6				
78	3	149	1	250	7
		150	2	251	4
88	7	151	2		
89	17	152	2	268	10
90	5	153	4	269	3
				270	1
100	4	165	2		
101	2	166	25	315	0.5
103	28	167	2		
104	9			332	0.4
105	10	176	4	333	0.1
		177	1		
108	1	178	2		

Infrared Spectrum

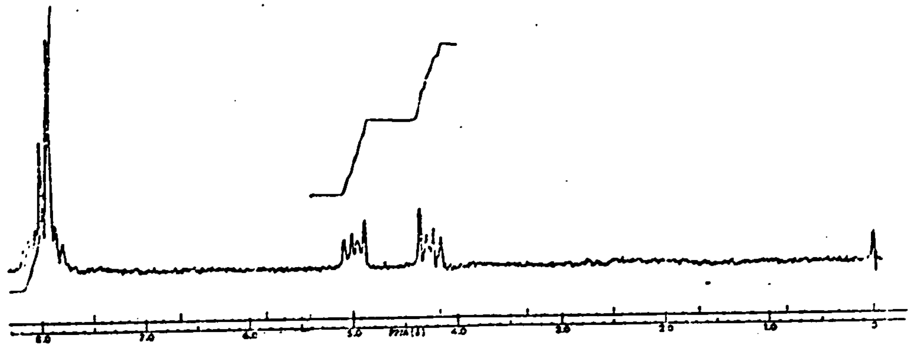
4b, 4c, 9b, 9c–Tetrahydrocyclobuta–[1,2-b:3,4-b']-bis-[1]-benzothiophene-5,5,10,10-tetraoxide (138)





Nuclear Magnetic Resonance Spectrum

4b, 4c, 9b, 9c-Tetrahydrocyclobuta-[1,2-b:3,4-b']-bis-[1]-benzothiphene-5,5,10,10-tetraoxide (138)

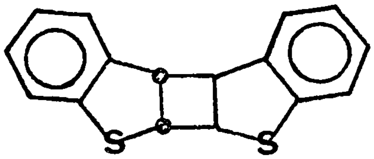


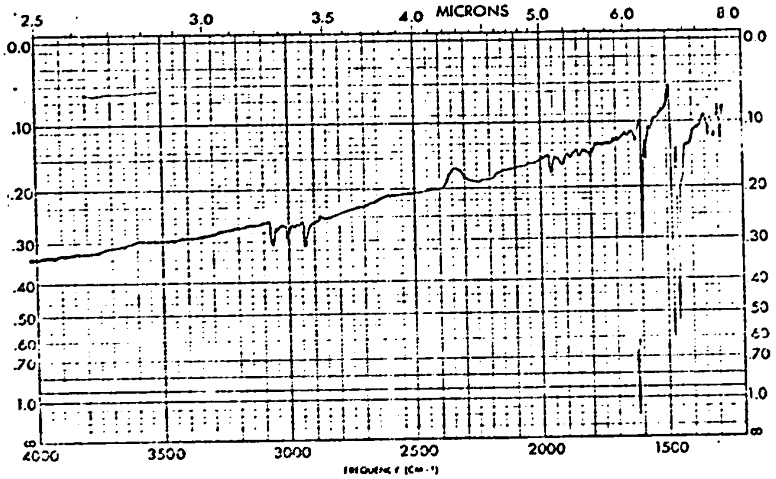
The Mass Spectrum of the Head-To-Tail, Anti Photodimer, 138

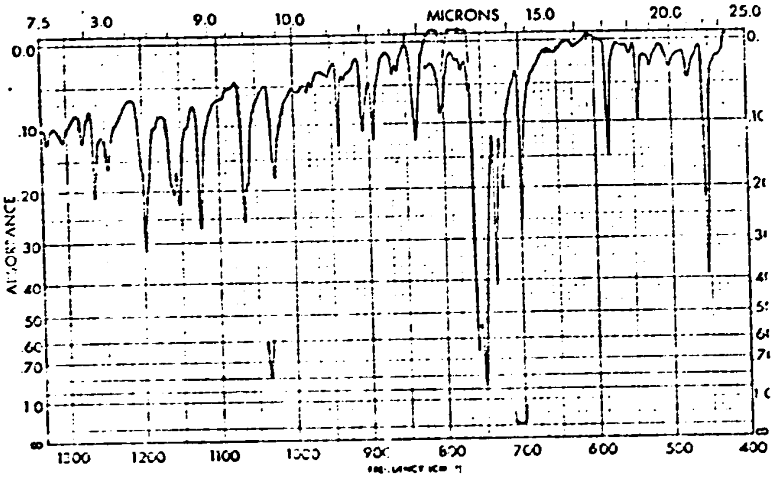
m/e	% Abundance	m/e	% Abundance	m/e	% Abundance
50	12	116	4	200	10
51	15			201	9
52	8	118	20	202	35
				203	30
62	1	121	10	204	20
63	14			205	10
64	1	134	5		
65	10	135	3	220	1
		136	10	221	10
67	1	137	100	222	5
		138	20	223	12
69	1	139	10	224	2
74	10	148	1	233	2
75	12	149	2		
76	20	150	4	239	35
77	12	151	3	240	8
78	4	152	3	241	4
		153	2		
87	2			250	7
88	10	163	7	251	10
89	20				
90	12	165	5	268	35
		166	50	269	10
100	2	167	8	270	5
101	15	168	5		
102	10			284	2
103	3	176	5		
104	3	177	1	302	2
105	10	178	4		
				332	1
108	2	189	7	333	0.2
109	35	190	1		
110	4	191	3		

Infrared Spectrum

5a, 5b, 10b, 10c-Tetrahydrocyclobuta-[1,2-b:4,3-b']-bis-[1]-benzothiphene (139)

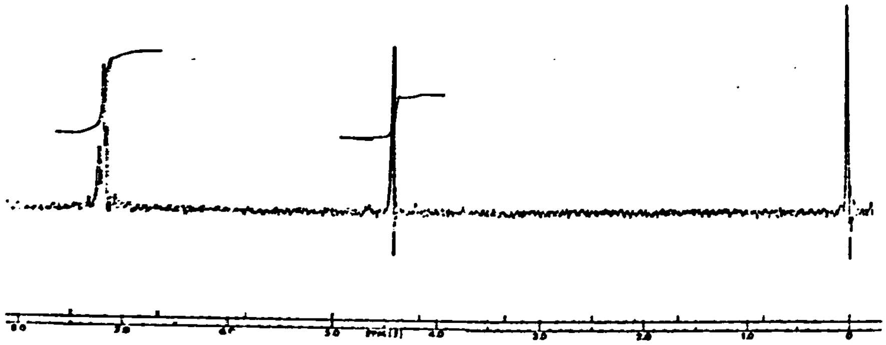






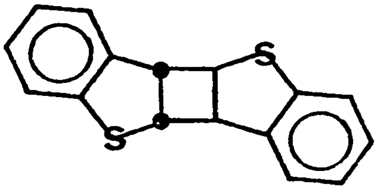
Nuclear Magnetic Resonance Spectrum

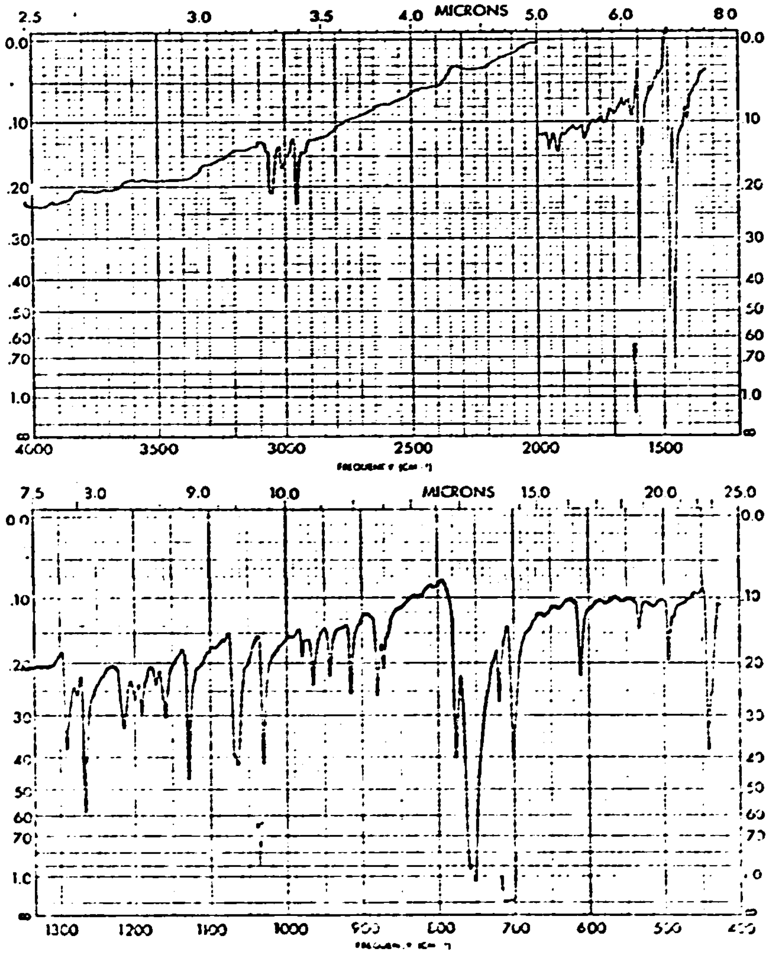
5a, 5b, 10b, 10c–Tetrahydrocyclobuta-[1,2-b:4,3-b']-bis-[1]-benzothiophene (139)



