ABSTRACT

REACTIONS OF IRON PENTACARBONYL WITH ORGANIC COMPOUNDS

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Department of Chemistry, Ph.D. Thesis

The iron-tricarbonyl complexes of some steroid dienes have been prepared by reaction of the diene with iron pentacarbonyl. Heteroannular dienes can be isomerized to homoannular dienes *via* diene-iron tricarbonyl complexes. A number of cross-conjugated dienone-iron tricarbonyl complexes have been synthesized. The spectral properties of the diene and dienone complexes are discussed. The behavior of iron pentacarbonyl towards various functional groups was investigated. N-Oxides, azoxy compounds, nitrones, nitroso and nitro compounds are deoxygenated by iron pentacarbonyl. Nitrosamines having at least one phenyl group afford secondary amines while non-aromatic nitrosamines give tetrasubstituted ureas. Iron pentacarbonyl treatment of oximes regenerates the corresponding carbonyl compounds. Primary amides and thionamides give nitriles. Thionbenzanilide, N-deuteriothionbenzanilide and benzanilide all form N-benzylideneaniline on reaction with the metal carbonyl. 1,1-Diphenyl-2-thiourea gives diphenylamine. Acid chlorides in butyl ether, tetrahydrofuran or 2-methyltetrahydrofuran react with iron pentacarbonyl to give the corresponding esters. Mechanisms are proposed for many of these reactions.

REACTIONS OF IRON PENTACARBONYL WITH ORGANIC COMPOUNDS

by

Howard Alper

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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To my wife

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INTRODUCTION

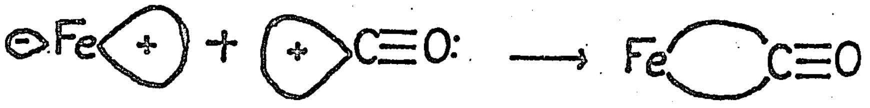
In 1891, Berthelot[1] and Mond and Quincke[2] found that reaction of metallic iron with carbon monoxide produced iron pentacarbonyl, a toxic yellow liquid having a melting point of -21°C and a boiling point of

$$Fe + 5CO \longrightarrow Fe(CO)_5$$

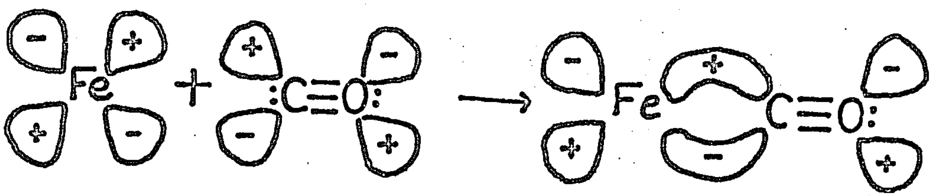
103°C.[3] It is diamagnetic and has a trigonal bipyramidal structure. Evidence for this structure comes from infrared[4] and Raman[5] spectra which show, in accordance with group theory predictions, two infrared active absorptions for terminal carbonyl groups at 2028 and 1994 cm^{-1} and three Raman active carbonyl stretching bands at 2114, 2031, and 1984 cm^{-1}. Further support for a trigonal bipyramidal structure for the metal carbonyl comes from the electron-diffraction studies of Evans and Lister[6] and from the X-ray analysis of Hanson.[7] The iron-carbon bond distance is 1.84 Å while the carbon-oxygen bond distance is 1.15 Å.[6]

The sigma bonds of iron in iron pentacarbonyl result from dsp^3 hybridization; the remaining d_{xz}, d_{yz}, d_{xy}, $d_{x^2-y^2}$ orbitals are involved in the metal π-bonding electron pairs. The bonding in the metal carbonyl can be visualized as follows: there is a dative overlap of the filled carbon sigma orbital (I) with an empty metal sigma orbital, and a dative overlap of a filled $d\pi$ or hybrid $dp\pi$ iron orbital with an empty antibonding $p\pi$

orbital of the carbonyl ligand (II). Thus, the drift of metal electrons into CO orbitals will tend to make the CO as a whole negative and hence increase its basicity. The acceptor strength of the π orbitals is at the same time enhanced by the drift of electrons to iron in the sigma



I



II

bond, tending to make the CO positive. As a result, the effects of sigma bond formation can strengthen the π bonding and vice versa.

The chemical properties of iron pentacarbonyl have been only slightly investigated. A review of its reactions with inorganic and various types of organic compounds follows. By itself, neat or in solution, iron pentacarbonyl is photolyzed with formation of diiron enneacarbonyl.[8]

$$2\,Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

I. REACTIONS WITH INORGANIC COMPOUNDS

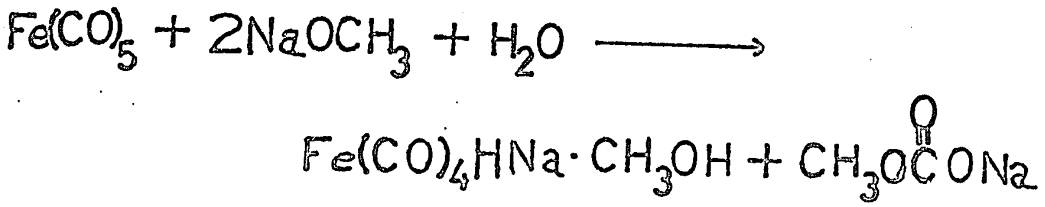
Reaction of iron pentacarbonyl with sodium hydroxide yields the metal carbonyl hydride, $HFe(CO)_4^-$. Treatment of this anion with oxidizing agents such as hydrogen peroxide, manganese (IV) oxide and potassium permanganate followed by acidification gives triiron dodecacarbonyl.[9] The latter carbonyl can also be

$$Fe(CO)_5 + 3OH^- \longrightarrow HFe(CO)_4^- + CO_3^{-2} + H_2O$$

$$3HFe(CO)_4^- + 3MnO_2 + 3H_2O \longrightarrow Fe_3(CO)_{12} + 3Mn^{+2} + 9OH^-$$

obtained by the action of triethylamine on iron pentacarbonyl followed by acidification.[10]

A metal carbonyl hydride can also be obtained by the action of sodium methoxide on iron pentacarbonyl followed by hydrolysis.[11]



$$Fe(CO)_5 + 2NaOCH_3 + H_2O \longrightarrow Fe(CO)_4HNa \cdot CH_3OH + CH_3O\overset{\overset{O}{\|}}{C}ONa$$

Hein and Pobloth[12] investigated the behavior of calcium and magnesium hydroxide towards iron pentacarbonyl and observed the formation of $\left[Fe(CO)_4H\right]_2M$ where M is either magnesium or calcium. The barium derivative has also been prepared in a similar manner.[11]

The dianion, $Fe(CO)_4^{-2}$, is obtained by reaction of the metal carbonyl with either sodium in liquid ammonia,[13]

$$Fe(CO)_5 + 2Na \xrightarrow{liq.\ NH_3} Na_2[Fe(CO)_4] + CO$$

with liquid ammonia at 20°C,[14]

$$Fe(CO)_5 + 4NH_3 \longrightarrow (NH_4)_2[Fe(CO)_4] + CO(NH_2)_2$$

or with alkali hydroxide.[15] The urea formed in the liquid ammonia

$$Fe(CO)_5 + 4OH^- \longrightarrow Fe(CO)_4^{-2} + CO_3^{-2} + 2H_2O$$

reaction can be accounted for by:

$$CO + 4NH_3 \longrightarrow CO(NH_2)_2 + 2NH_4^+ + 2e$$

Acidification of the dianion with hydrochloric acid produces iron tetracarbonyl dihydride, a very unstable compound which decomposes below -10°C.[15]

In the presence of hydroxylamine or pyridine,[16] iron pentacarbonyl and aqueous ammonia react to form $\left[\mathrm{Fe(NH_3)_6}\right]\left[\mathrm{Fe_2(CO)_8}\right]$.

Iron dicarbonyl dinitrosyl is formed by reaction of the metal carbonyl with nitrosyl chloride.[17] The nitrosyl compound

$$\mathrm{Fe(CO)_5 + 2NOCl \longrightarrow Fe(CO)_2(NO)_2}$$

may also be obtained by reaction of iron pentacarbonyl with sodium nitrite and sodium hydroxide in water (or potassium nitrite in absolute methanol) to form $\mathrm{Fe(CO)_3NO^-}$, followed by acidification of this anion with glacial acetic acid.[18]

$$\mathrm{Fe(CO)_5 + NaNO_2 + 2NaOH \xrightarrow{H_2O} [Fe(CO)_3NO]Na + CO\uparrow + Na_2CO_3 + H_2O}$$

$$\mathrm{Na[Fe(CO)_3NO] + NaNO_2 + 2CH_3COOH \longrightarrow Fe(CO)_2(NO)_2 + CO\uparrow + 2CH_3COONa + H_2O}$$

Iron pentacarbonyl does not react with sulfur chloride pentafluoride[19] but antimony trichloride[20] displaces two carbon monoxide ligands to form

$Fe(CO)_3\ (SbCl_3)_2$. Mercuric sulfate reacts with the metal carbonyl to form $Fe(CO)_4Hg$.[17]

Treatment of the metal carbonyl with sulfur trioxide[21] yields what is believed to be the pyrosulfato-complex, $(CO)_3Fe\ O(SO_3)_2$.

Hal~~ides~~ogens react with iron pentacarbonyl in ether to form iron tetracarbonyl dihalides.[22]

$$Fe(CO)_5 + Br_2 \xrightarrow{(C_2H_5)_2O} Fe(CO)_4Br_2 + CO$$

The substitution of CO groups in iron pentacarbonyl by phosphorus trifluoride has been studied by Clark.[23] Compounds of the series $Fe(PF_3)_n(CO)_{5-n}$ $(0 \leq n \leq 5)$ were obtained by treating the metal carbonyl with phosphorus trifluoride under various conditions. The yellow liquid compounds, $Fe(PF_3)_n(CO)_{5-n}(0 \leq n \leq 4)$, are obtained in various mixtures by heating the metal carbonyl with the phosphorus compound at 170-275°C and 10-30 atm. pressure. The degree of PF_3 substitution increased with the temperature.

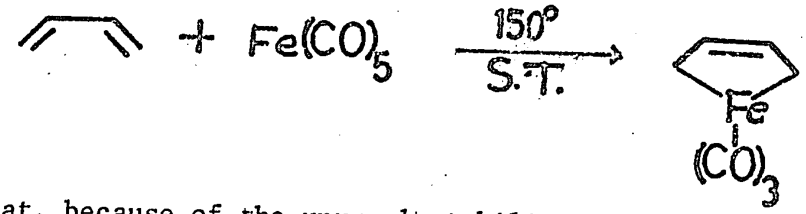
Iron pentacarbonyl does not undergo rapid exchange with labelled carbon monoxide.[24]

$$Fe(CO)_5 + {}^{*}CO \xrightarrow[25^{\circ}]{C_6H_6} \text{4 years for exchange.}$$

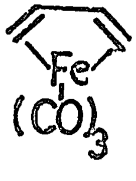
II. REACTIONS WITH OLEFINS

Numerous papers have appeared on the reaction of olefins with iron pentacarbonyl and since only a few of these will be cited here, the reader is referred to an excellent review of this topic by Pettit and Emerson.[25]

In 1930, Reihlen and co-workers[26] found that when butadiene and iron pentacarbonyl were heated together in a sealed tube, a complex, $C_4H_6Fe(CO)_3$ was formed to which they assigned the structure (III). Later, Hallam and Pauson[27] extended the reaction to other diene systems. It was proposed



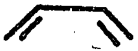
that, because of the unusual stability of these compounds and by analogy with ferrocene and other sandwich complexes, structure (IV) best represented the bonding within the complex. Here the butadiene moiety is planar, or nearly



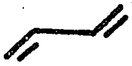
IV

so, and the iron atom lies below the plane and is approximately equidistant from the four carbon atoms of the diene system.

In order to form diene-iron tricarbonyl complexes, the diene must be able to adopt a cisoid (Va) rather than a transoid (Vb) conformation. Thus, for instance, 3-methylenecyclohexene does not form a stable complex.



Va



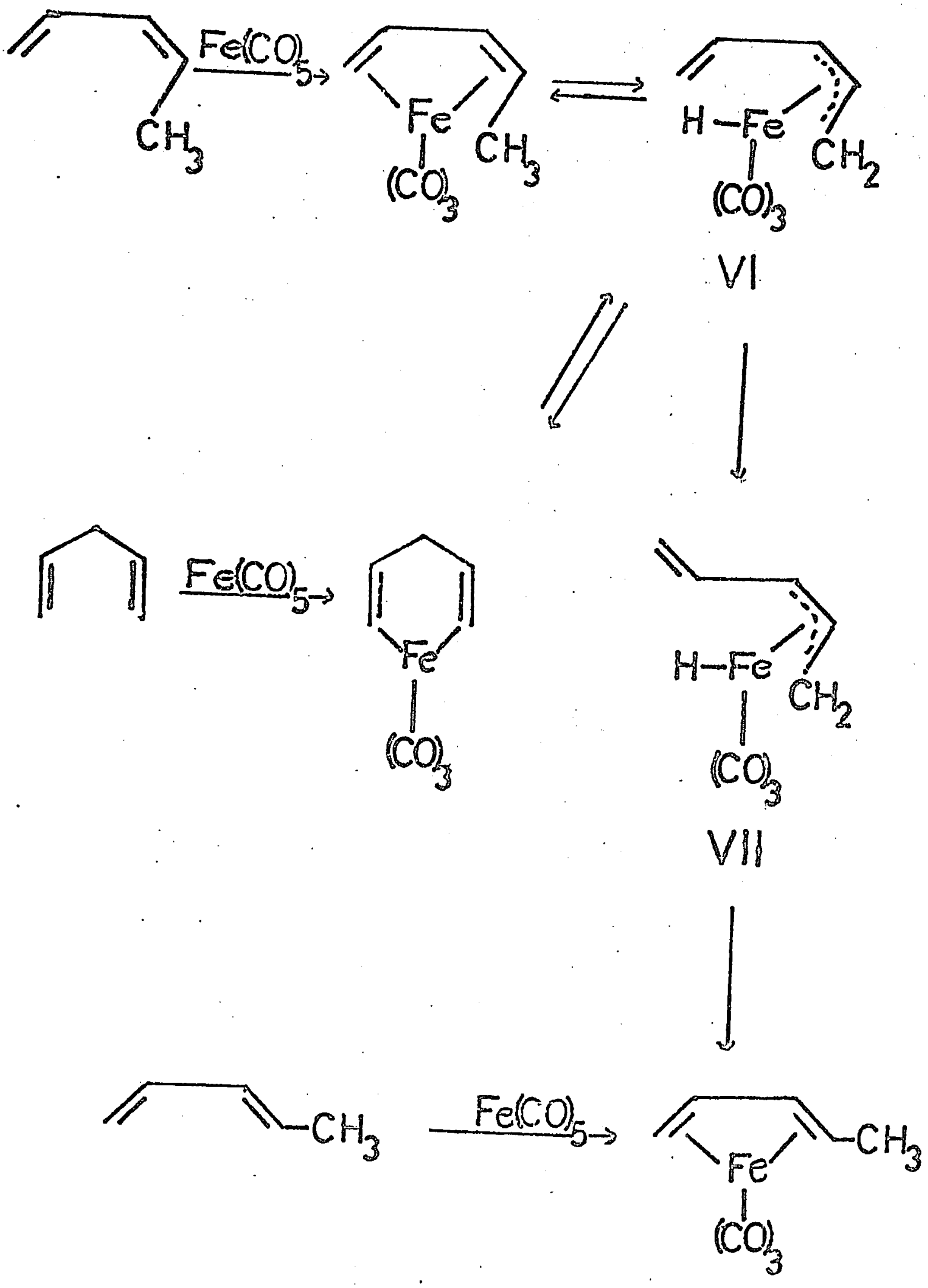
Vb

Non-conjugated dienes can rearrange under the influence of iron pentacarbonyl to form conjugated complexes. For example, 1,4-pentadiene reacts with the metal carbonyl to give trans-1,3-pentadiene-iron tricarbonyl, which can also be obtained by treating either cis or trans-1,3-pentadiene with iron pentacarbonyl[28] (Scheme 1). A postulated mechanism for formation of the trans-1,3 complex initially involves the generation of a diene-iron tricarbonyl complex, from which the iron atom can abstract an allylic proton to form a π-allyl-hydroiron-tricarbonyl (VI). In this compound the olefinic bond is free to rotate to give the more stable conformer (VII). Hydrogen transfer then occurs giving the trans complex which is the thermodynamically most stable complex.

III. REACTIONS WITH ORGANIC NITROGEN COMPOUNDS

Sternberg and co-workers[29] proposed that iron pentacarbonyl disproportionates in various amines such as piperidine into $Fe(CO)_6^{+2}$ and $Fe(CO)_4^{-2}$. Reaction of the metal carbonyl and piperidine at liquid nitrogen temperatures gave a substance which analyzed for $Fe(CO)_5 \cdot 3C_5H_{10}NH$. The product was viewed as a loose association of the reagents, which gave the

SCHEME 1

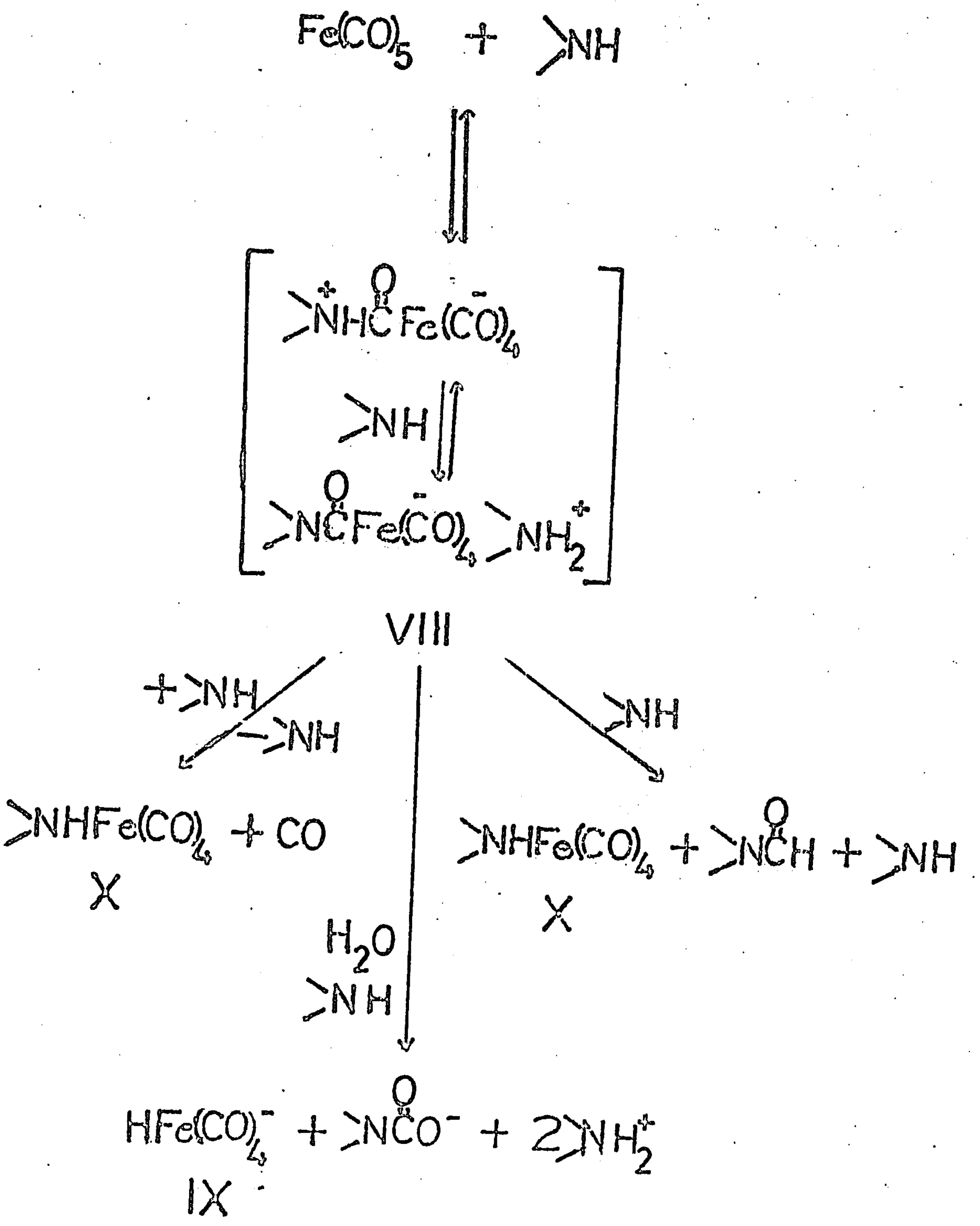

Fe(CO)5
CH3
Fe
(CO)3
CH3
H–Fe
(CO)3
CH2
VI
Fe(CO)5
Fe
(CO)3
H–Fe
CH2
(CO)3
VII
CH3
Fe(CO)5
Fe
CH3
(CO)3

infrared spectrum of unmodified iron pentacarbonyl and piperidine when dissolved in ether or cyclohexane. When dissolved in piperidine, this substance was presumably converted into the mononuclear carbonylferrate anion and a cationic iron carbonyl complex by a disproportionation mechanism.[30,31] Attack by the amine on the complex liberated carbon monoxide with subsequent formylation of the amine while the anion was transformed rapidly into polynuclear carbonylferrates.

Edgell and co-workers,[32] however, observed the following three species to appear successively with time from the reaction of piperidine with iron pentacarbonyl at room temperature: $Fe(CO)_5(NHC_5H_{10})_3$ (VIII), $HFe(CO)_4^-$ (IX) and $Fe(CO)_4(NHC_5H_{10})$ (X). The first product was shown to be identical with Hieber and Kahlen's[30] compound since it exhibited the same spectral properties in cyclohexane and ether solution. An infrared spectrum of the solid at -78^oC indicated that the bands corresponding to piperidine were altered and shifted. Thus (VIII) is not the metal carbonyl and amine loosely held together but a substance in which the Fe-C and C-O bonds of the metal carbonyl moiety are modified and in which at least one of the amine moieties participates rather directly. The formation of IX is accompanied by piperidine carbamate. Similar results were obtained when n-butylamine or pyrrolidine[33] was treated with iron pentacarbonyl.

A mechanism was proposed by Edgell and co-workers involving an initial almost instantaneous and reversible reaction between the metal carbonyl and amine to form VIII (Scheme 2). Hydrolysis of VIII in the presence of traces of water can give piperidine hydrogen tetracarbonylferrate (IX)

SCHEME 2


Fe(CO)5 + >NH
>N⁺HC(=O)Fe(CO)4⁻
>NH
>NC(=O)Fe(CO)4⁻ >NH2⁺
VIII
+ >NH
− >NH
>NH
>NHFe(CO)4 + CO
X
>NHFe(CO)4 + >NC(=O)H + >NH
X
H2O
>NH
HFe(CO)4⁻ + >NC(=O)O⁻ + 2>NH2⁺
IX

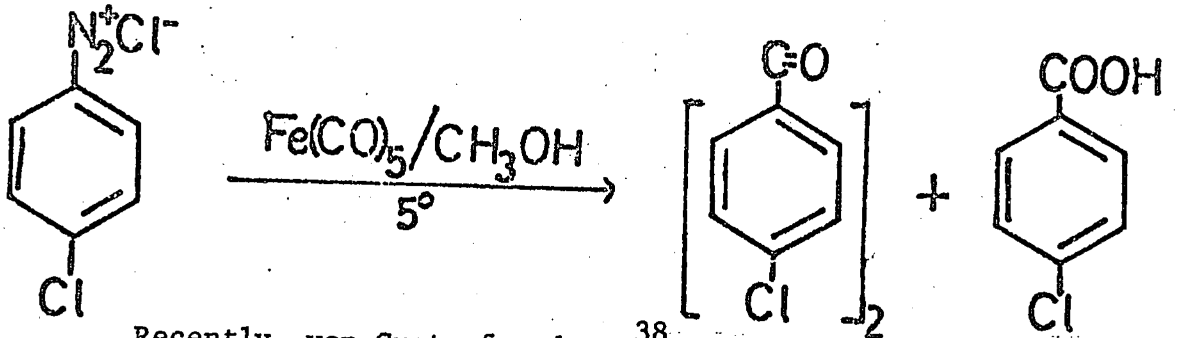
and piperidine carbamate, while X can be slowly formed from VIII with evolution of carbon monoxide. It can also be obtained by reaction of VIII with more piperidine, in which case formylpiperidine is also formed as a by-product.

Pyridine on irradiation with iron pentacarbonyl or treatment with triiron dodecacarbonyl at room temperature gives $\left[Fe(py)_6\right]\left[Fe_4(CO)_{13}\right]$. This is a convenient means of preparing the $Fe_4(CO)_{13}^{-2}$ ion.[31] Isoquinoline reacts in the same manner.[34] When the ultraviolet irradiation of pyridine and iron pentacarbonyl was conducted in a nonpolar solvent such as n-hexane, tetracarbonyl-(pyridine)-iron (0) was obtained; 2- and 4-picoline reacted similarly.[35] Hence, reactions carried out in polar solvents favor the formation of ionic complexes while those conducted in nonpolar solvents give substituted carbonyls.

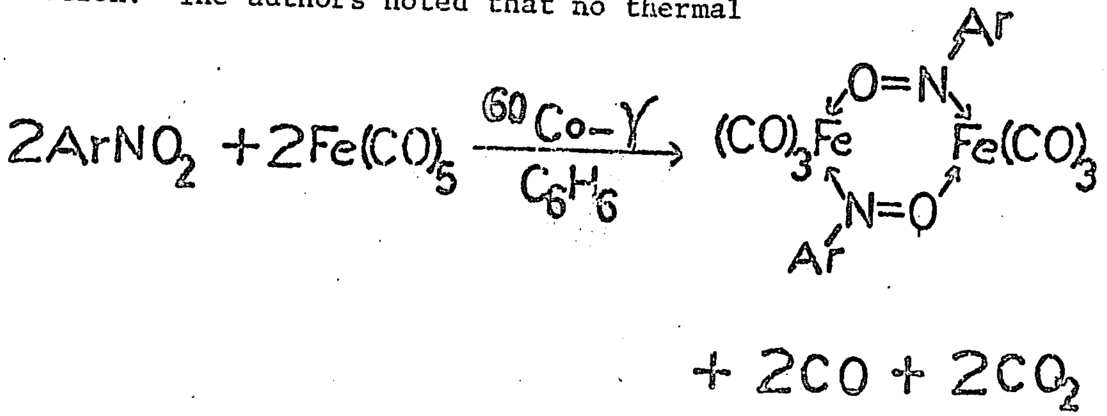
Pyridine-N-oxide has been shown to react with triiron dodecacarbonyl in benzene to give brown pyrophoric $\left[Fe(C_5H_5NO)_6\right]\left[Fe_4(CO)_{13}\right]$.[36]

When iron pentacarbonyl and o-phenanthroline are heated in acetone at 65° for a short time, a blue unstable compound $Fe(CO)_5$(o-phen) of unknown structure is obtained; however, if the reaction is carried out for a longer period of time, $\left[Fe(\underline{o}\text{-phen})_3\right]\left[Fe_2(CO)_8\right]$ is produced.[34]

Schrauzer[37] has shown that diazonium chlorides react with iron pentacarbonyl in methanol or acetone at 5°C to give mixtures of the corresponding acid and ketone in fair yield. For example, p-chlorobenzenediazonium chloride reacts with the metal carbonyl to give 4,4'-dichlorobenzophenone as the major product and p-chlorobenzoic acid as the minor product.



Recently, von Gustorf and Jun[38] prepared dimeric substituted nitrosobenzene-iron tricarbonyl by ultraviolet or cobalt-60 irradiation of the aromatic nitro compound and iron pentacarbonyl, the formation of the iron tricarbonyl complex evidently shielding the nitroso group from further reduction. The authors noted that no thermal reaction occurred between the two reactants. The following mechanism was postulated:



$$C_6H_6 \rightsquigarrow C_6H_6^{*}$$

$$C_6H_6^{*} + Fe(CO)_5 \longrightarrow Fe(CO)_5^{*} + C_6H_6$$

$$\mathrm{Fe(CO)_5^{*} + ArNO_2 \longrightarrow ArNO_2Fe(CO)_4 + CO}$$

$$\mathrm{ArNO_2Fe(CO)_4 + C_6H_6^{*} \longrightarrow ArNOFe(CO)_3 + CO_2 + C_6H_6}$$

$$\mathrm{2ArNOFe(CO)_3 \longrightarrow [ArNOFe(CO)_3]_2}$$

Reaction of 2,2'-dinitrobiphenyl with iron pentacarbonyl led to reduction of only one nitro group. Attempts to decompose these complexes to form the corresponding nitroso compounds have failed and hence the usefulness of this reaction is limited.

Displacement of a carbon monoxide ligand occurs when the metal carbonyl is treated with an equimolar quantity of isocyanide at 50-60°C.[39] When a 2:1 mole ratio of isocyanide to metal carbonyl is heated at 80-90°C

$$\mathrm{Fe(CO)_5 + RN{\equiv}C \xrightarrow{50-60^\circ} Fe(CO)_4(CNR)}$$

the disubstitution product is obtained.