Infrared Spectrum

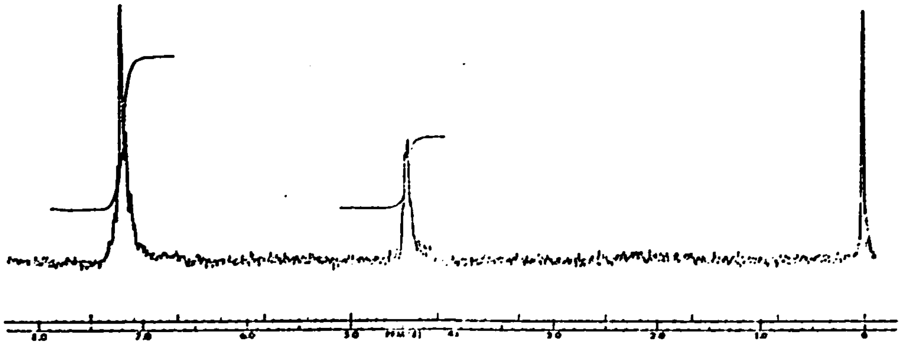
4b, 4c, 9b, 9c-Tetrahydrocyclobuta-[1,2-b:3,4-b']-bis-[1]-benzothiophene (145)





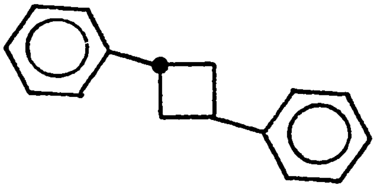
Nuclear Magnetic Resonance Spectrum

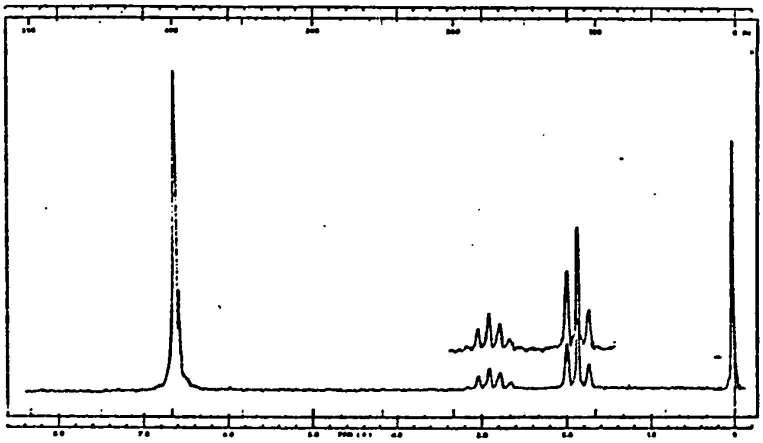
4b, 4c, 9b, 9c-Tetrahydrocyclobuta-[1,2-b:3,4-b']-bis-[1]-benzothiophene (<u>145</u>)



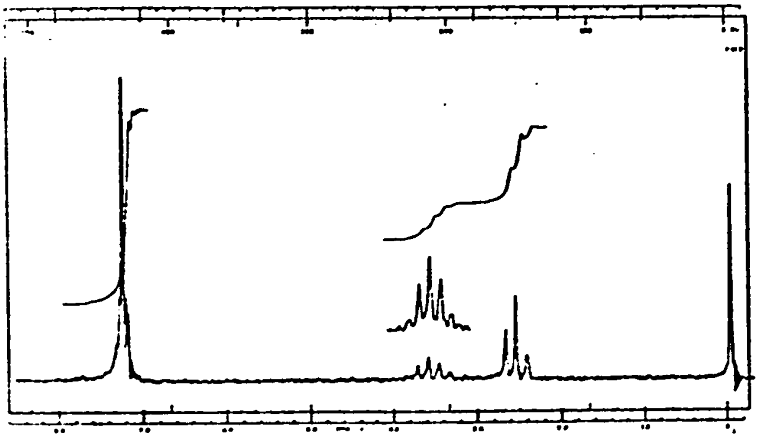
Nuclear Magnetic Resonance Spectra

trans-1,3-Dipehnylcyclobutane (147)





(C_6D_6)



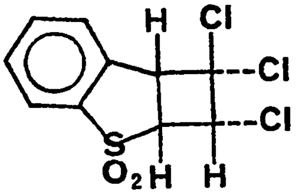
$(CDCl_3)$

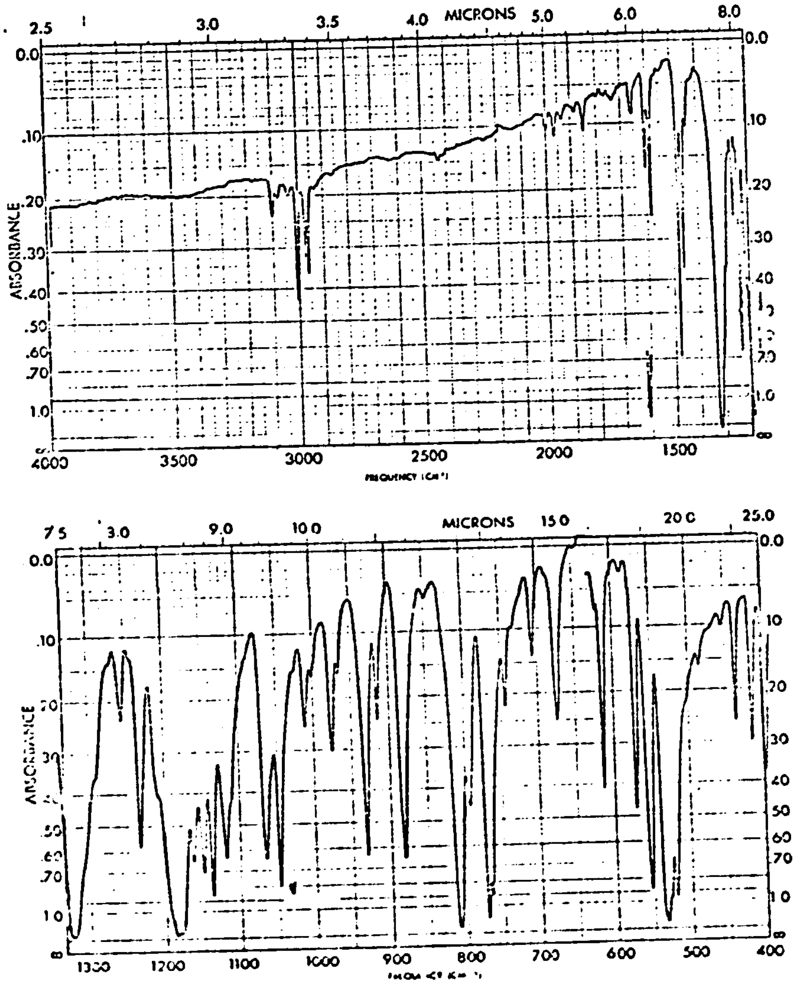
The Mass Spectrum of trans-1,3-Diphenylcyclobutane (<u>147</u>)

m/e	% Abundance	m/e	% Abundance
39	3.6	89	1.2
50	2.4	91	4.8
51	5.0		
52	2.4	102	2.4
		103	12.0
62	2.4	104	100.0
		105	11.5
64	3.6		
		113	2.4
75	1.2		
76	1.2	115	3.0
77	7.2		
78	10.8	208	9.6
79	1.2	209	1.2

Infrared Spectrum

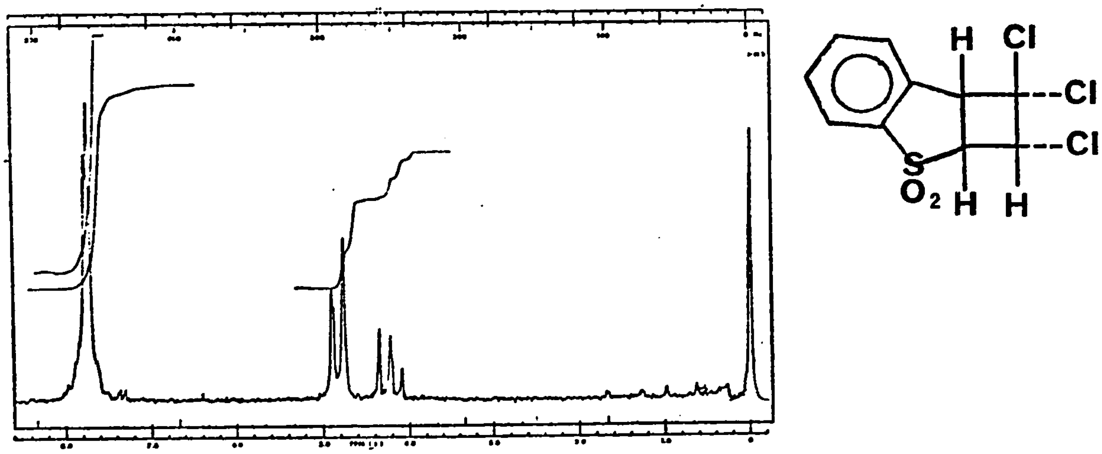
3,4,4-Trichloro-2,5-dihydrocyclobuta-[b]-thianaphthene-1,1-dioxide (206a)



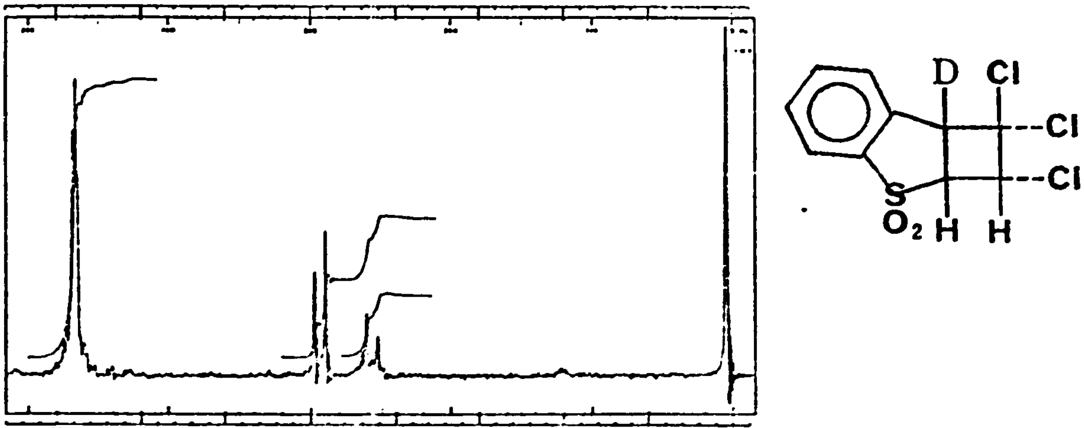


Nuclear Magnetic Resonance Spectra

3,4,4-Trichloro-2,5-dihydrocyclobuta-[b]-thianaphthene-1,1-dioxide (206a)