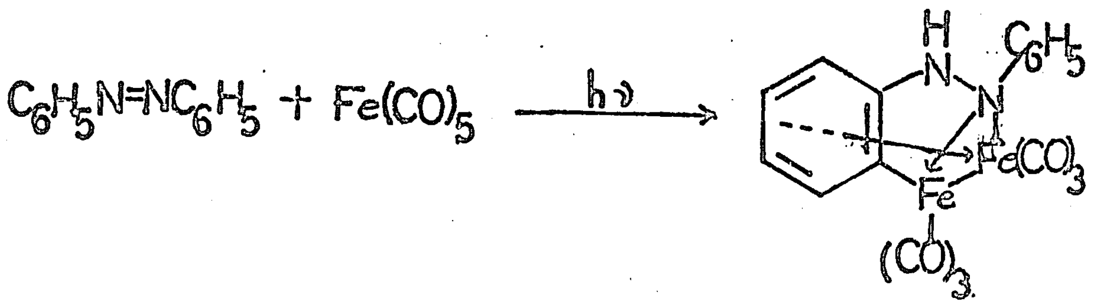
$$Fe(CO)_5 + RN{\equiv}C \xrightarrow{80\text{-}90^\circ} Fe(CO)_3(CNR)_2$$

Similar monosubstituted metal carbonyls were obtained by Seyferth and Kahlen[40] when R was $(CH_3)_3$ Si, $(CH_3)_3$ Ge and $(CH_3)_3Sn$.

Sodium bistrimethylsilylamide reacts vigorously with iron pentacarbonyl to form a carbonylcyano complex and bistrimethylsilyl ether. This is the first example of a reaction of iron pentacarbonyl in which substitution of the carbonyl oxygen occurs without cleavage of the metal-carbon bond.[41]

$$Fe(CO)_5 + NaN[Si(CH_3)_3]_2 \longrightarrow [Fe(CO)_4CN]^- Na^+ + O[Si(CH_3)_3]_2$$

Pauson and co-workers[42] have published a preliminary communication on the photolysis of azobenzene and substituted azobenzenes with iron pentacarbonyl to give complexes having the structure shown:



XI

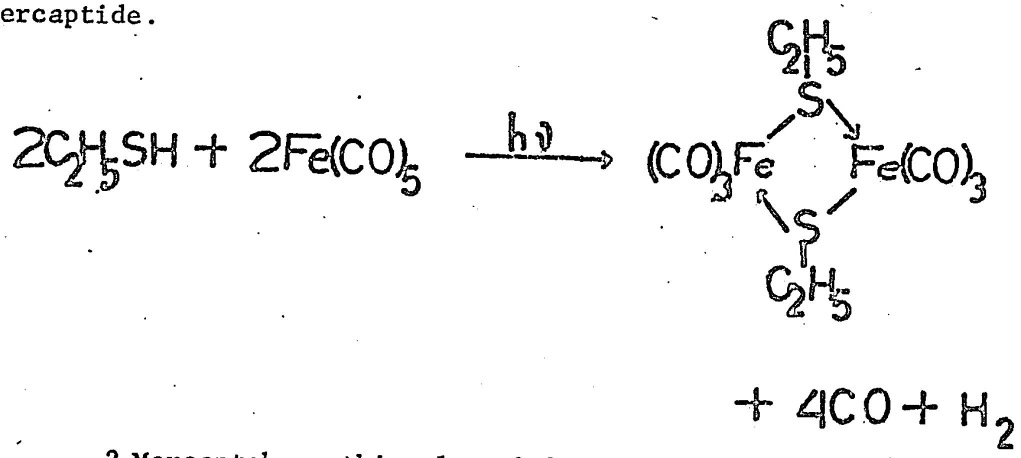
However, no description of the properties of these complexes was included.

IV. REACTIONS WITH ORGANIC SULFUR COMPOUNDS

Hieber and co-workers[43] have shown that mercaptans react with iron pentacarbonyl to give iron tricarbonyl mercaptides which may exist in mono, di, tri, or tetrameric forms, depending on the nature of the mercaptan.

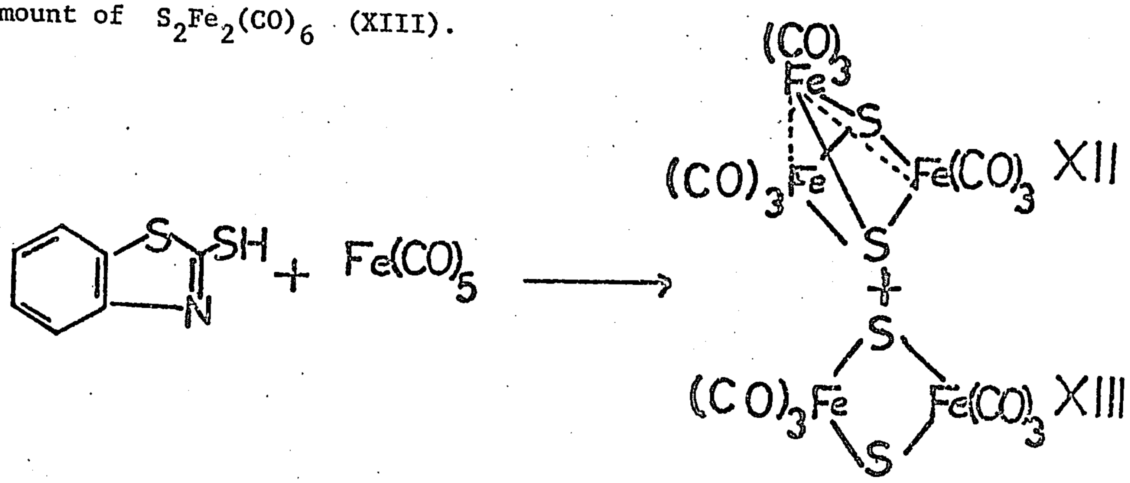
$$RSH + Fe(CO)_5 \longrightarrow [RSFe(CO)_3]_n \qquad n = 1-4$$

Photolysis of ethyl mercaptan and the metal carbonyl[44] gives the dimeric mercaptide.

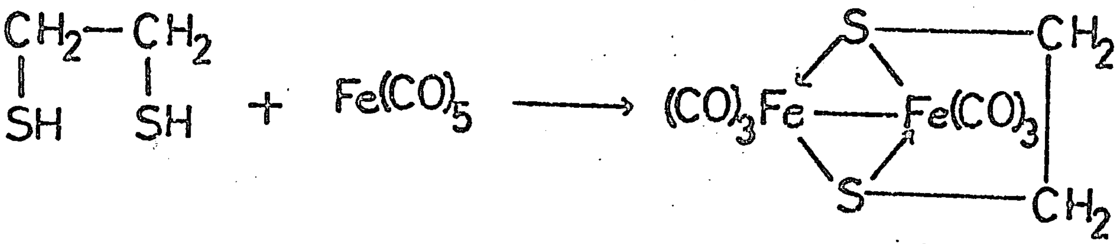


2-Mercaptobenzothiazole exhibits anomalous behaviour towards iron pentacarbonyl. Hieber and Gruber[45] obtained a product which they reported had the empirical formula $CH_2S_2Fe_3(CO)_{10}$. This product was later shown to be identical with that obtained by Havlin and Knox[46] from the same reaction and to that obtained by King[47] on treatment of cyclohexene sulfide with iron pentacarbonyl. However, this product has the empirical formula $S_2Fe_3(CO)_9$

and the structure XII. Havlin and Knox[46] also observed formation of a minor amount of $S_2Fe_2(CO)_6$ (XIII).



King[48] has shown that 1,2-ethanedithiol reacts with iron pentacarbonyl to give the red, volatile, diamagnetic, air-stable complex XIV. Analogous complexes are formed with 3,4-toluenedithiol and bis-(trifluoromethyl)-dithietane.



XIV

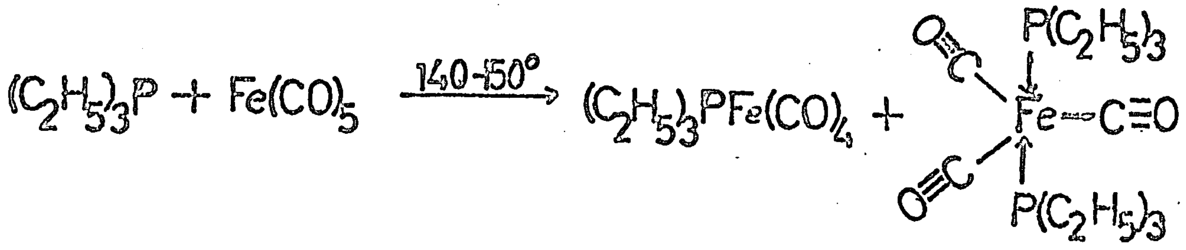
When dimethyldisulfide is treated with iron pentacarbonyl in an autoclave, the polymer $\left[(CH_3S)_2\ Fe(CO)_2\right]_n$ is the major product, with the dimeric mercaptide $(CH_3SFe(CO)_3)_2$ being formed in low yield. When this reaction is carried out in the presence of carbon monoxide, the dimeric mercaptide is the major product.[49]

Irradiation of iron pentacarbonyl and dimethylsulfoxide in benzene solution at 80°C gives the red-black, slightly air-sensitive $[Fe((CH_3)_2SO)_6][Fe_4(CO)_{13}]$.[36]

V. REACTIONS WITH ORGANIC PHOSPHORUS COMPOUNDS

Photolysis of a mixture of iron pentacarbonyl and triphenylphosphine in cyclohexane results in carbon monoxide ligand displacement and formation of $Fe(CO)_4(P\Phi_3)$ as the major product and $Fe(CO)_3(P\Phi_3)_2$ as the minor product.[50] Analogous substitution products are formed by the use of triphenylarsine under photolytic conditions or of Φ_3M(M=P,As,Sb) under thermal conditions.[51,52] Triphenylphosphine-iron tetracarbonyl, dissolved in a mixture of trifluoroacetic acid and 1,2-dichloroethane, undergoes rapid carbon monoxide exchange with iron pentacarbonyl at -20°C.[53] There is slow exchange of bis-(triphenylphosphine)-iron tricarbonyl with iron pentacarbonyl, the predominant process being formation of triphenylphosphine-iron tetracarbonyl.

Reckziegel and Bigorgne[54] have shown that reaction of triethylphosphine with iron pentacarbonyl at 140-150°C produces triethylphosphine-iron tetracarbonyl and trans-$[(C_2H_5)_3P]_2\ Fe(CO)_3$.



Trimethylphosphite reacts in an analogous manner; however on heating excess trimethylphosphite with the metal carbonyl, a dicarbonyl of composition $\left[(CH_3O)_3P \right]_3Fe(CO)_2$ is obtained.

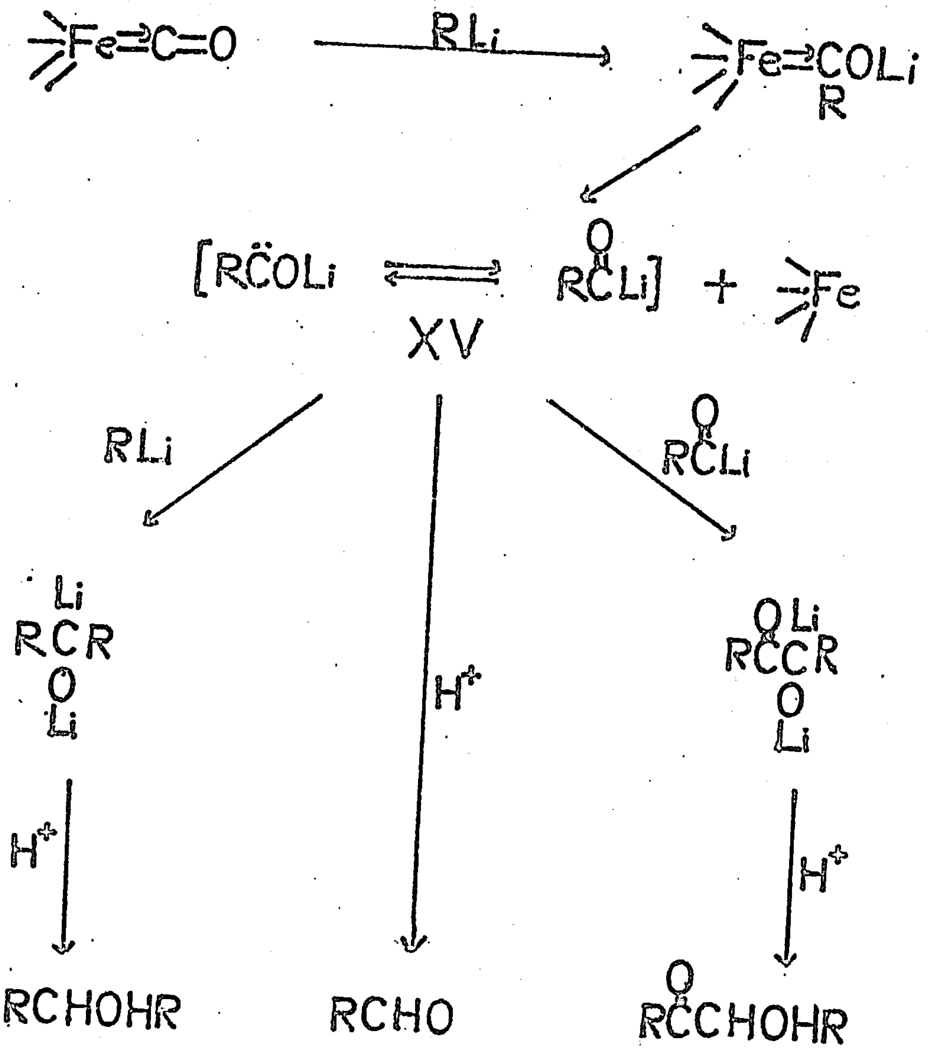
When iron pentacarbonyl and triphenylphosphine oxide or triphenylarsin oxide are irradiated in benzene solution at 80°C, dark red materials formulated as $\left[Fe((C_6H_5)_3PO)_2 \right]\left[Fe_2(CO)_8 \right]$ or $\left[Fe((C_6H_5)_3AsO)_2 \right]\left[Fe_2(CO)_8 \right]$, respectively, are formed.[36]

Tetraphenyldiphosphine, on treatment with iron pentacarbonyl, gives the complex $(C_6H_5)_2P\text{-}P(C_6H_5)_2 \cdot 2Fe(CO)_4$.[55]

VI. OTHER REACTIONS

Iron pentacarbonyl reacts with organolithium compounds in an ethereal solution at -50°C to give a number of products.[56] In general, aryllithiums yielded the corresponding aldehydes, benzhydrol derivatives and benzoin derivatives by reaction with iron pentacarbonyl (Scheme 3) but the alkyllithiums and p-tolyllithium gave symmetrical ketones. The following reaction mechanism for the aryllithium reaction was postulated: addition of aryllithium to the carbonyl double bond of iron pentacarbonyl resulted in the fission of the iron-carbon bond of the metal carbonyl producing an unstable aroyllithium intermediate. The aroyllithium could then be hydrolyzed to the aldehyde, react further with the aryllithium to form the benzhydrol derivative or dimerize to form the benzoin product. By carrying out the reaction under conditions where the dimerization reaction and the reaction

SCHEME 3



of the intermediate with aryllithium are suppressed, i.e. rapid addition of the metal carbonyl to a diluted solution of aryllithium in ether at -60°C and subsequent hydrolysis with ethanolic hydrochloric acid, the corresponding aldehydes were obtained in good yields.[57]

Coffey[58] has shown that tetraarylethylenes can be obtained from dihaloarylmethanes and iron pentacarbonyl in benzene. The metal carbonyl will react with organic halides as long as there are two halogen atoms on

$$2Ar_2CCl_2 + 2Fe(CO)_5 \longrightarrow Ar_2C{=}CAr_2 + 2FeCl_2 + 10CO$$

the same carbon atom or in very close proximity to one another. In addition, the halide must be activated by the presence of groups such as halo, cyano, carbalkoxy or phenyl. Iron pentacarbonyl reacts with diethyl dibromomalonate to give a near quantitative yield of deep purple tris-(diethyl bromomalonato)-iron (III), $Fe\left[BrC(COOC_2H_5)_2\right]_3$ while reaction of the metal carbonyl with dibromomalononitrite gave a complicated mixture of products.