3,4,4-Trichloro-5-deutero-2-hydrocyclobuta-[b]-thianaphthene-1,1-dioxide (206b)



The Mass Spectrum of Compound 206a

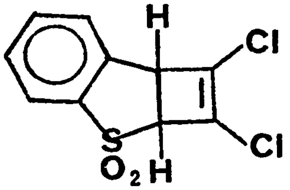
m/e	% Abundance	m/e	% Abundance	m/e	% Abundance
50	9.0	97	1.4	134	3.5
51	9.0	98	3.5	135	2.1
52	2.1	99	5.0	136	11.9
		100	2.1	137	100.0
61	2.5	101	4.3	138	11.9
62	4.5	102	2.9	139	4.2
63	13.6				
		109	2.1	161	7.7
65	3.0	110	15.0	162	16.1
		111	2.9	163	4.2
68	1.4	112	2.1	164	4.9
69	2.1				
		114	1.4	166	84.0
73	2.1	115	7.7	167	9.1
74	6.9	116	0.7	168	5.6
75	9.3				
76	5.0	118	10.0	196	1.8
77	6.4			197	2.1
78	2.1	121	2.9		
		122	1.4	261	2.9
80	2.1	123	1.4		
81	3.5			263	1.4
		125	8.0		
84	0.7	126	11.4	296	4.9
85	2.9	127	10.7	297	4.9
86	2.9	128	1.4	298	1.4
87	2.9				
		130	2.1		
89	4.3				
90	2.1	132	2.1		
91	0.7				

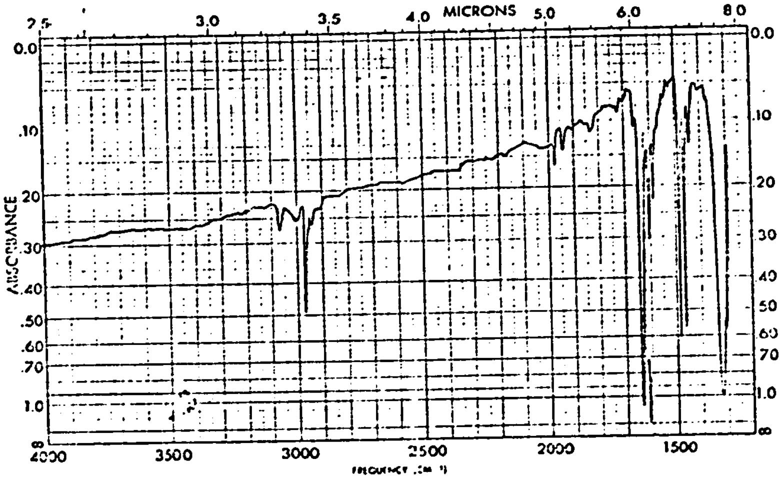
The Mass Spectrum of Compound 206b

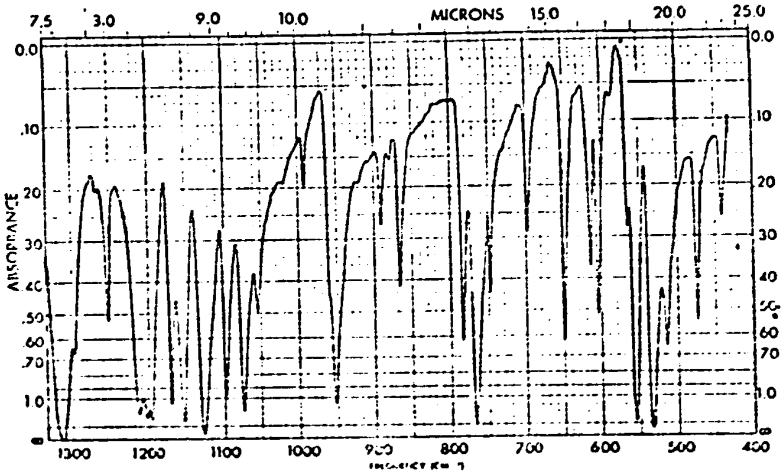
m/e	% Abundance	m/e	% Abundance
50	7.8	129	3.6
51	8.4	130	3.6
52	4.2		
		132	4.2
60	0.6	133	2.4
61	1.8		
62	4.2	135	4.8
63	9.0	136	6.0
		137	36.0
69	2.4	138	98.2
70	18.0	139	7.8
		140	7.2
90	1.2		
		161	3.6
97	2.4	162	4.8
98	6.0	163	12.0
99	2.4	164	4.8
100	2.4	165	4.8
101	3.0	166	30.0
102	2.4	167	100.0
103	1.8	168	16.2
		169	6.0
108	1.2		
109	6.0	192	2.4
110	13.2	193	3.0
111	6.0		
112	1.8	251	0.6
		252	2.4
119	10.0	253	0.6
120	1.2	254	1.8
121	1.8		
122	2.4	296	0.6
		297	3.6
126	6.0	298	1.2
127	12.0	299	4.2
128	12.0	300	0.6
		301	1.2

Infrared Spectrum

3,4-Dichloro-2,5-dihydrocyclo-3-butena-[b]-thianaphthene-1,1-dioxide (212)

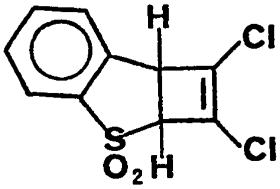


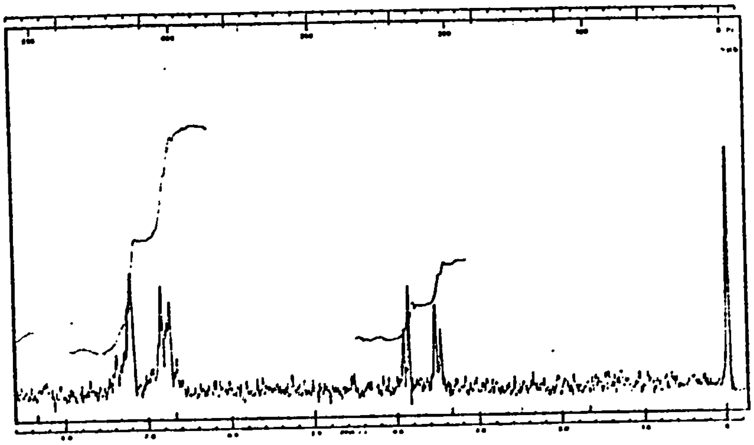




Nuclear Magnetic Resonance Spectrum

3,4-Dichloro-2,5-dihydrocyclo-3-butena-[b]-thianaphthene-1,1-dioxide (212)

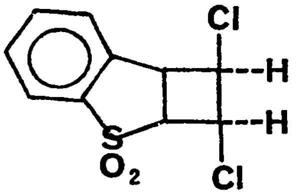


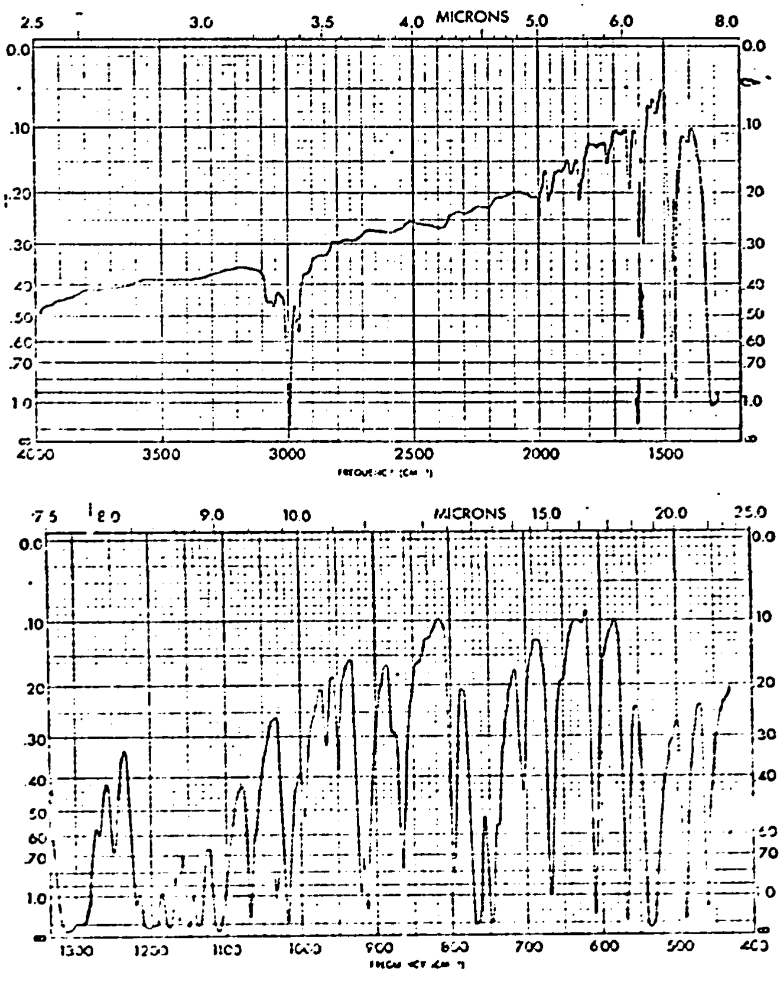


(C_6D_6)