Iron pentacarbonyl has been shown to react with carbon tetrachloride[59] to produce mostly tar and some hexachloroethane. Carbon tetrabromide, ethyl dibromoacetate and benzotrichloride undergo similar reactions with the metal carbonyl.

Phenylmercuric chloride reacts with iron pentacarbonyl to produce a mercury-iron carbonyl complex,[18] which is convertible to diphenylmercury and $Fe(CO)_4Hg$, which is the same product formed by reaction of the metal carbonyl with mercuric sulfate in aqueous media.[17] An entirely analogous reaction

$$2C_6H_5HgCl + Fe(CO)_5 \longrightarrow Fe(CO)_4(HgC_6H_5)_2 + COCl_2$$

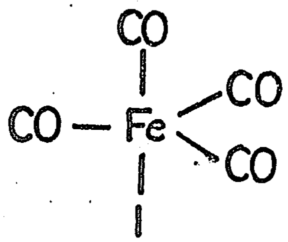
$$Fe(CO)_4(HgC_6H_5)_2 \longrightarrow Fe(CO)_4Hg + (C_6H_5)_2Hg$$

occurs between phenylmercuric hydroxide and the metal carbonyl. Diphenylmercury can also react with the metal carbonyl, forming $Fe(CO)_4Hg$ and a carbonyl insertion product, benzophenone.

Iron pentacarbonyl reacts with perfluoroalkyl iodides either in benzene solution at atmospheric pressure[60] or preferably in a closed system in the absence of solvent to give perfluoroalkyliron tetracarbonyl iodides. When the product iodides are heated at temperatures below 75°C, they decompose quantitatively to the dimeric perfluoroalkyliron tricarbonyl iodides.

$$2R_FFe(CO)_4I \xrightarrow{\Delta} [R_FFe(CO)_3I]_2 + 2CO$$

When iron pentacarbonyl is treated with tetraethylammonium iodide in diglyme at 90°C for 2 hours, deep red crystals of $(C_2H_5)_4N^+[Fe(CO)_4I]^-$ are obtained.[62] This ionic complex decomposes rapidly in air and in solution but is stable under nitrogen in darkness. The structure of the iodotetracarbonyliron anion, determined by infrared spectroscopy, is as indicated.



Under reflux conditions, iron pentacarbonyl reacts with pentane-2,4-dione to give $Fe(C_5H_7O_2)_3$ where $C_5H_7O_2^-$ is the enol anion of the β-diketone.[63]

Finally, iron pentacarbonyl is reported to behave as a base in boron trifluoride—trifluoroacetic acid solution.[64]

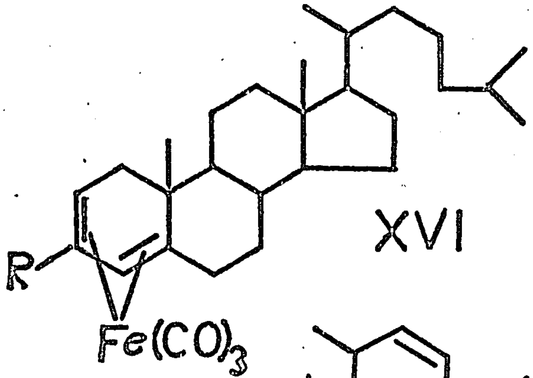
This review indicates that the reaction of iron pentacarbonyl with only a few of the functional groups of organic chemistry has been investigated. The present thesis reports an investigation of the reaction of several of these groups under different conditions, as well as the reaction of several other groups hitherto untested. As wide a variety of types of compounds as possible was investigated in the time available, in an attempt to discern a pattern in the reactions of iron pentacarbonyl. This has prevented a detailed study of the mechanisms of the reactions.

DISCUSSION

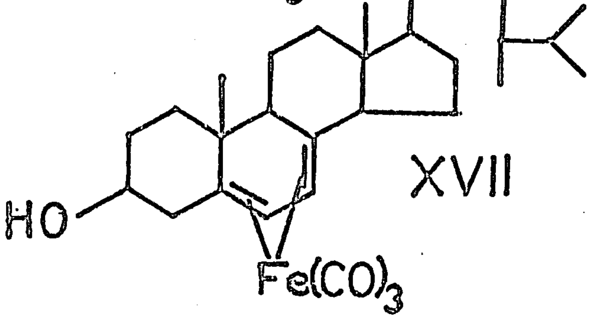
I. Diene Complexes

While the formation of diene-iron tricarbonyl complexes has been reported for a wide variety of dienes of simple systems,[25] there is only one example of the formation of a steroid diene-iron tricarbonyl complex. Nakamura and Tsutsui[65] prepared ergosterol acetate-iron tricarbonyl by reaction of the parent diene with iron pentacarbonyl in benzene. However, their attempts to prepare the complex of the alcohol itself failed. It was decided to investigate the preparation of ergosterol-iron tricarbonyl and other steroid complexes and to determine their infrared, nuclear magnetic resonance and ultraviolet spectral characteristics; the latter have been reported for only a few diene-iron tricarbonyl complexes.[65,89]

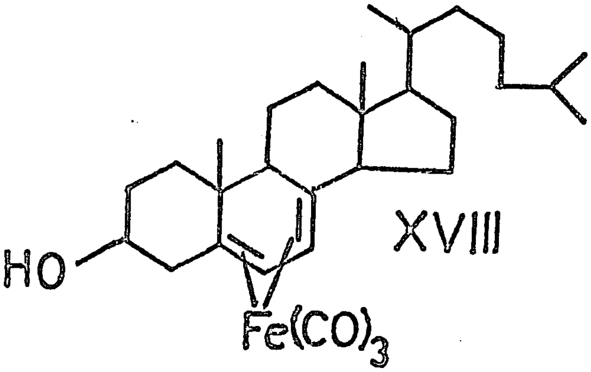
The iron-tricarbonyl complexes of cholesta-2,4-diene (XVI, R=H), ergosterol (XVII) and cholesta-5,7-dien-3β-ol (XVIII) were obtained in 38.8-62.6% yield by refluxing a mixture of the diene and iron pentacarbonyl in isooctane, cyclohexane or butyl ether. The crude complexes were purified by column chromatography. In the case of ergosterol, the chromatography must be carried out under nitrogen to avoid decomposition to starting material and it is essential that the pure complex be stored under nitrogen. No special precautions have to be taken in the work-up of the other complexes to ensure isolation of the product.



XVI



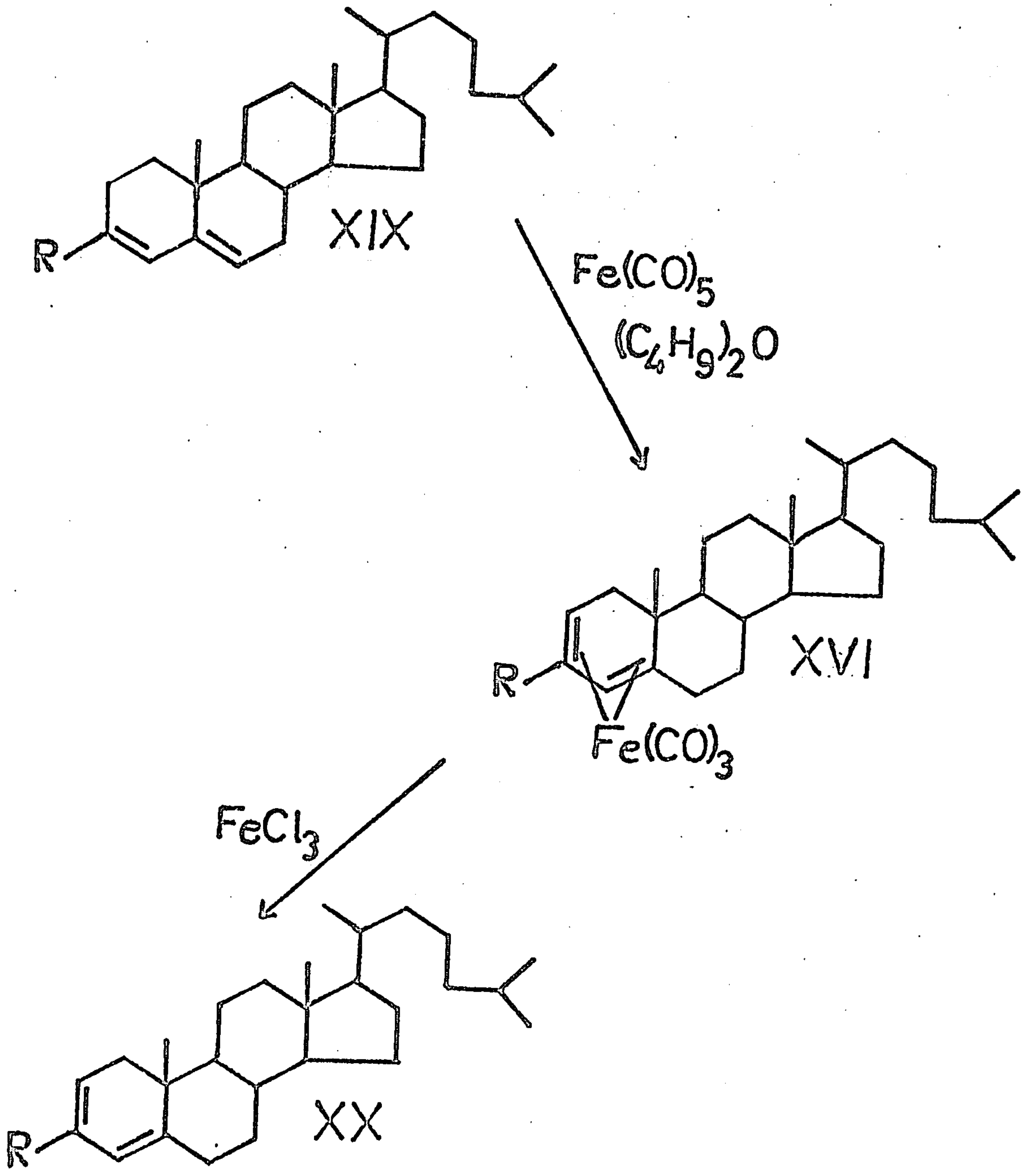
XVII



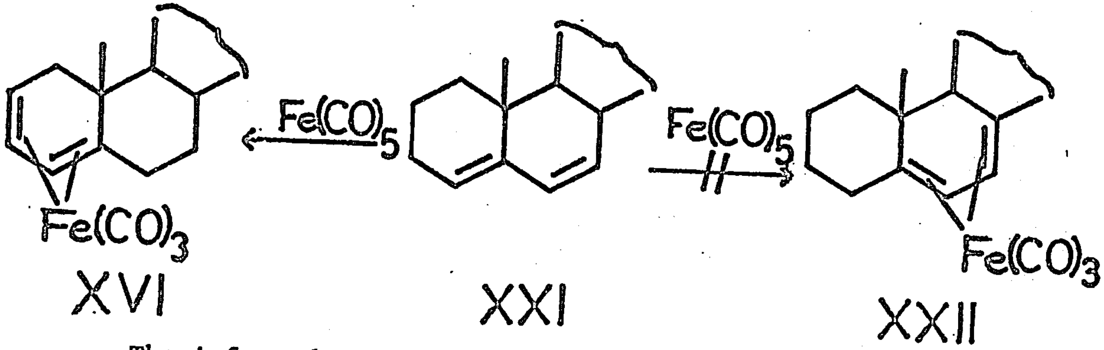
XVIII

Although no successful preparation of a trans diene-iron tricarbonyl complex has been reported, it was nevertheless decided to investigate the behavior of a number of trans dienes towards iron pentacarbonyl. It seemed conceivable that isomerization to the cis complex might occur,[28] the driving force of the reaction being the necessity of the diene to possess a cis conformation to enable complex formation to occur.

When the cholesta-3,5-dienes XIX (R=H, CH_3, OCH_3) reacted with iron pentacarbonyl in butyl ether, the corresponding cholesta-2,4-diene-iron tricarbonyl complexes XVI (R=H, CH_3, OCH_3) were obtained in 53.0-71.4% yield (Table III). Treatment of cholesta-4,6-diene (XXI) with iron pentacarbonyl also gave complex XVI (R=H) in 33.7% yield.



The failure to obtain any of the 5,7-diene complex (XXII) is probably due to the greater stability of complex XVI.



The infrared spectra of the diene-iron tricarbonyl complexes is of interest particularly in the metal carbonyl region. The maximum symmetry can be C_{3v} for a molecule of the type (Ligand) $Fe(CO)_3$, leading to two infrared active carbonyl frequencies (a_1 + e). A lower symmetry would lead to loss of the degeneracy of the vibration. Hence, two or three frequencies may be anticipated depending on the nature of the ligand.[66] Usually there is a sharp band at 2100-2000 cm.$^{-1}$ and a broad band, sometimes resolvable into two bands, at 2000-1900 cm.$^{-1}$ The positions of the bands due to metal carbonyl stretching in the complexes investigated are listed in Table I. The sharp band of the complexes occurs in the region of 2029-2040 cm.$^{-1}$ while the broad band, resolvable into two bands for complex XVI (R=H), shows absorption in the region of 1938-1970 cm.$^{-1}$ The infrared spectrum of XVII in chloroform solution is shown as a representative example (Figure 1).

In the ultraviolet spectrum, the occurrence of a considerable shift to lower frequency and an increase in intensity is noted for the steroids upon complex formation (Table II). The ultraviolet spectrum of

XVII is given in Figure 2.

Green and co-workers[67] have shown that in the nuclear magnetic resonance spectra (N.M.R.) of cyclic diene-iron tricarbonyl complexes, the protons on the central carbons of the diene system give a signal in the region between 5.1 and 5.4 p.p.m. being largely unaltered by complex formation. The absorption of the terminal protons, on the other hand, is shifted to higher field and lies between 2.7 and 3.4 p.p.m. The positions of the protons on the central carbons of the diene system in the complexes prepared are indicated in Table II. The direction of the small shift in the positions of the protons on the central carbons of the diene system upon complex formation is in accordance with the ultraviolet spectral results in indicating less olefinic character in the diene system on complexation. The band for the outer olefinic proton of cholesta-2,4-diene, which occurs in the region 5.32-5.75 p.p.m. is shifted to the steroidal methylene region of the spectrum upon complex formation. The N.M.R. spectrum of XVIII in deuteriochloroform solution is shown in Figure 3.

In summary, the infrared and N.M.R. spectra of the complexes are similar to those reported for other diene-iron tricarbonyl complexes. The ultraviolet spectra of the dienes show a marked hypsochromic shift upon complex formation. Similar shifts would be expected in other similar diene-iron tricarbonyl complexes.

TABLE I

INFRARED SPECTRAL PROPERTIES OF STEROID DIENE-IRON TRICARBONYL COMPLEXES

Steroid Diene-Iron Tricarbonyl Complex	Metal Carbonyl Stretching Frequency Intensity CM^{-1}	Phase
Cholesta-2,4-diene (XVI, R=H)	2036(s), 1964(s), 1938(s), 1925sh, 1916sh	NEAT
3-Methylcholesta-2,4-diene (XVI, R=CH_3)	2040(s), 1970(s)	CCl_4
3-Methoxycholesta-2,4-diene (XVI, R=OCH_3)	2038(s), 1966(s)	KBr
Ergosterol (XVII)	2032(s), 1958(s), 1928(w)	KBr
	2034(s), 1962(s), 1928(w)	$CHCl_3$
Cholesta-5,7-dien-3β-ol (XVIII)	2029(s), 1957(s)	KBr
	2031(s), 1960(s)	$CHCl_3$

s = strong w = weak sh = shoulder

TABLE II

ULTRAVIOLET AND NUCLEAR MAGNETIC RESONANCE SPECTRAL PROPERTIES OF STEROID DIENES AND THE CORRESPONDING IRON TRICARBONYL COMPLEXES

Compound	Ultraviolet			Nuclear Magnetic Resonance	
	Absorption Maximum mμ	Log ϵ	Solvent	Positions of Protons on the Central Carbons of Diene System p.p.m.	Solvent
Cholesta-2,4-diene	267, 275	3.8[68]	--	5.32-5.75 (Multiplets)	CCl_4
Cholesta-2,4-diene-Iron Tricarbonyl (XVI, R=H)	231.0	4.24	Isooctane	5.03-5.72 (Broad Multiplet)	CCl_4
3-Methylcholesta-2,4-diene-Iron Tricarbonyl (XVI, R=CH_3)	233.0	4.28	Isooctane	--	--
3-Methoxycholesta-2,4-diene	277.0	4.08	Ethanol	--	--
3-Methoxycholesta-2,4-diene-Iron Tricarbonyl (XVI, R=OCH_3)	237.5	4.37	Ethanol	--	--
Ergosterol	281.0	4.00	Isooctane[69]	5.2-5.8 (Broad Multiplet)	$CDCl_3$
Ergosterol-Iron Tricarbonyl (XVII)	238.0	4.33	Isooctane	4.8-5.7 (Broad Multiplet)	$CDCl_3$
Cholesta-5,7-dien-3β-ol	281.5	4.04	Hexane[70]	5.30-5.75 (Multiplets)	$CDCl_3$
Cholesta-5,7-dien-3β-ol-Iron Tricarbonyl (XVIII)	238.0	4.34	Isooctane	4.99, 5.25 (Multiplets)	$CDCl_3$

The facile decomposition of diene-iron tricarbonyl complexes can usually be accomplished with ferric chloride to give the parent diene.[71] When complexes XVI-XVIII were treated with ferric chloride in ethanol, the parent dienes were obtained in 58.7-90.1% yield. The parent dienes of complexes XVI (R=H), XVII, XVIII were identified by comparison with authentic samples. 3-Methylcholesta-2,4-diene (XX, $R=CH_3$) was identical to a sample prepared by treating cholest-4-en-3-one first with methyl magnesium iodide followed by ammonium chloride.[72]

3-Methoxycholesta-2,4-diene (XX, $R=OCH_3$) has not been previously reported. This homoannular diene showed an ultraviolet maximum at 277 mμ in comparison to the corresponding heteroannular diene where the principal absorption occurred at 239.0 mμ ($\log \epsilon = 4.30$).[73] Therefore, iron pentacarbonyl provides a useful means of isomerizing a heteroannular diene to the less stable homoannular compound. The greater stability of a heteroannular diene is indicated by the thermal conversion of cholesta-5,7-diene to XXI.[74]

With certain diene-iron tricarbonyl complexes, hydride abstraction can take place with surprising ease, e.g. cyclohexa-1,3-diene-iron tricarbonyl:[75]

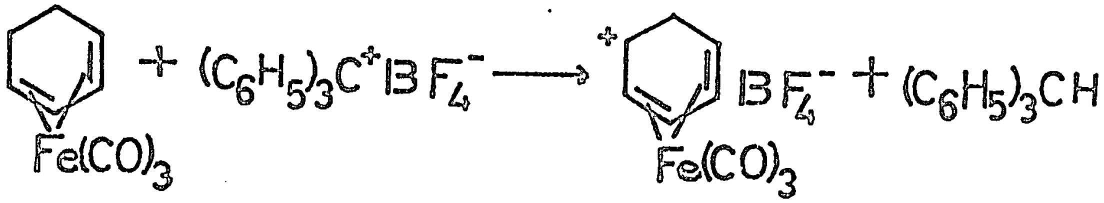


TABLE III

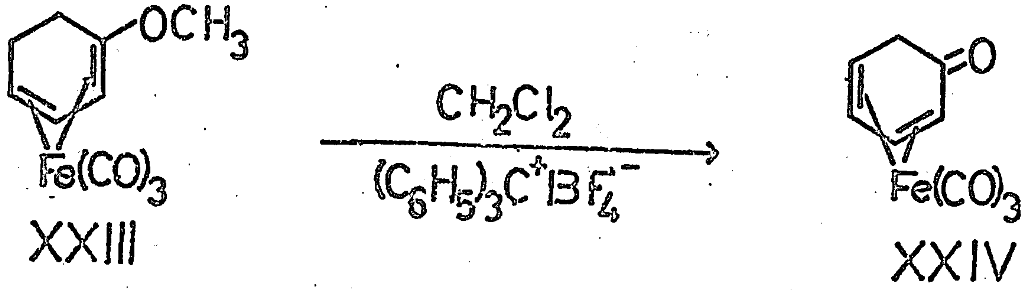
REACTION OF DIENES WITH IRON PENTACARBONYL

Product	Reactant	Reaction Time hrs.	Solvent	Yield %	Melting Point °C	Analysis Calculated		Analysis Found	
						Carbon %	Hydrogen	Carbon %	Hydrogen
Cholesta-2,4-diene-Iron Tricarbonyl (XVI, R=H)	Cholesta-2,4-diene	40	Isooctane	62.6	18.0-20.0	70.86	8.72	70.84	8.93
	Cholesta-3,5-diene	36	Butyl Ether	63.7					
	Cholesta-4,6-diene	108	Butyl Ether	33.7					
3-Methylcholesta-2,4-diene-Iron Tricarbonyl (XVI, $R=CH_3$)	3-Methylcholesta-3,5-diene	36	Butyl Ether	53.0	18.0-20.0	71.25	8.89	71.01	8.88
3-Methoxycholesta-2,4-diene-Iron Tricarbonyl (XVI, $R=OCH_3$)	3-Methoxycholesta-3,5-diene	36	Butyl Ether	71.4	24.0-27.0	69.14	8.61	69.35	8.44
Ergosterol-Iron Tricarbonyl (XVII)	Ergosterol	30-33	Isooctane or Cyclohexane	38.8	70.0-71.0	69.39	8.27	69.19	7.91
Cholesta-5,7-dien-3β-ol-Iron Tricarbonyl (XVIII)	Cholesta-5,7-dien-3β-ol	14 26	Butyl Ether Isooctane	42.4	49.0-51.0	68.68	8.46	68.58	8.71

However, complexes XVI (R=H) and XVIII did not react with triphenylmethyl tetrafluoroborate to give a fluoroborate salt. Cholesta-2,4-diene-iron tricarbonyl (XVI, R=H) gave a single (thin layer chromatography) non-complexed organic product which had an empirical formula of $C_{28}H_{37}O$ according to carbon, hydrogen elemental analysis and to a positive ferrox test[76] for oxygen. Infrared absorption (KBr disc) at 1600, 1500, 750 and 704 cm^{-1} suggested the presence of a monosubstituted phenyl group. Integration of the N.M.R. spectrum (CCl_4 solution) indicated the presence of one phenyl group per steroid nucleus. The product did not exhibit any absorption in the olefinic proton region of the N.M.R. spectrum. Mass spectrometry shows a multiplet of unidentifiable peaks in mass region 606-612 and a peak at 91 mass units for the tropylium ion with the remainder of the fragmentation pattern being the removal of methylene groups. Because of the contradictory data, the nature of the product was not further investigated. Complex XVIII, on similar treatment, gave two unidentifiable non-complexed products. These products were not further investigated.

II. Dienone Complexes

Iron carbonyl complexes of a few dienones have been prepared. Hubel and co-workers[77] reported the formation of a large number of derivatives of cyclopentadienone-iron tricarbonyl principally from reaction of acetylenes with the metal carbonyl. Birch and co-workers[78] have observed that cyclohexa-2,4-dienone-iron tricarbonyl could be obtained via the 1-methoxycyclohexa-1,3-diene complex.



XXIII XXIV

The complex of tropone, where iron is bonded to two of the three double bonds, was synthesized by reaction of iron carbonyls either with tropone[79] or acetylene.[80] However, no complexes of cross-conjugated dienones have been reported.* Therefore, it was considered of interest to attempt the synthesis of complexes of cross-conjugated dienones and to investigate their properties. The behavior of a simple dienone, 4,4-dimethylcyclohexa-2,5-dienone towards iron pentacarbonyl was first investigated.

4,4-Dimethylcyclohexa-2,5-dienone (XXVI) has been prepared by a lengthy route involving bromination of 4,4-dimethylcyclohexanone or

---

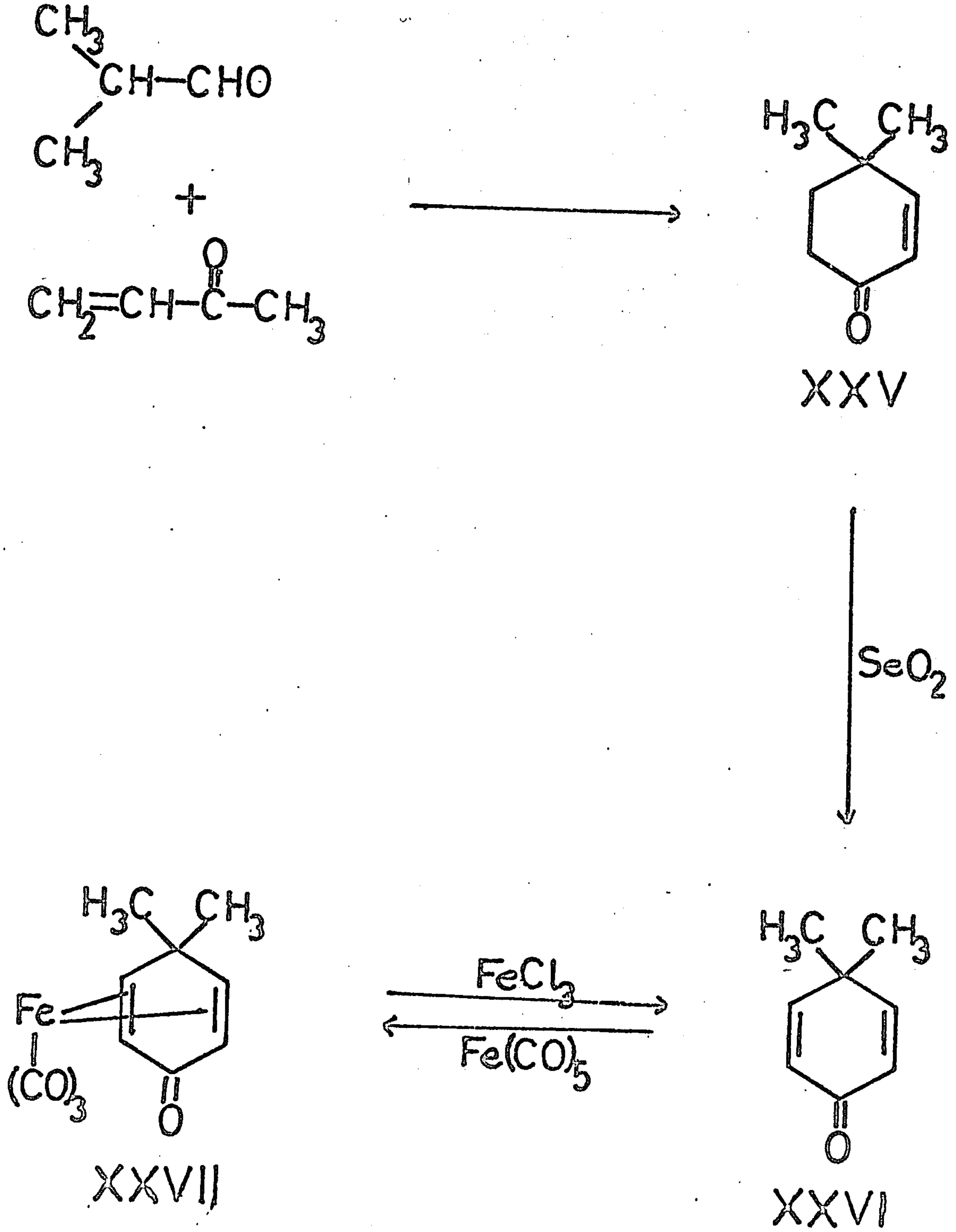
*Duroquinone-iron tricarbonyl[83] has been prepared by photolysis of 2-butyne and iron pentacarbonyl.

its ketal and subsequent dehydrohalogenation.[81,82] A simplified synthesis of this compound was accomplished in the following way (Scheme 4): reaction of isobutyraldehyde with methyl vinyl ketone according to Bordwell and Wellman[84] gave 4,4-dimethylcyclohex-2-enone (XXV). This monoenone was dehydrogenated with selenium dioxide[85] to give the desired dienone (XXVI) as a colorless liquid with an absorption maximum in the ultraviolet at 225.0 mμ (log $\mathcal{E}$ = 4.20 in isooctane). It exhibited N.M.R. absorption (carbon tetrachloride solution) at 1.23 p.p.m. (singlet) for the two methyl groups, at 6.00 p.p.m. for the protons <u>alpha</u> to the carbonyl function, and at 6.72 p.p.m. for the protons <u>beta</u> to the carbonyl group.

When a mixture of XXVI and iron pentacarbonyl was refluxed in isooctane for 49 hours, the dienone-iron tricarbonyl complex XXVII was obtained in 36.1% yield. Cholesta-1,4-dien-3-one-iron tricarbonyl (XXVIII) was prepared in a similar manner or by stirring a mixture of the dienone with diiron enneacarbonyl in dry benzene at 40-50°C for four hours. The latter method gave a somewhat lower yield of XXVIII than the use of iron pentacarbonyl (EXPERIMENTAL). Androsta-1,4-diene-3,11,17-trione-iron tricarbonyl (XXIX) and santonin-iron tricarbonyl (XXXI) were obtained in yields of 22.1% and 41.8%, respectively, by refluxing the dienone with iron pentacarbonyl in dioxane.