Infrared Spectrum

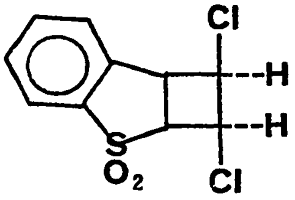
cis-3,4-Dichloro-2,5-dihydrocyclobuta-[b]-thianaphthene-1,1-dioxide (207)

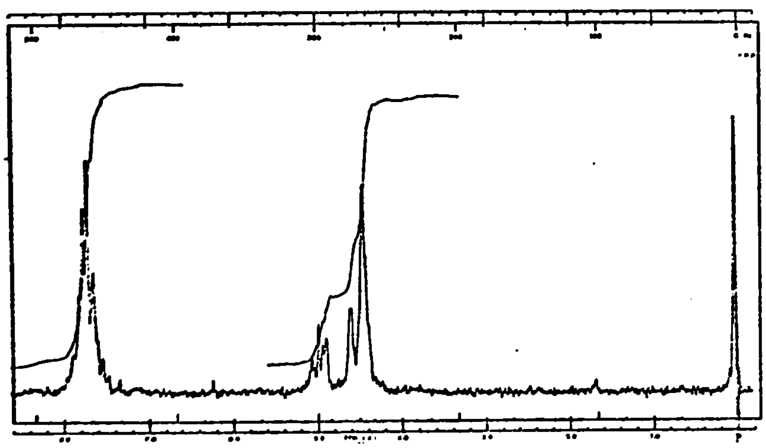




Nuclear Magnetic Resonance Spectrum

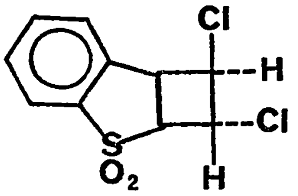
cis-3,4-Dichloro-2,5-dihydrocyclobuta-[b]-thianaphthene-1,1-dioxide (207)

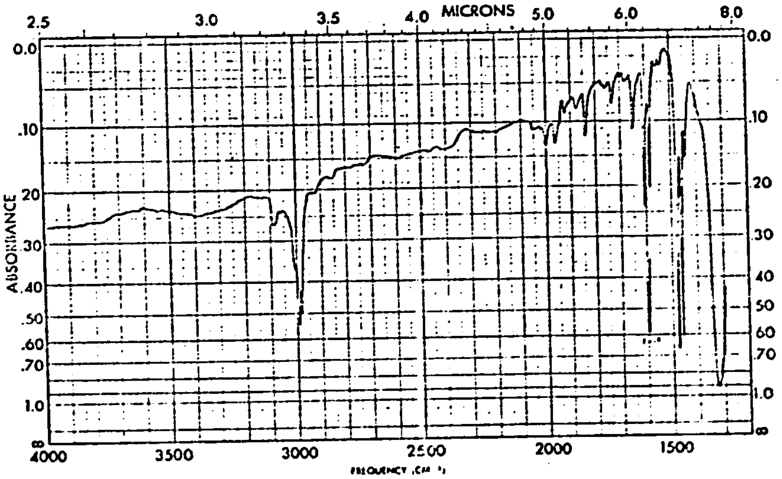


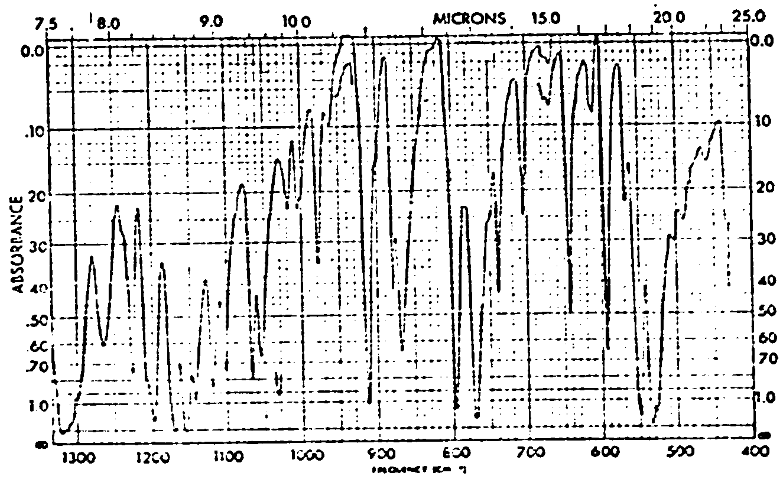


Infrared Spectrum

trans-3,4-Dichloro-2,5-dihydrocyclobuta-[b]-thianaphthene-1,1-dioxide (208)

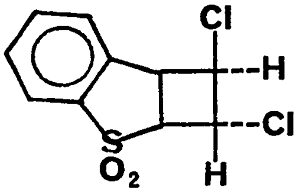


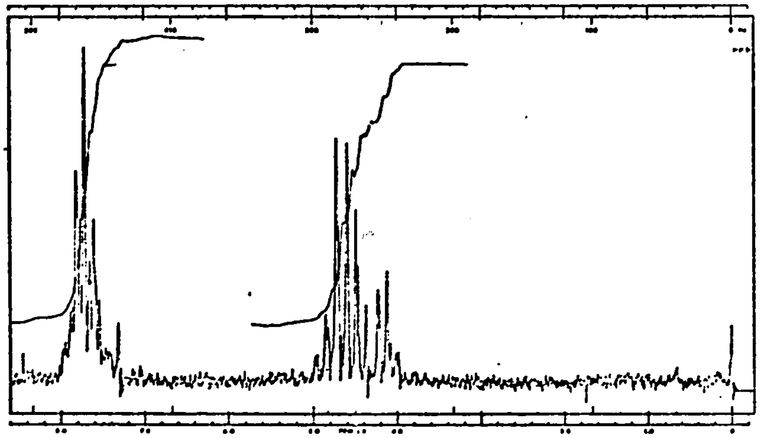




Nuclear Magnetic Resonance Spectrum

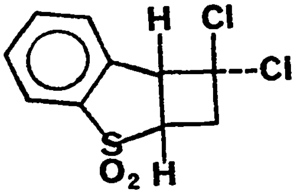
trans-3,4-Dichloro-2,5-dihydrocyclobuta-[b]-thianaphthene-1,1-dioxide (208)

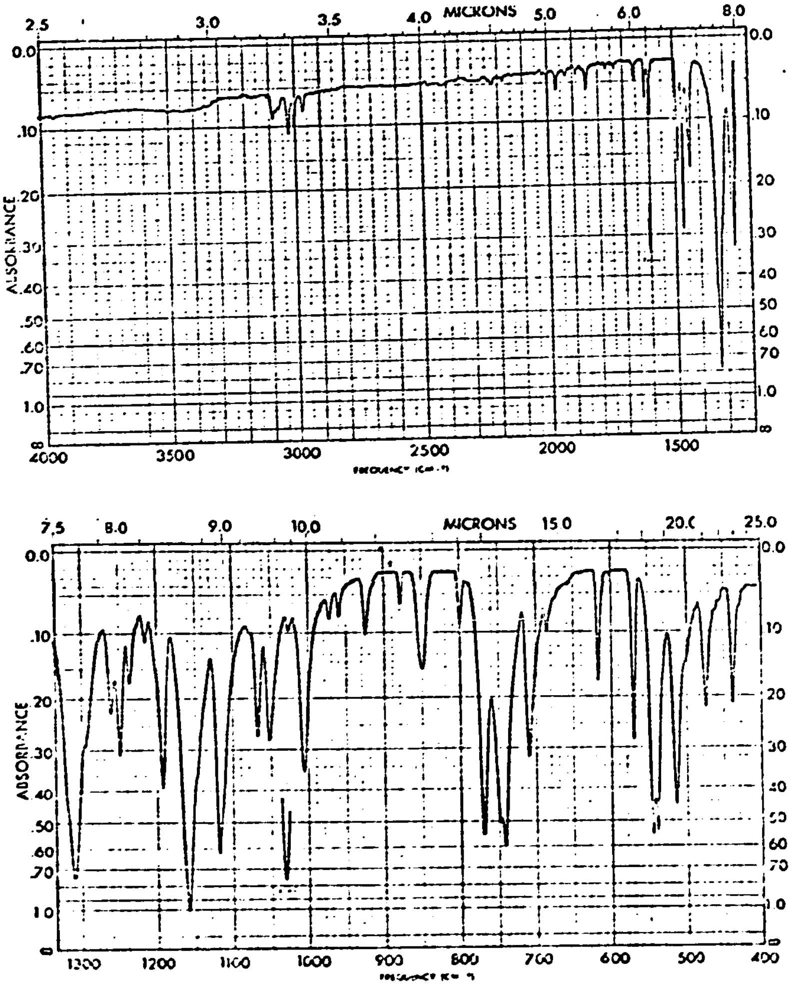




Infrared Spectrum

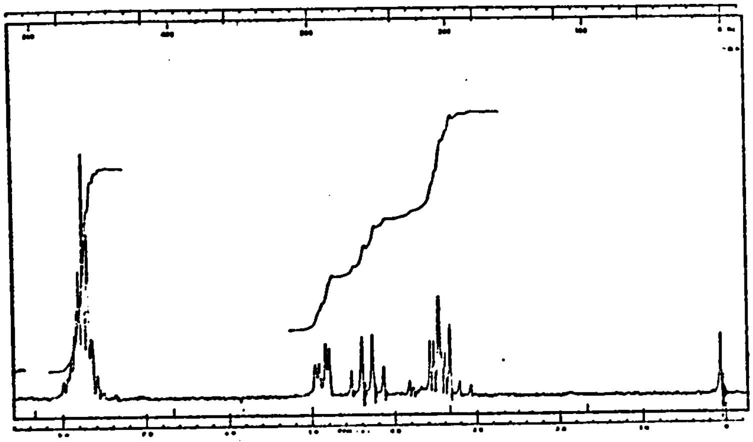
4,4-Dichloro-2,5-dihydrocyclobuta-[b]-thianaphthene-1,1-dioxide (209a)

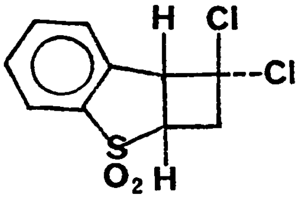




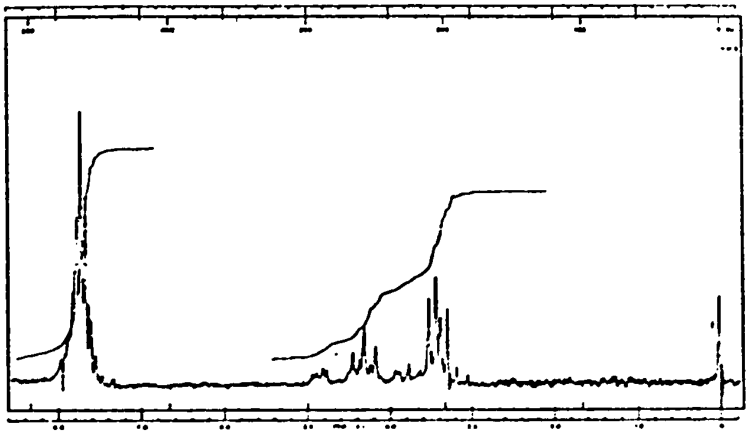
Nuclear Magnetic Resonance Spectra

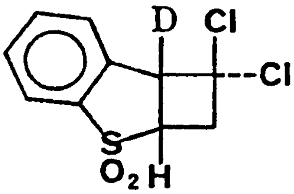
4,4-Dichloro-2,5-dihydrocyclobuta-[b]-thianaphthene-1,1-dioxide (209a)





4,4-Dichloro-5-deutero-2-hydrocyclobuta-[b]-thianaphthene-1,1-dioxide (209b)





The Mass Spectrum of Compound <u>209a</u>

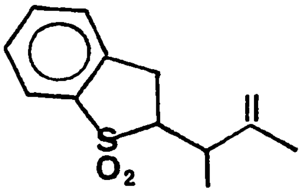
m/e	% Abundance	m/e	% Abundance
39	8.3	118	10.4
50	16.2	127	3.4
51	11.7	128	6.2
52	2.1	129	5.5
		130	1.4
63	11.7		
64	1.4	134	1.4
65	2.1	135	0.7
66	0.7	136	1.4
		137	100.0
73	2.1	138	6.9
74	4.1	139	3.4
75	5.5		
76	4.1	147	0.7
77	4.1		
78	1.4	149	0.7
81	2.1	153	6.9
84	0.7	162	2.1
85	1.4	163	1.4
86	1.4	164	1.4
87	0.7	165	0.7
		166	31.0
89	2.8	167	2.8
90	2.1	168	1.4
91	0.7		
		181	2.1
100	0.7	182	0.5
101	3.4	183	0.7
102	4.1		
		227	0.7
108	0.7		
109	11.0	262	4.8
110	2.1		
111	1.4	264	2.1

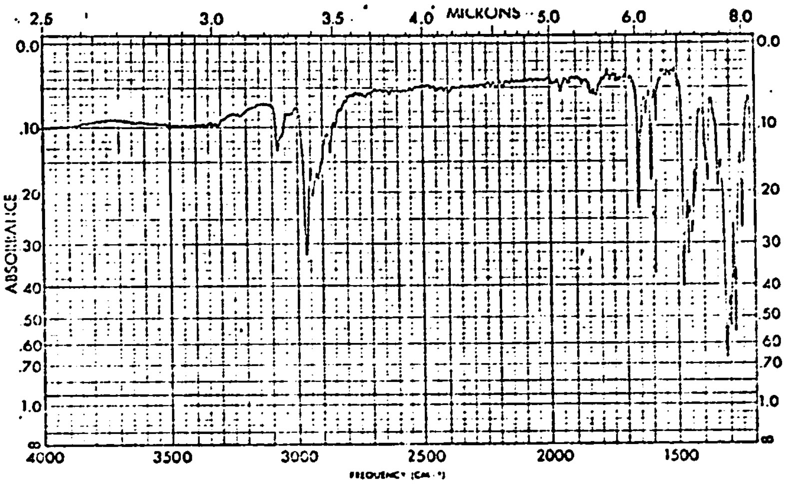
The Mass Spectrum of Compound <u>209b</u>

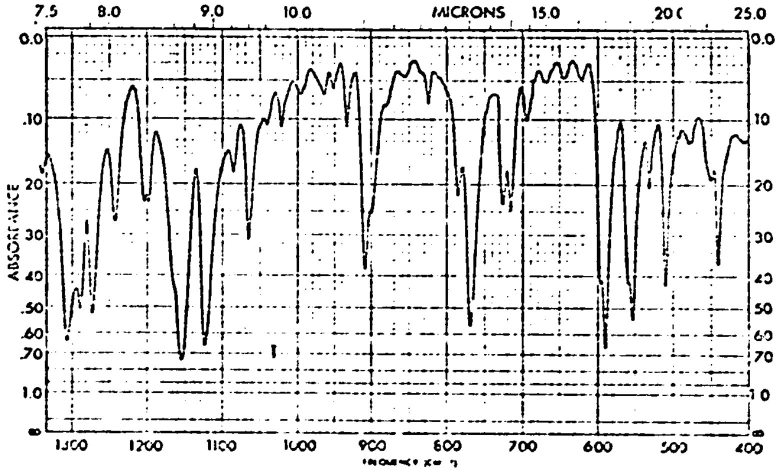
m/e	% Abundance	m/e	% Abundance
39	5.6	118	7.5
		119	10.6
50	7.5		
51	9.3	127	7.5
52	5.6	128	11.2
		129	10.0
61	3.1	130	1.2
62	3.1		
63	8.1	137	34.5
64	6.2	138	100.0
65	2.5	139	13.5
66	2.5	140	6.2
73	1.2	147	2.5
74	5.0	148	1.2
75	6.2	149	1.2
76	6.2	150	0.6
77	3.8		
78	3.8	162	1.9
79	1.2	163	5.0
		164	3.8
81	0.6	165	1.2
82	0.6	166	16.0
83	6.2	167	47.5
84	0.6	168	6.2
85	4.4	169	3.8
86	1.2		
87	2.5	181	1.8
88	1.2	182	2.5
89	1.9	183	0.7
90	3.8	184	0.6
91	3.1		
		227	1.9
100	1.2		
101	2.5	262	0.6
102	3.8	263	5.0
103	3.8	264	1.2
104	1.9	265	3.8
109	7.5		
110	16.2		
111	3.8		
112	1.9		

Infrared Spectrum

2(1,2-Dimethyl-2-propenyl)-2,3-dihydrothianaphthene-1,1-dioxide (210a)

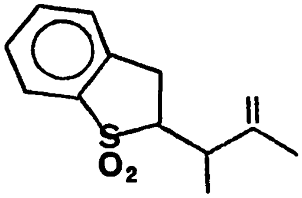


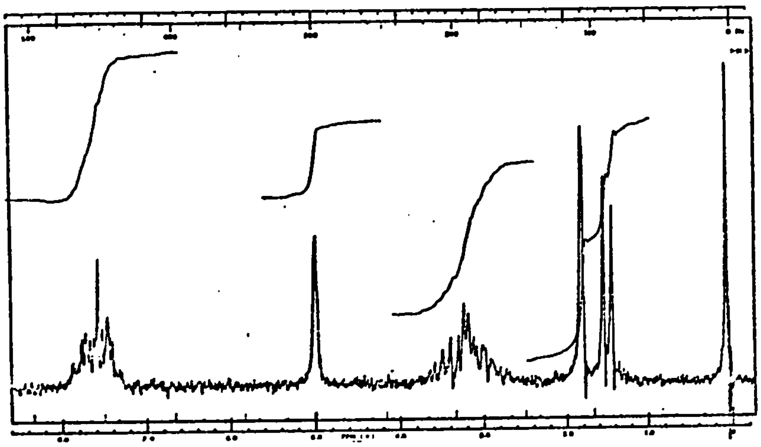




Nuclear Magnetic Resonance Spectrum

2(1,2-Dimethyl-2-propenyl)-2,3-dihydrothianaphthene-1,1-dioxide (210a)





The Mass Spectrum of Compound <u>210a</u>

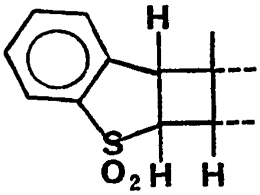
m/e	% Abundance	m/e	% Abundance	m/e	% Abundance
39	17.4	89	5.2	151	2.6
40	2.6	90	2.6	152	5.2
41	28.6	91	13.0	153	13.0
42	10.4	92	2.1	154	2.6
43	7.8			155	7.0
44	2.2	102	2.6	156	7.8
45	2.2	103	5.2	157	44.2
		104	2.6	158	5.6
50	2.6				
51	6.5	109	2.6	165	7.8
52	2.6	110	2.1	166	2.6
53	6.5	111	5.2	167	26.0
54	2.6			168	7.8
55	15.6	115	15.6	169	2.0
56	2.6	116	7.8		
57	9.1	117	2.6	171	5.2
58	2.1			172	5.2
59	2.6	127	5.2		
		128	18.2	174	2.6
63	4.4	129	27.2		
64	2.1	130	10.4	184	2.6
65	7.8	131	7.8	185	2.6
				186	7.8
67	5.0	134	10.4		
68	2.1	135	7.8	193	5.2
69	13.0	136	2.6	194	2.6
70	100.0	137	23.4		
71	7.8	138	10.4	201	7.8
				202	2.6
76	2.1	140	10.4	203	2.6
77	10.4	141	5.2		
78	3.9	142	15.6	219	2.6
79	3.9	143	31.2		
		144	36.4	236	31.2
81	5.2	145	2.6	237	5.2
82	2.3			238	2.6
83	8.0				
84	2.3				
85	2.3				