The spectral properties of the dienone complexes are given in Tables IV and V. There is little difference between the positions of the metal carbonyl stretching frequencies for the dienone and diene-iron

SCHEME 4

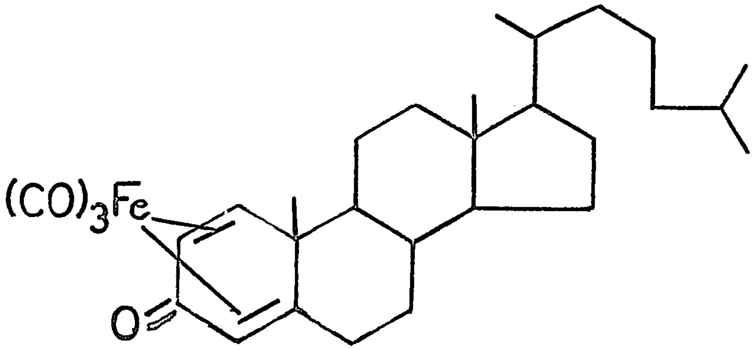


CH3
CH—CHO
CH3
+
CH2=CH—C(=O)—CH3
H3C CH3
XXV
SeO2
H3C CH3
XXVI
FeCl3
Fe(CO)5
H3C CH3
Fe
(CO)3
XXVII

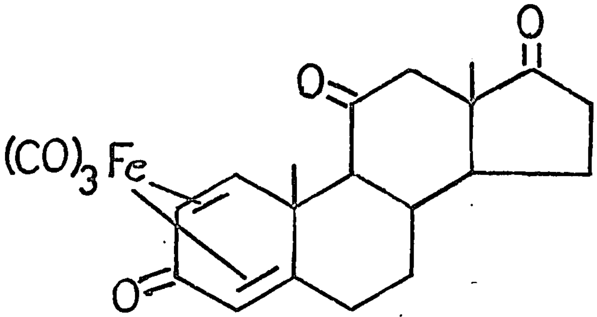
tricarbonyl complexes. In contrast to the steroid diene-iron tricarbonyl complexes, there is only a small hypsochromic shift of the ultraviolet absorption maxima of the dienones upon complex formation. The ultraviolet spectrum of complex XXIX is remarkably different from the ultraviolet spectra of the other dienone complexes (Figure 4) because of the appearance of absorption maxima in the region of 316.0-348.0 mμ in addition to the principal absorption at 215.5 mμ. We are unable to offer any explanation for the remarkable difference in the spectra of such closely related compounds as XXVIII and XXIX; presumably the 11-carbonyl group of the latter is responsible.

The positions of the olefinic protons of the dienones are only slightly shifted upon complex formation (Table VI). For instance, the protons alpha to the carbonyl group in complex XXVII appeared at only 0.04 p.p.m. higher field than XXVI; the protons beta to the carbonyl function gave a doublet at 6.58 p.p.m., a shift of 0.14 p.p.m. from the uncomplexed form. The spin-spin coupling constant is 10 cycles per second for the AB protons in all of the spectra of the dienones and the corresponding iron tricarbonyl complexes.

Complexes XXVII-XXIX were readily decomposed to the corresponding dienones with ferric chloride in yields of 86.0-94.2%. However, treatment of santonin-iron tricarbonyl (XXXI) with ferric chloride in ethanol gave no isolable product. The complex could be decomposed via its oxime (Scheme 5). Reaction of the complex with hydroxylamine gave santonin oxime-iron tricarbonyl (XXXII), identical to the product obtained in low



XXVIII



XXIX

TABLE IV

INFRARED SPECTRAL PROPERTIES OF DIENONE-IRON TRICARBONYL COMPLEXES

Dienone-Iron Tricarbonyl Complex	Metal Carbonyl Stretching Frequency Intensity cm^{-1}	Phase
4,4-Dimethylcyclohexa-2,5-dienone (XXVII)	2075(w), 2040(s), 2004(w-m), 1967(s)	CCl_4
Cholesta-1,4-dien-3-one (XXVIII)	2030(s), 1952(s)	KBr
Androsta-1,4-diene-3,11,17-trione (XXIX)	2034(s), 1961(s), 1943(s)	$CHCl_3$
Santonin (XXXI)	2044(s), 1970(s)	CH_2Cl_2

s = strong m = medium w = weak

TABLE V

ULTRAVIOLET & NUCLEAR MAGNETIC RESONANCE SPECTRAL PROPERTIES OF DIENONES & THE CORRESPONDING IRON TRICARBONYL COMPLEXES

Compound	Ultraviolet			Nuclear Magnetic Resonance	
	Absorption Maximum mμ	Log ε	Solvent	Olefinic Protons p.p.m.	Solvent
4,4-Dimethylcyclohexa-2,5-dienone (XXVI)	225.0	4.20	Isooctane[82]	6.00 (H_2, H_6) 6.72 (H_3, H_5)	CCl_4
4,4-Dimethylcyclohexa-2,5-dienone-Iron Tricarbonyl (XXVII)	218.5	4.29	Isooctane	5.96 (H_2, H_6) 6.58 (H_3, H_5)	CCl_4
Cholesta-1,4-dien-3-one	233.5	4.19	Isooctane	6.88 (H_1) 6.01 (H_2, H_4)	$CDCl_3$
Cholesta-1,4-dien-3-one-Iron Tricarbonyl (XXVIII)	219.0	4.27	Isooctane	6.82 (H_1) 5.94 (H_2, H_4)	$CDCl_3$
Androsta-1,4-diene-3,11,17-trione	238.0	4.14	Ethanol[86]	--	--
Androsta-1,4-diene-3,11,17-trione-Iron Tricarbonyl (XXIX)	215.5	4.26	Ethanol	--	--
	227.0sh	4.24			
	316.0	3.68			
	334.0sh	3.65			
	348.0sh	3.50			
Santonin (XXX)	239.0	4.03	Methylene Chloride	6.81 (H_1) 6.28 (H_2)	$CDCl_3$
Santonin-Iron Tricarbonyl (XXXI)	231.0	4.16	Methylene Chloride	6.74 (H_1) 6.20 (H_2)	$CDCl_3$

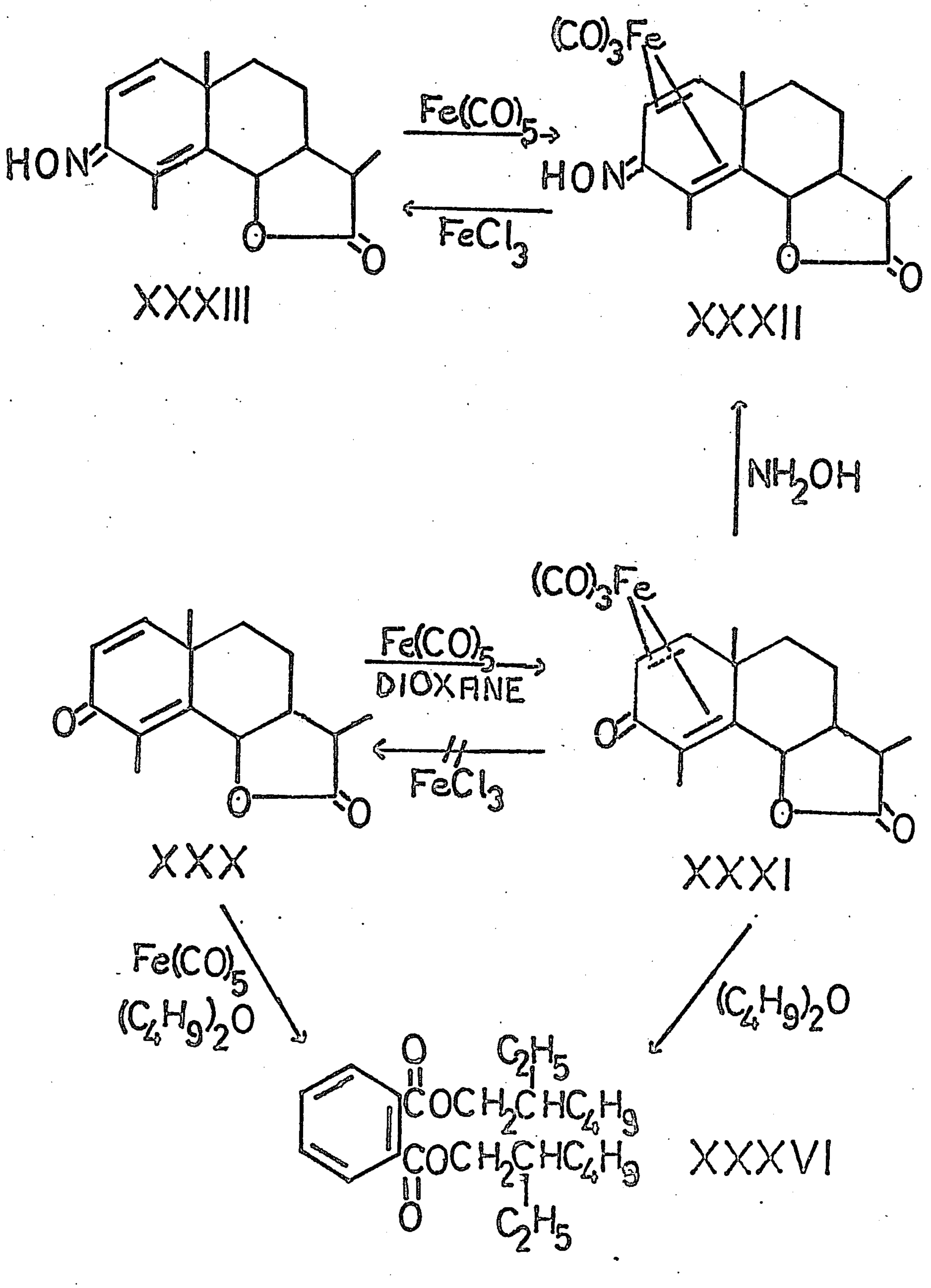
sh = shoulder

yield when a mixture of santonin oxime and iron pentacarbonyl was refluxed in either dioxane or butyl ether. Ferric chloride treatment of complex XXXII regenerated santonin oxime (XXXIII) from which santonin can be regenerated by reaction with iron pentacarbonyl and boron trifluoride in butyl ether (see next chapter).

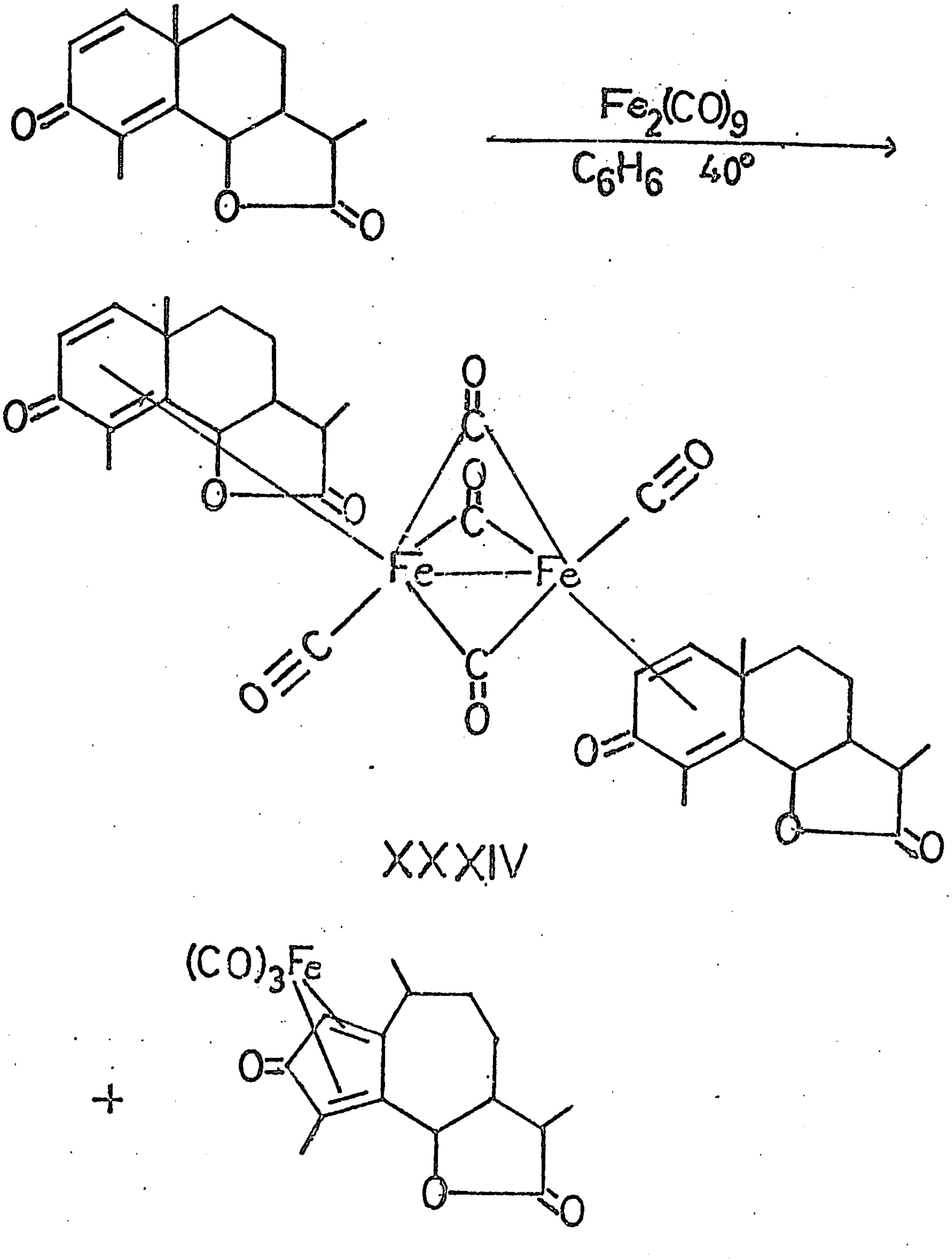
Santonin oxime-iron tricarbonyl was an orange, reasonably air-stable complex exhibiting terminal metal carbonyl absorption at 2070(w), 2030(s), 1958sh, and 1946(s) cm^{-1} (KBr disc). Complex XXXII showed an ultraviolet absorption maximum at 237.0 mμ in ethanol, a hypsochromic shift of 10 mμ from that of the parent oxime. Complex XXXII also showed a weak absorption at 290.0 mμ (log ϵ = 2.06).

Attempts to form the dienone-iron tricarbonyl complex of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone failed. When a mixture of iron pentacarbonyl and dienone was refluxed in isooctane or methyl cyclohexane for 40-65 hours, a brown solid was obtained. Purification by chromatography gave a compound which analyzed (by two laboratories) for $C_{11}H_{18}Cl_5O_6Fe_2$. The infrared spectrum (KBr disc) lacked absorption in the 2100-1900 cm.$^{-1}$ region for terminal metal carbonyl stretching and at 1675 cm.$^{-1}$ due to the carbonyl stretching of an α, β, α',β' diunsaturated ketone. There was broad absorption in the region of 3500-3300 cm.$^{-1}$ and a strong band at 1545 cm.$^{-1}$ which is close to the region (1550-1562 cm.$^{-1}$) where metal chelates of β-diketones exhibit strong carbonyl stretching.[87] The ultraviolet absorption spectrum (in ethanol) showed maxima at 231.0 (log ϵ = 4.01) and 317.0 mμ (log ϵ = 3.54) while the starting

SCHEME 5


(CO)$_3$Fe
HON
Fe(CO)$_5$
FeCl$_3$
XXXIII
XXXII
NH$_2$OH
(CO)$_3$Fe
Fe(CO)$_5$
DIOXANE
FeCl$_3$
XXX
XXXI
Fe(CO)$_5$
(C$_4$H$_9$)$_2$O
(C$_4$H$_9$)$_2$O
COCH$_2$CHC$_4$H$_9$
C$_2$H$_5$
XXXVI

SCHEME 5 (continued)

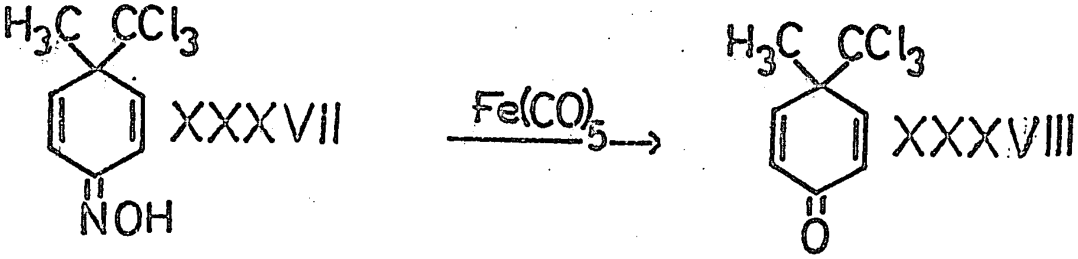


XXXIV

XXXV

material had its absorption maximum at 230.5 mμ (log ϵ = 4.25). The compound was insufficiently soluble in ordinary solvents to obtain a satisfactory N.M.R. spectrum, and was insufficiently volatile to allow mass spectral analysis.

As the above data indicate that the carbonyl group of the dienone had reacted, the behavior of the corresponding oxime towards iron pentacarbonyl was investigated in an attempt to shed light on the structure of the brown solid. When a mixture of the oxime and metal carbonyl was refluxed in isooctane or preferably butyl ether for 8-10 hours, no complex was obtained. Instead, XXXVIII was regenerated in 72% yield. This unexpected result led to the broad investigation of the reactions of iron pentacarbonyl towards different functions described in the next chapter.

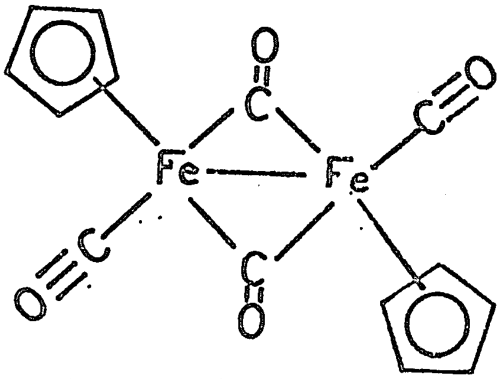


XXXVII

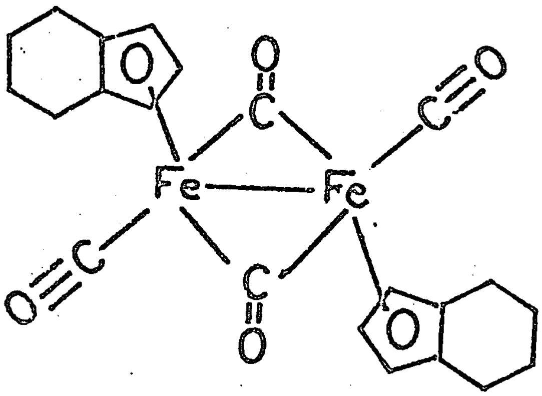
XXXVIII

The structure of the brown solid was not further investigated.

As mentioned previously, cholesta-1,4-dien-3-one reacted with diiron enneacarbonyl to give the corresponding dienone-iron tricarbonyl complex (XXVIII). The reaction of santonin with the enneacarbonyl followed a different pathway. When a mixture of santonin and diiron enneacarbonyl was stirred in benzene at 40°C for four hours (optimum reaction conditions), two air-stable products were obtained: a pale-brown complex in 7.8% yield and a yellow complex in 0.022% yield. The structures of the products were ~~identified~~ elucidated on the basis of analysis and spectral properties. The major product analyzed for $C_{35}H_{36}O_{11}Fe_2$ and is soluble in both polar and non-polar solvents. Its infrared spectrum (KBr disc - Figure 5) exhibited not only the characteristic strong terminal metal carbonyl bands at 2038(s), 1974(s), 1967(s) and 1950(m) cm.$^{-1}$ but also a strong band at 1760 cm.$^{-1}$ due to bridging metal carbonyl groups (lactone carbonyl stretching occurred at 1780 cm.$^{-1}$). The complexes, cyclopentadienyl-iron dicarbonyl dimer (XXXIX)[88,153] and the tetrahydroindene-iron dicarbonyl dimer (XL)[89] show bridging metal carbonyl absorptions at 1756 and 1754 cm.$^{-1}$, respectively. The major complex from santonin showed an ultraviolet absorption maximum at 230.0 mμ (log ε = 4.20 in methylene chloride), so that the structure XXXIV seems likely.



XXXIX

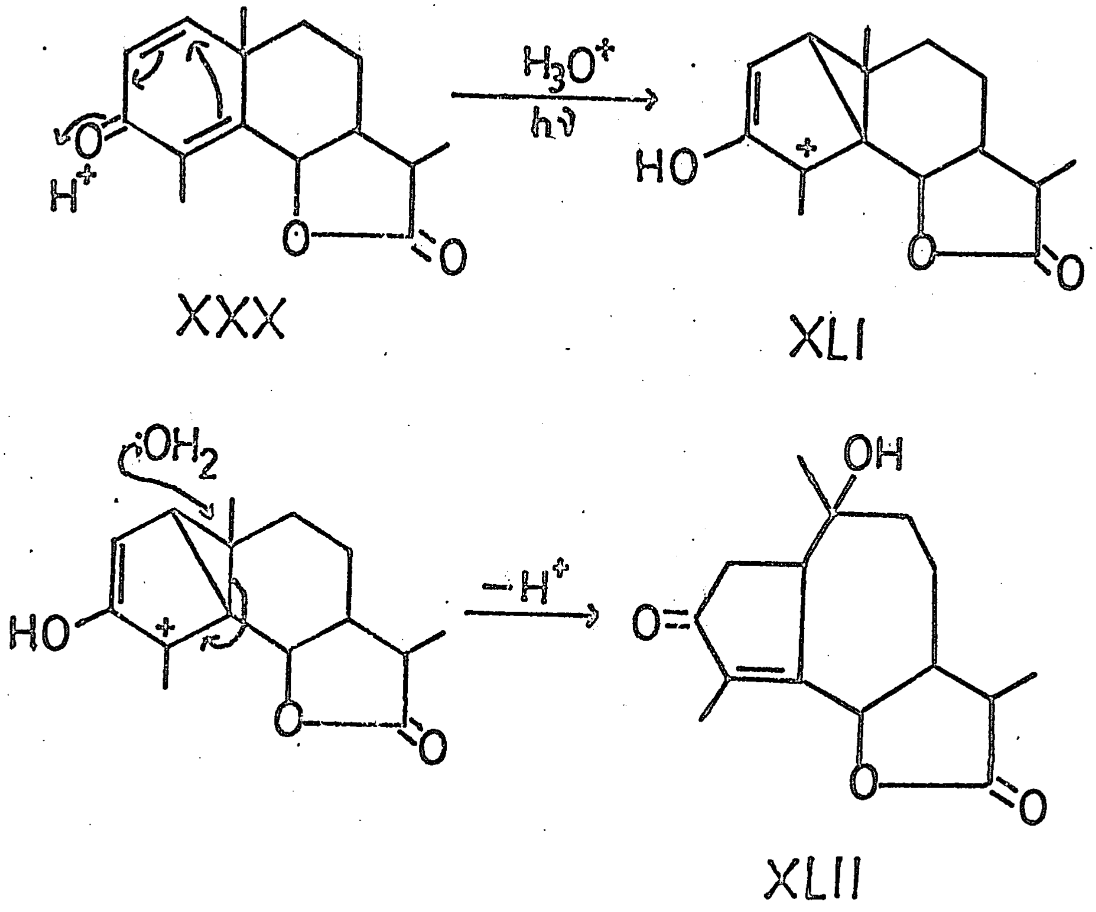


XL

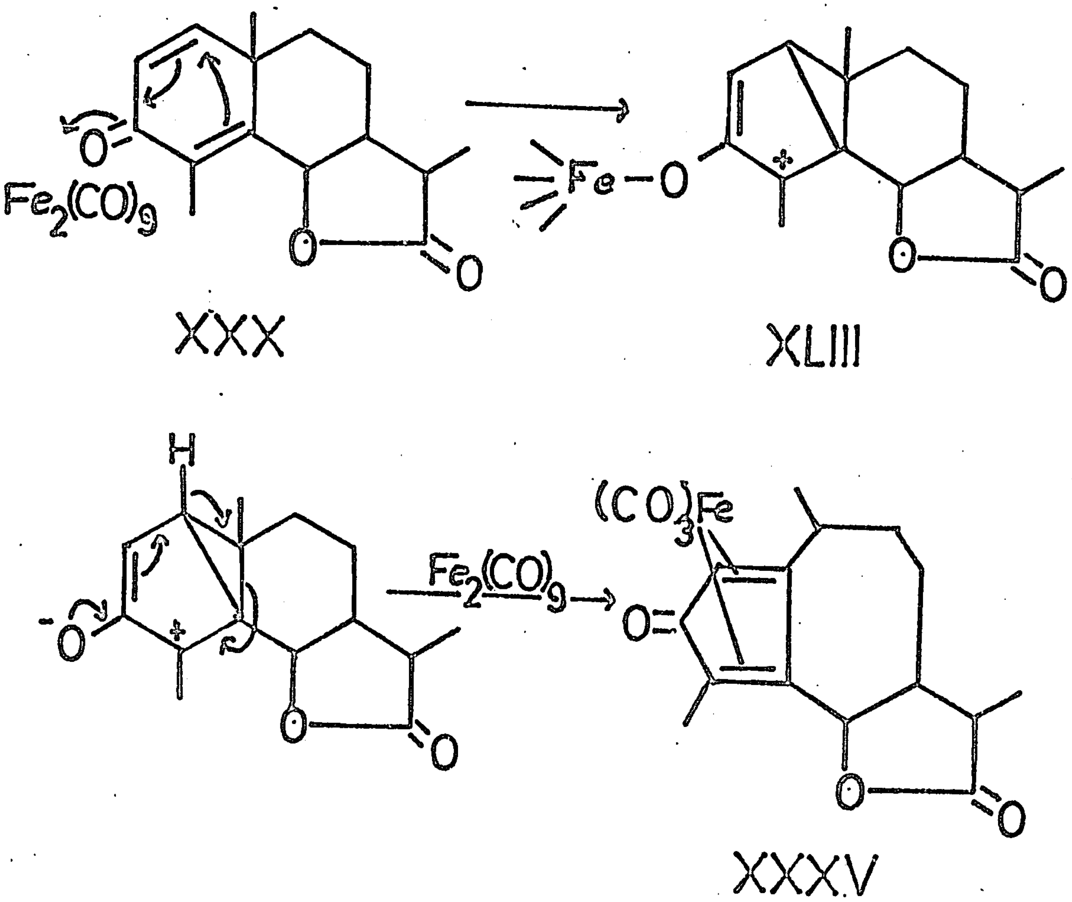
The minor product, soluble in polar but not in non-polar solvents, analyzed for $C_{18}H_{18}O_6Fe$. The infrared spectrum (KBr disc - Figure 6) showed terminal carbonyl stretching bands at 2060(s), 2022sh, 2011(s), 1995 sh, 1983(s) and carbonyl stretching at 1605 cm.$^{-1}$ These bands occur at different positions from those for the cyclohexadienone-iron tricarbonyl complexes (Table IV). Similar absorption bands were observed by Weiss and Hubel for cyclopentadienone-iron tricarbonyl complexes.[77,90] Three bands appeared in the terminal metal carbonyl stretching region at: 4.83-4.85 μ (2062-2070 cm.$^{-1}$), 4.97-4.99 μ (2004-2012 cm.$^{-1}$), and at 5.00-5.04 μ (1984-2000 cm.$^{-1}$) and the dienone carbonyl stretching occurred at 6.05-6.23 μ (1605-1653 cm.$^{-1}$). Hence the infrared spectrum of the minor product indicated a cyclopentadienone type complex. The ultraviolet absorption spectrum of the complex in absolute ethanol showed only end absorption down to 203 mμ, with a shoulder at 223 mμ, also indicative of a cyclopentadienone complex.

Due to the low yield of the minor product, it was necessary to take the nuclear magnetic resonance spectrum ($CDCl_3$) in a microtube. The resolution was not good but certain features were notable. Absorption occurred at 1.04 p.p.m. which can be ascribed to a CH_3-C-C=C type of system.[91] Absorption at 1.38 p.p.m. and 2.23 p.p.m. can be assigned to the methyl groups of the lactone and dienone rings respectively of structure XXXV. In santonin, by comparison, the methyl groups in the lactone ring and at the 4-position occur at 1.33 and 2.14 p.p.m. respectively, while the protons of the angular methyl group exhibit a singlet at 1.21 p.p.m. Because of the weak spectrum, the peak expected from the lone olefinic hydrogen of XXXV could not be observed. However, on the basis of the available N.M.R. data, structure XXXV seems very probable for the minor product from santonin.