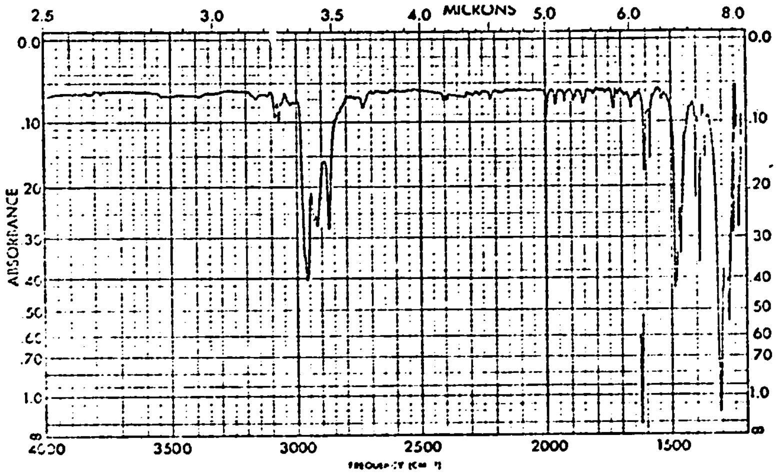
The Mass Spectrum of Compound <u>210b</u>

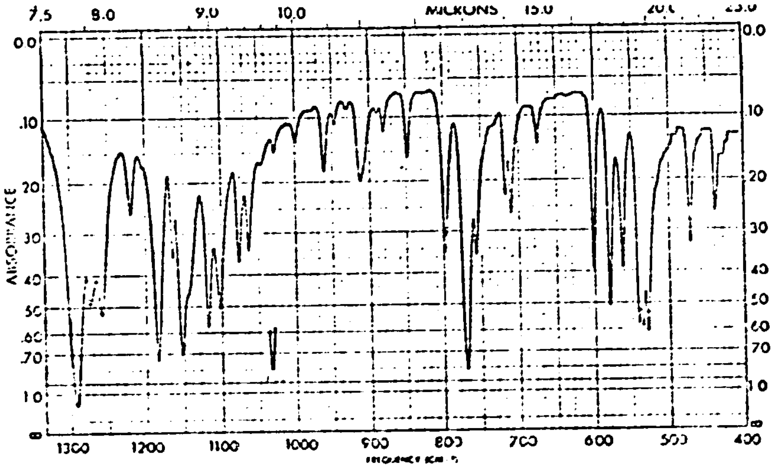
m/e	% Abundance	m/e	% Abundance	m/e	% Abundance
39	7.6	89	2.3	154	2.9
40	4.2	90	3.6	155	2.9
41	16.8	91	6.3	156	2.9
42	4.4	92	6.8	157	6.8
43	5.9			158	18.5
44	1.0	102	1.4	159	3.2
45	1.7	103	2.7		
		104	4.5	161	1.4
50	4.2	105	2.3	162	2.3
51	8.4				
52	4.2	109	2.3	167	4.5
53	8.4	110	2.3	168	14.4
54	1.3			169	4.5
55	11.3	115	5.4		
56	1.7	116	8.6	172	3.2
57	4.2	117	3.4	173	3.2
58	1.0	118	1.7		
59	1.1			175	2.3
		127	2.3	176	3.2
63	2.9	128	7.2		
64	2.5	129	14.4	185	1.0
65	2.9	130	17.6	186	2.3
66	2.5	131	5.4	187	1.3
67	2.5	132	4.5	188	1.0
69	12.6	135	4.0	194	1.0
70	100.0	136	4.0	195	1.8
71	6.7	137	5.4		
		138	6.8	201	2.7
76	2.1	139	3.2	202	2.7
77	5.9	140	2.5	203	1.3
78	5.9	141	2.5		
79	3.4	142	6.8	219	2.3
		143	9.0		
81	3.1	144	7.2	236	3.2
				237	20.7
83	5.9	152	3.4	238	3.4
84	4.5	153	4.5		

Infrared Spectrum

3,4,4-Trimethyl-2,5-dihydrocyclobuta-[b]-thianaphthene-1,1-dioxide (211a)

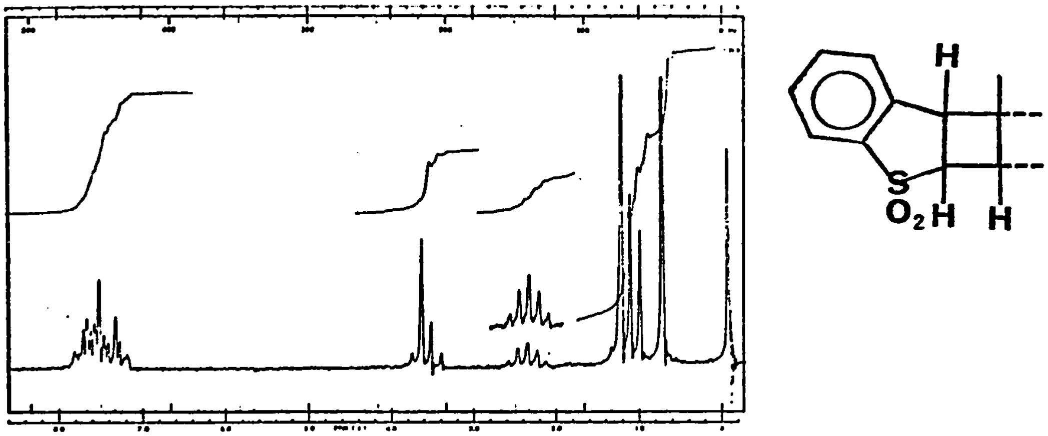




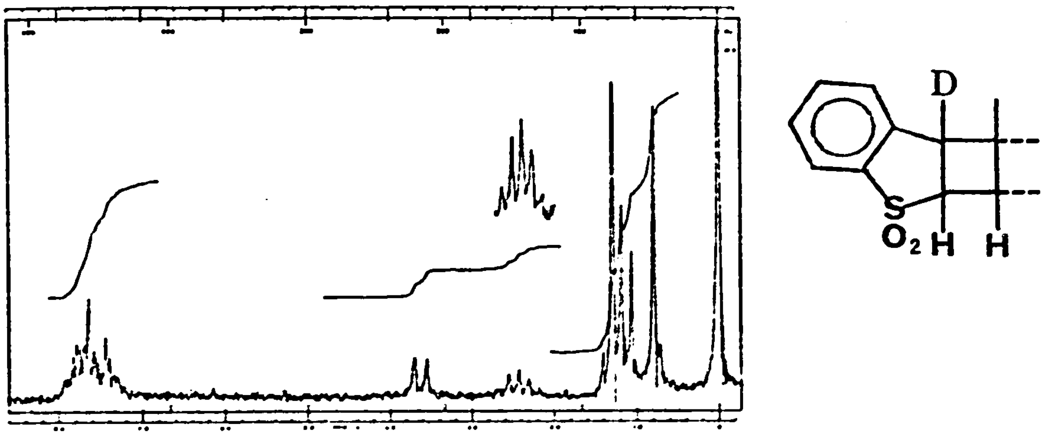


Nuclear Magnetic Resonance Spectra

3,4,4-Trimethyl-2,5-dihydrocyclobuta-[b]-thianaphthene-1,1-dioxide (211a)



3,4,4-Trimethyl-5-deutero-2-hydrocyclobuta-[b]-thianaphthene-1,1-dioxide (211b)



The Mass Spectrum of Compound <u>211a</u>

m/e	% Abundance	m/e	% Abundance	m/e	% Abundance
39	11.0	89	5.0	152	2.8
40	1.6	90	3.3	153	6.6
41	22.0	91	11.0	154	1.6
42	3.8			155	2.2
43	3.8	96	1.1	156	3.3
44	1.1			157	20.4
45	1.6	98	2.2	158	3.9
50	2.2	102	2.2	167	14.3
51	5.0	103	4.4	168	4.4
52	1.6	104	2.8	169	1.1
53	5.0			170	0.6
		115	6.8	171	3.3
55	9.9	116	5.5	172	3.3
		117	2.8		
57	2.2			201	3.9
		127	3.3	202	0.6
69	13.8	128	11.0	203	0.6
70	100.0	129	18.2		
71	6.6	130	5.5	219	2.2
		131	3.3	220	0.6
76	2.2			221	0.6
77	8.2	134	2.2		
78	3.9	135	2.8	236	20.9
79	3.9	136	0.6	237	4.4
		137	9.4	238	1.6
81	3.3	138	4.4		
		139	3.3		
83	9.9				
84	1.6	151	2.2		

The Mass Spectrum of Compound <u>211b</u>

m/e	% Abundance	m/e	% Abundance	m/e	% Abundance
39	5.5	89	0.6	140	1.0
40	1.6	90	1.1	141	1.1
41	8.2	91	2.4		
42	9.9	92	2.1	152	1.6
43	2.2			153	2.8
44	0.6	102	0.6	154	1.1
45	0.6	103	1.6	155	1.1
		104	3.3	156	1.1
50	1.6	105	1.0	157	3.3
51	2.8			158	7.7
52	1.6	115	2.8	159	1.6
53	2.2	116	5.5		
54	1.1	117	1.1	167	4.4
55	24.8	118	0.6	168	19.3
56	1.6	119	0.6	169	3.9
57	1.6			170	1.6
		121	0.6	171	1.1
69	5.0	122	1.0	172	1.1
70	100.0	123	0.6	173	1.6
71	7.7				
		127	1.1	186	0.6
75	0.6	128	2.8		
76	1.1	129	6.0	201	1.1
77	3.3	130	7.2	202	0.6
78	2.8	131	2.2		
				219	0.6
83	4.4	134	0.6	220	1.2
84	1.6	135	1.6	221	0.6
85	1.1	136	1.1		
		137	1.6	236	1.6
		138	3.9	237	13.2
		139	1.1	238	2.2
				239	0.6

APPENDIX B

Sample Calculation

Quantum Yield of the Photodimerization of Thianaphthene-1,1-dioxide (3.67×10^{-2} M) Sensitized by Benzophenone (1.99×10^{-2} M).

	ABSORBANCE			
Actinometer	1	2	3	4
Before irradiation	1.26	1.26	1.26	1.26
After irradiation	1.19	1.20	1.19	1.19
Decrease in Absorbance	0.07	0.06	0.07	0.07
Moles of actinometer reacted ($\times 10^3$)	5.15	4.41	5.15	5.15

Thianaphthene-1,1-dioxide	1	2	3	4
Before irradiaton	1.01	1.01	1.01	1.01
After irradiation	0.79	0.79	0.77	0.79
Decrease in Absorbance	0.22	0.22	0.22	0.22
Moles of Thianaphthene-1,1-dioxide reacted ($\times 10^3$)	7.72	7.72	8.40	7.72
Q_{TND}	1.03	1.03	1.08	1.03

$$Q_{TND} = \frac{\text{moles of thianaphthene-1,1-dioxide reacted}}{\text{moles of actinometer reacted}} \times Q_{act}$$

Q_{TND} (Mean) = 1.03 ± 0.01

$Q_{DIM} = Q_{TND}/2 = 0.56 \pm 0.01$.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Trecker, D.J., Organic Photochemistry, Vol. 2 (O.L. Chapman, ed.), Dekker, New York, (1969), p. 63.

2. Scharf, D. and Korte, F., Tetrahedron Letters, 1963, 821.

3. Arnold, D.R., Trecker, D.J. and Whipple, E.B., J. Am. Chem. Soc., 87, 2596 (1965).

4. Trecker, D.J., Henry J.P. and McKeon, J.E., J. Am. Chem. Soc., 87, 3261 (1965).

5. Trecker, D.J., Foote, R.S., Henry, J.P. and McKeon, J.E., J. Am. Chem. Soc., 88, 3021 (1966).

6. Trecker, D.J., Organic Photochemistry, Vol. 2 (O.L. Chapman, ed.), Dekker, New York, (1969), p. 67.

7. Srinivasan, R. and Hill, K.A., J. Am. Chem. Soc., 88, 3765 (1966).

8. Stechl, H.H., Ber. 97, 2681 (1964).

9. Scharf, H.D. and Korte, F., Ber., 97, 2425 (1964).

10. Hartmann, W. and Steinmetz, R., Ber., 100, 217 (1967).

11. Arnold, D.R. and Abraitys, V.Y., Chem. Comm., 1967, 1053.

12. Turro, N.J. and Hammond, G.S., J. Am. Chem. Soc., 84, 2841 (1962).

13. Baldwin, J.E. and Nelson, J.P., J. Org. Chem., 31, 336 (1966).

14. Schenk, G.O., Kuhls, J. and Krauch, C.H., Z. Naturforsch, 20b, 635 (1965).

15. Mannsfeld, S.P., Doctoral Dissertation, Univ. of Gottingen, 1963.

16. Eaton, P.E., J. Am. Chem. Soc., 84, 2344 (1962); 2454 (1962).

17. Eaton, P.E. and Hurt, W.S., J. Am. Chem. Soc., 88, 5038 (1966).

18. Ruhlen, J.L. and Leermakers, P.A., J. Am. Chem. Soc., 88, 5672 (1968); 89, 4944 (1967).

19. Lam, E.Y., Valentine, D., and Hammond, G.S., J. Am. Chem. Soc., 89, 3482 (1967).

20. Ziffer, H. and Mathews, B.W., Chem. Comm., 1970, 294.

21. Ziffer, H., Sharpless, N.E. and Kan, R.O., Tetrahedron, 22, 3011 (1966).

22. Trecker, D.J., Griswold, A.A. and Chapman, O.L., 152nd National Meeting of American Chemical Society, New York, Sept. 1966.

23. Chapman, O.L., 20th National Organic Chemistry Symposium, Burlington, Vt., June 1967.

24. Chapman, O.L.· Nelson, P.J., King, R.W., Trecker, D.J. and Griswold, A.A., Rec. Chem. Progress, 28, 167 (1967).

25. Mukai, T., Oine, T. and Sukawa, H., Chem. Comm., 1970, 271.

26. Chapman, O.L., Smith, H.G. and King, R.W., J. Am. Chem. Soc., 85, 803 (1963); 85, 806 (1963).

27. Mukai, T. and Shishido, T., J. Org. Chem., 32, 2744 (1967).

28. Stobbe, H. and Bremer, K., J. Prakt. Chem., 123, 1 (1929).

29. Sugayama, N., Yamada, K., Watari, Y. and Koyama, T., Nippon Kagaku Zasshi, 87, 737 (1966).

30. Cookson, R.C., Cox, D.A. and Hudec, J., J. Chem. Soc., 1961, 4499.

31. Bryce-Smith, D. and Gilbert, A., J. Chem Soc., 1964, 2428.

32. Cookson, R.C. and Nudec, J., Proc. Chem. Soc., 1959, 11.

33. Guia, M. and Civera, M., Gazz. Chim. Ital., 81, 875 (1951); Chem. Abstr. 47, 4335f (1951).

34. Yates, P. and Jorgenson, M.J., J. Am. Chem. Soc., 80, 6150 (1958), 85, 2956 (1963).

35. Rubin, M.B., Hipps, G.E. and Glover, D., J. Org. Chem., 29, 68 (1964).

36. Throndson, H.C., Cainelli, G., Arigoni, D. and Jeger, O., Helv. Chim. Acta, 45, 2342 (1962).

37. Stobbe, H. and Farber, E., Ber., 58, 1548 (1925).

38. Corse, J., Finkle, B.J. and Lundin, R.E., Tetrahedron Letters, 1961, 1.

39. Mukai, T., Tezuka, T. and Akasaki, Y., J. Am. Chem. Soc., 88, 5025 (1966).

40a. Kende, A.S. and Lancaster, J.E., J. Am. Chem. Soc., 89, 5283 (1967).

b. Tezuka, T., Akasaki, Y. and Mukai, T., Tetrahedron Letters, 1967, 1397.

41. Mustafa, A., Kamel, M. and Allam, M.A., J. Org. Chem., 22, 888 (1957).

42. Anet, R., Can. J. Chem., 40, 1249 (1962).

43. Hammond, G.S., Stout, C.A. and Lamola, A.A., J. Am. Chem. Soc., 86, 3103 (1964).

44. Morrison, H., Curtis, H. and McDowell, T., J. Am. Chem. Soc., 88, 5415 (1966).

45. Krauch, C.H., Farid, S. and Schenk, G.O., Ber., 99, 625 (1966).

46. de Mayo, P. and Yip, R.W.. Proc. Chem. Soc., 1964, 84.

47. Taylor, E.C. and Paudler, W.W., Tetrahedron Letters, 1960, 1.

48. Buchardt, O., Acta. Chem. Scand., 17 1461 (1963); 18, 1389 (1964).

49. Elliott, I.W., J. Org. Chem., 29, 305 (1964).

50. Fahr, E., Furst, G., Dorhofer, G. and Popp, H., Angew. Chem. Intern. Ed. Engl., 6, 250 (1967).

51. Blackburn, G.M. and Davies, R.J.H., Chem. Comm., 1965, 215; J. Am. Chem. Soc., 89, 5941 (1967).

52. Anet. R., Tetrahedron Letters, 1965, 3713.

53. Blackburn, G.M. and Davies, R.J.H., J. Chem. Soc., C1966, 1342; C1966, 2239.

54. Mantione, M.J. and Pullman, B., Biochim. Biophys. Acta, 91, 387 (1964).

55. Ruber, C.N., Ber., 35, 2415 (1902).

56. Stoermer, R. and Laage, E., Ber., 54, 77 (1922).

57. Stobbe, H. and Steinberger, F.K., Ber., 55, 2225 (1922).

58. Bernstein, H.I. and Quimby, W.C., J. Am. Chem. Soc., 65, 1845 (1943).

59a. Cohen, M.D. and Schmidt, G.M.J., J. Chem. Soc., 1964, 1996;

b. Cohen, M.D., Schmidt, G.M.J. and Sonntag, F.I., J. Chem. Soc., 1964, 2000.

60. Schmidt, G.M.J., J. Chem. Soc., 1964, 2014.

61. Bregman, J., Osaki, K., Schmidt, G.M.J. and Sonntag, F.I., J. Chem. Soc., 1964, 2021.

62. Rennert, J. Ruggiero, E.M. and Rapp, J., Photochem. Photobiol., 6, 29 (1967).

63. Filippakis, S.E. and Schmidt, G.M.J., J. Chem. Soc., B1967, 229.

64. Block, S., Filippakis, S.E. and Schmidt, G.M.J., J. Chem. Soc., B1967, 233

65. Lahav, M. and Schmidt, G.M.J., J. Chem. Soc., B1967, 239.

66. Griffin, G.W., Vellturo, A.F. and Furukawa, K., J. Am. Chem. Soc., 83, 2725 (1961).

67. Griffin, G.W., U.S. Pat. 3,139,395 (to American Cyanamid), 1964; Chem. Abstr. 61, 6937b (1964).

68. Griffin, G.W., U.S. Pat. 3,203,886 (to American Cyanamid), 1965; Chem. Abstr. 64, 613h (1966).

69. Schenk, G.O., Hartmann, W., Mannsfeld, S.R., Metzner, W. and Krauch, C.H., Ber., 95, 1642 (1962).

70. Bryce-Smith, D., Bullen, G.J., Clark, N.H., Connett, B.E. and Gilbert, A., J. Chem. Soc., C1966, 167.

71. Coulson, C.A., Orgel, L.E., Taylor, W. and Weiss, J., J. Chem. Soc., 1955, 2961.

72. Clar, E., Ber., 65, 503 (1932).

73. Schönberg, A., Trans. Faraday Soc., 32, 514 (1936).

74. Greene, F.D., Misrock, S.L. and Wolfe Jr., J.R., J. Am. Chem Soc., 77, 3852 (1955).

75. Applequist, D.E., Little, R.L., Friedrich, E.C. and Wall, R.E., J. Am. Chem. Soc., 81, 452 (1959).

76. Dziewonski, K. and Paschalski, C., Ber., 46, 1986 (1913).

77. Bowen, E.J. and Marsh, J.D.F., J. Chem. Soc., 1947, 109.

78. Schenk, G.O. and Walgast, R., Naturwiss., 48, 737 (1961); 49, 36 (1962).

79. Schönberg, A., Södtke, U. and Praefcke, K., Tetrahedron letters, 1968, 3669.

80. Not assigned.

81. Anastassiou, A.G. and Griffin, G.W., J. Org. Chem., 33, 3441 (1968).

82. Bowyer, J. and Porter, Q.N., Aust. J. Chem., 19, 1455 (1966).

83. McCullough, J.J., Can. J. Chem., 46, 43 (1968).

84. Krauch, C.H., Metzner, W. and Schenk, G.O., Ber., 99, 1723 (1966).

85. Bauman, R.P., "Absorption Spectroscopy", John Wiley & Sons, Inc., New York, N.Y.,(1962),p. 462.

86. Ziffer, H. and Levin, I.W., J. Org. Chem. 34, 4056 (1969).

87. Fleming, I. and Williams, D.H., Tetrahedron, 23, 2747 (1967).

88. Not assigned.

89. Paolillo, L., Ziffer, H. and Buchardt, O., J. Org. Chem., 35, 38 (1970).

90. Field, F.H., Acc. of Chem. Res., 1, 48 (1968).

91. Ziffer, H., Fales, H.M., Milne, G.W.A. and Field, F.H. J. Am. Chem. Soc., 92, 1597 (1970).

92. Wagner, P.J. and Buchek, D.J., J. Am. Chem. Soc., 91, 5090 (1969).

93. Livingston, R. and Wei, K.S., J. Phys. Chem., 71, 541 (1967).

94. Davies, W. and James, F.C., J. Chem. Soc., 1955, 314

95a. Mustafa, A., Nature, 175, 992 (1955).

b. Mustafa, A. and Zayed, S.M.A.D., J. Am. Chem. Soc., 78, 6174 (1956).

96. Corey, E.J., Bass, J.D., Le Mahieu, R. and Mitra, R.B., J. Am. Chem. Soc., 86, 5570 (1967).

97. Dodson, R.M. and Zielske, A.G., J. Org. Chem., 32, 28 (1967).

98. Fletcher, Jr., H.G. and Richtmyer, N.K., Adv. Carbohydrate Chem. 5, 1 (1950).

99. Bonner, W.A. and Kahn, J.E., J. Am. Chem. Soc., 73, 2241 (1951).

100. Mozingo, R., Wolf, D.E., Harris, S.A. and Folkers, K., J. Am. Chem. Soc., 65. 1013 (1943).

101. Chatterjee, R., Cook, A.H., Heilbron, I. and Levy, A.L., J. Chem. Soc., 1948, 1337.

102. Fonken, G. and Mozingo, R., J. Am. Chem. Soc., 69, 1212 (1947).

103. Birch, S.F. and Dean, R.A., Ann. 585, 234 (1954).

104. Birch, S.F., Dean, R.A. and Whitehead, E.V., J. Org. Chem., 19, 1449 (1954).

105. Hussey, A.S., Liao, H.P. and Baker, R.H., J. Am. Chem. Soc., 75, 4727 (1953).

106. Stork, G., van Tamelen, E.E., Friedman, L.J. and Burgstathler, A.W., J. Am. Chem. Soc., 75, 384 (1953).

107. Ford, J.F., Pitkethly, R.C. and Young, V.O., Tetrahedron, 4, 325 (1958).

108. Weitkamp, A.W., J. Am. Chem. Soc., 81, 3434 (1959).

109. Wiberg, K.B. and Lampman, G.M. J. Am. Chem. Soc., 88, 4429 (1966).

110. von E. Doering, W. and Coburn, J.F., Tetrahedron Letters, 1965, 991.

111. Griesbaum, K., Naegele, W. and Wanless, G.G., J. Am. Chem. Soc., 87, 3151 (1965).

112. Dodson, R.M. and Klose, G., Chem. & Ind., 1963, 450.

113. Trost, B.M., Schinski, W.L. and Mantz, I.B., J. Am. Chem. Soc., 91, 4320 (1969).

114. Conant, J.B. and Blatt, A.H., J. Am. Chem. Soc., 50, 555 (1928).

115. "Dictionary of Organic Compounds", Eyre & Spottiswoods, Ltd., London, 3, 1274 (1965).

116. Schaefer, J.P., J. Org. Chem., 25, 2027 (1960).

117. Budzikiewicz, H., Djerassi, C. and Williams, D.H., "Mass Spectrometry of Organic Compounds", Holden-Day Inc., New York,(1967),pp. 558-560.

118. Hammond, G.S., Saltiel, J., Lamola, A.A., Turro, N.J., Bradshaw, J.S., Cowan, D.O., Counsell, R.C., Vogt, V. and Dalton, C., J. Am. Chem. Soc., 86, 3197 (1964).

119. Turro, N.J., "Molecular Photochemistry", W.A. Benjamin, Inc., New York, (1965), p. 95.

120. Young, H.D., "Statistical Treatment of Experimental Data", McGraw-Hill Company Inc., New York, (1962).

121. Berson, J.A., Hamlet, Z. and Mueller, W.A., J. Am. Chem. Soc., 84, 297 (1962).

122. Moore, W.M. and Ketchum, M., J. Am. Chem. Soc., 84, 1368 (1962).

123. Ullman, E.F. and Henderson, W.A., J. Am. Chem. Soc., 88, 4942 (1966).

124. Evans, T.R., "Energy Transfer and Organic Photochemistry", (A.A. Lamola and N.J. Turro, editors), Interscience, New York, (1969), pp. 318-319.

125. Parker, C.A. and Goddart, A.P., Anal. Chim. Acta, 4, 517 (1950).

126. Dilling, W.L., Tabor, T.E., Boer, F.P. and North, P.P., J. Am. Chem. Soc., 92, 1399 (1970).

127. Eaton, P.E., Acc. Chem. Res., 1, 50 (1968).

128. Chapman, O.L., Koch, T.H., Klein, F., Nelson, P.J. and Brown, E.L., J. Am. Chem. Soc., 90, 1657 (1968).

129. Nelson, P.J., Ostram, D., Lassila, J.D. and Chapman, O.L., J. Org. Chem., 34, 811 (1969).

130. Cantrell, T.S., Haller, W.S. and Williams, J.C., J. Org. Chem., 34, 509 (1969).

131. Barltrop, J.A. and Robson, R., Tetrahedron Letters, 1963, 597.

132. de Mayo, P., Reid, S.T. and Yip, R.W., Can. J. Chem., 42, 2828 (1964).

133. Hara, M. Odaira, Y. and Tsutsumi, S., Tetrahedron, 22, 95 (1966).

134. Evanega, G.R. and Fabing, D.L., J. Org. Chem., 35, 1757 (1970).

135. Metzner, W., Tetrahedron Letters, 1968, 1321.

136. McCullough, J.J. and Huang, C.W., Can. J. Chem., 47, 757 (1969).

137. Neckers, D.C., Dopper, J.H. and Wynberg, H., J. Org. Chem., 35, 1582 (1970).

138. Corey, E.J. and Nozoe, S., J. Am. Chem. Soc., 86, 1652 (1964).

139. Corey, E.J., Mitra, R.B. and Uda, H., J. Am. Chem. Soc., 86, 485 (1964).

140. White, J.D. and Gupta, D.N., J. Am. Chem. Soc., 90, 6171 (1968).

141. Lange, G.L. and de Mayo, P., Chem. Comm. 1967, 704.

142. Bagli, J.F. and Bogri, T. Tetrahedron Letters, 1969, 1639.

143. Challand, B.D., Kornis, G., Lange, G.L. and de Mayo, P., Chem. Comm., 1967, 704.

144. Wiesner, K., Uyeo, S., Philipp, A. and Valenta, Z., Tetrahedron Letters, 1968, 6279.

145. Wiesner, K., Jirkovsky, I., Fishman, M. and Williams, C.A.J., Tetrahedron Letters, 1967, 1523.

146. Nozaki, M. Kurita, M., Mori, T., and Noyori, N., Tetrahedron, 24, 1821 (1968).

147. Hikino, H. and de Mayo, P., J. Am. Chem. Soc., 86, 3582 (1964).

148. Porter, G., "Reactivity of the Photoexcited Molecule", Proceedings of the Thirteenth Conference on Chemistry, Interscience, New York, (1967), p. 79.

149. Banwell, C.N., "Nuclear Magnetic Resonance for Organic Chemists", (D.W. Mathieson, ed.) Academic Press Inc., London, (1967), p. 85.

150. Gould, E.S., "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, (1959), p. 732.

151. von Komppa, G., J. Prakt. Chem., 622, 319 (1929).