The mechanism of the formation of the cyclopentadienone complex can be rationalized by analogy with the photochemical reactions of santonin. Photolysis of santonin in aqueous acid media results in the formation of isophotosantonic lactone as the major product.[92,93] The



mechanism of the reaction apparently involves the cyclopropyl intermediate (XLI) which on cleavage of the C_5-C_{10} bond, reacts by nucleophilic attack of solvent at C_{10}.[94] Diiron enneacarbonyl apparently acts as a Lewis acid (further examples are given on pp. 56, 85) and hence formation of a similar cyclopropyl intermediate (XLIII) can be visualized. However,



since the reaction is carried out in an inert solvent (benzene) rather than a nucleophilic solvent (aqueous acetic acid), the C_{10} carbonium ion formed by cleavage of the 5,10-bond cannot stabilize itself by reaction with solvent, and instead reacts by a hydride transfer, as shown. The cyclopentadienone formed would ordinarily be unstable[95] but in the presence of the iron carbonyl can form the stable iron tricarbonyl complex XXXV.[77,90]

A most peculiar reaction occurred when a mixture of santonin and iron pentacarbonyl were refluxed in butyl ether for twelve hours. Routine purification of the crude product gave bis(2-ethylhexyl)-o-phthalate. The structure of the ester was supported by spectral evidence. The infrared spectrum (neat) showed carbonyl stretching of an ester at 1725 cm.$^{-1}$ and out-of-plane bending of an o-substituted phenyl at 747 cm.$^{-1}$ The ultraviolet spectrum exhibited an absorption maximum at 224.0 mμ (in isooctane), identical with the spectrum of an authentic sample. The N.M.R. spectrum (in CCl_4) was also identical with that obtained from bis(2-ethylhexyl)-o-phthalate. A parent peak was observed at 390 m/e units in the mass spectrum, in agreement with the assigned structure.

The knowledge that bis(2-ethylhexyl)-o-phthalate is used as diffusion pump oil makes one very cautious to accept the results described in the previous paragraph. However, no santonin was recovered from the reaction and furthermore the experimental conditions seemed to exclude contact of the reaction mixture with diffusion pump oil. When cholesta-5,7-dien-3β-ol was reacted with iron pentacarbonyl in the same dry butyl ether, only the diene-iron tricarbonyl complex (XVIII) was obtained.

When santonin-iron tricarbonyl (XXXI) was heated in butyl ether, the diester (XXXVI) was the only isolable product. Hence, it appears that the complex is an intermediate in the reaction of santonin and the metal carbonyl in butyl ether. In summary, bis(2-ethylhexyl)-o-phthalate seems to be an authentic product from the described reactions and not obtained from an external source.

III. Reactions of Iron Pentacarbonyl with Different Functional Groups

A. N-Oxides, Azoxy Compounds, and Nitrones

In a paper concerned with the reaction of oxides of organic nitrogen, sulfur, phosphorus and arsenic compounds with iron carbonyls to form ionic complexes (see p. 12), Hieber and Lipp[36] noted that pyridine-N-oxide reacts with iron pentacarbonyl at high temperature to form pyridine and iron oxide. However, neither experimental conditions nor references were given in this paper and no subsequent reports have appeared on this reaction. Hence, it was decided to investigate the possibilities of the general deoxygenation of N-oxides with iron pentacarbonyl.

It was found that, under the appropriate conditions, the metal carbonyl can be a useful reagent for the deoxygenation of heterocyclic N-oxides. The procedure involved is very simple (see EXPERIMENTAL) and gives yields of 51.8-79.1% of the parent amines (Table VI). This method is superior to some others reported in the literature (e.g. sulfur dioxide).[96]

The results obtained with the N-oxides led to an investigation of the deoxygenation of other functional groups with iron pentacarbonyl.

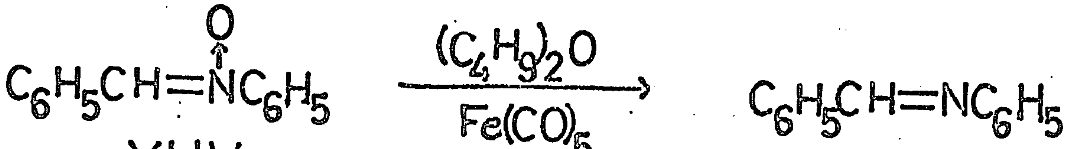
TABLE VI

YIELDS OF PRODUCTS FROM DEOXYGENATION OF N-OXIDES WITH IRON PENTACARBONYL IN BUTYL ETHER

N-Oxide	Yield of Deoxygenated Product %	Boiling Point °C	Boiling Point (Lit.)[3] °C
Pyridine	79.1	113-115	115
2-Picoline	62.2	129-131	128
4-Picoline	78.1	143-144	143
4-Methoxypyridine	51.8	193-195	191
Quinoline	60.1	236-238	237.7

Azoxybenzene could be readily deoxygenated to azobenzene by treatment with the metal carbonyl in butyl ether. (Butyl ether was employed as a solvent for this and other described reactions because of its fairly high boiling point (142°C) and because of the ability of many compounds to dissolve in it when hot.) Similarly, 2,2'-dimethylazobenzene was obtained from the corresponding azoxy compound in 65.0% yield. Optimum yields of azo compound were obtained using 0.8-1.0/1.0 mole ratios of metal carbonyl to azoxy compound.

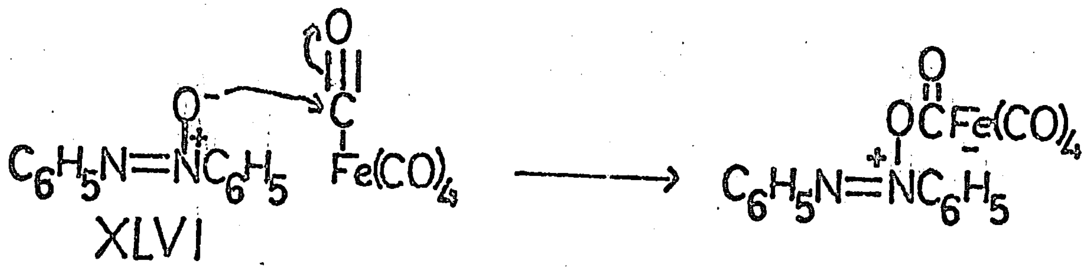
The behavior of the nitrone, α-phenyl-N-phenylnitrone (XLIV) towards iron pentacarbonyl was investigated. N-Benzylideneaniline (XLV) was obtained in 60.7% yield as a result of the deoxygenation of the nitrone.

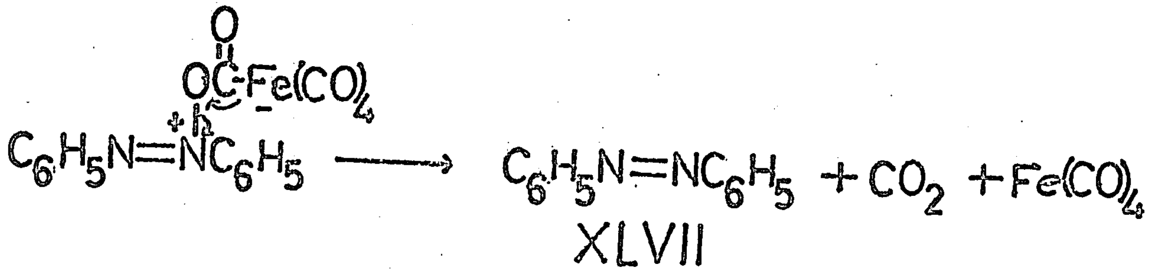


$$\mathrm{C_6H_5CH{=}\overset{\overset{O}{\uparrow}}{N}C_6H_5} \xrightarrow[\mathrm{Fe(CO)_5}]{\mathrm{(C_4H_9)_2O}} \mathrm{C_6H_5CH{=}NC_6H_5}$$

XLIV XLV

The deoxygenations of azoxybenzene and pyridine-N-oxide are accompanied by evolution of one equivalent amount of carbon dioxide, detected by bubbling the gas through a solution of barium hydroxide. A mechanism involving attack of the oxide on a terminal carbonyl of iron pentacarbonyl followed by elimination of carbon dioxide is proposed. The iron tetracarbonyl formed can trimerize to triiron dodecacarbonyl or decompose to iron oxide, whose formation was observed in both the investigations reported here and those by Hieber and Lipp.[36]

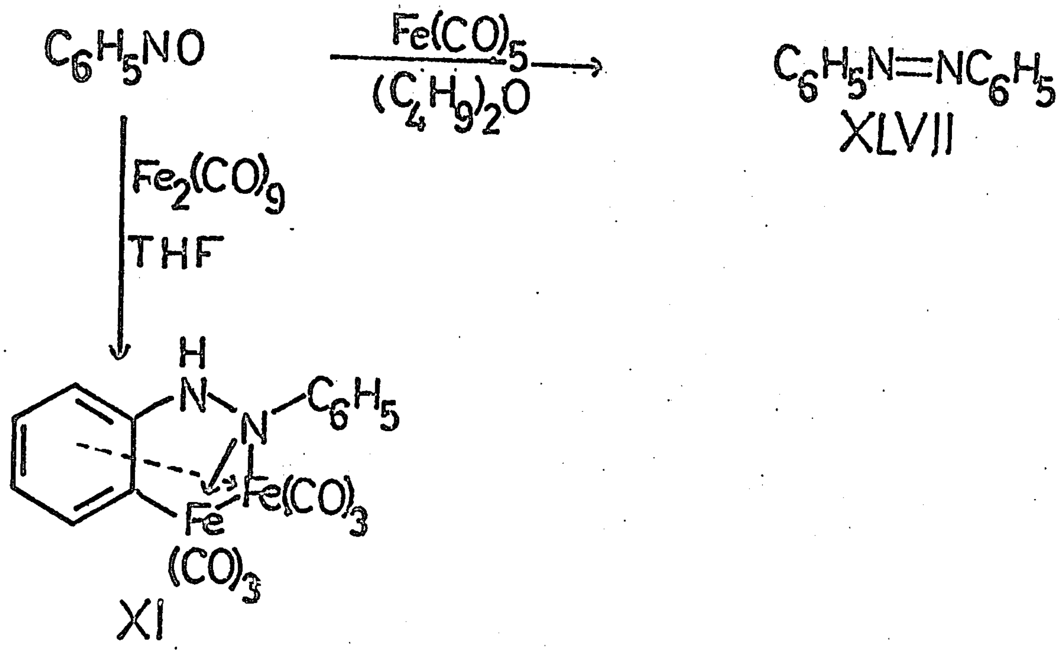




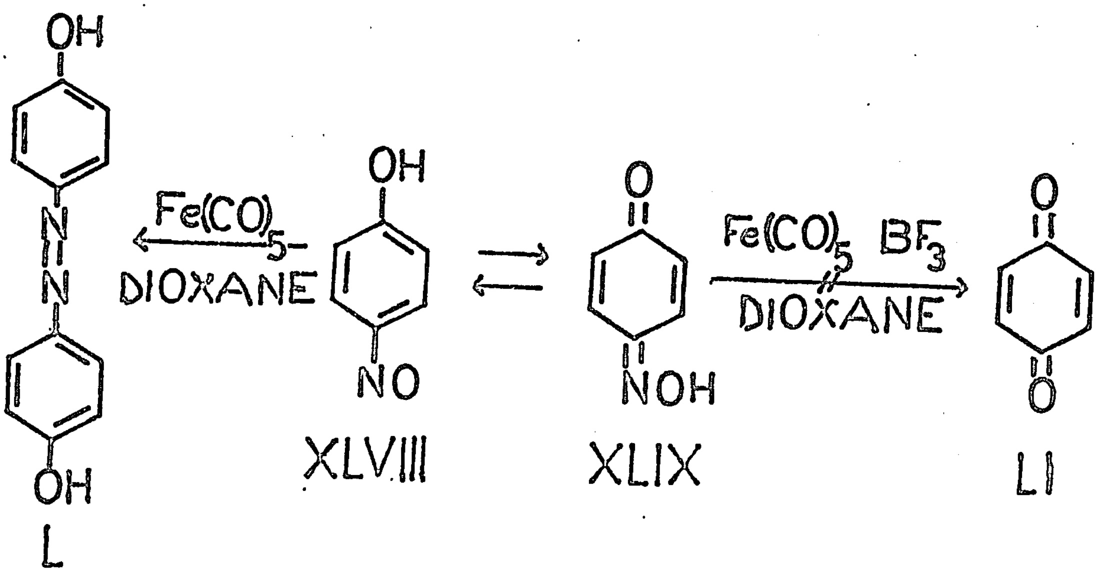
A similar mechanism can be written for the deoxygenation of α-phenyl-N-phenylnitrone.

B. Nitroso Compounds

Nitrosobenzene could be deoxygenated to azobenzene in 75% yield by refluxing equimolar quantities of nitroso compound and iron pentacarbonyl in butyl ether. When a mixture of nitrosobenzene and diiron enneacarbonyl was stirred in anhydrous tetrahydrofuran under nitrogen for twelve hours at room temperature, complex XI, previously prepared by Pauson et al[42] by photolysis of a mixture of azobenzene and iron pentacarbonyl (see p. 15) could be obtained in 11.0% yield. It is possible that nitrosobenzene could be reduced to azobenzene by using a smaller amount of diiron enneacarbonyl.

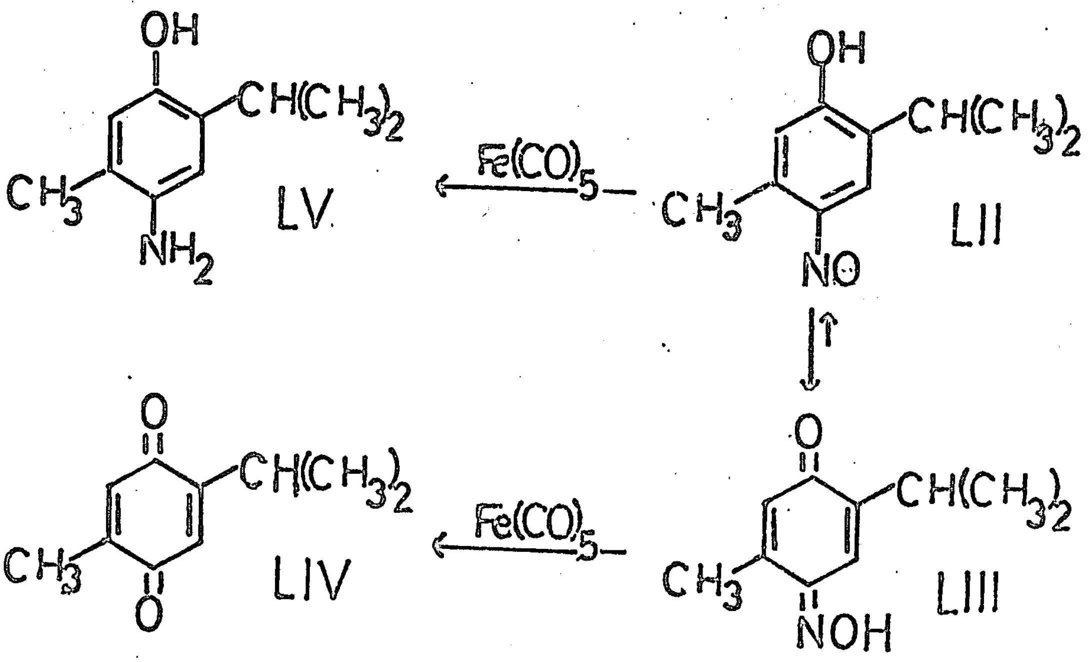


Nitrosophenols exhibited interesting behavior towards the metal carbonyl. *p*-Nitrosophenol has been shown, by near infrared[97] and nuclear magnetic resonance[98] experiments, to exist only to the extent of 14-17% as the nitroso form (XLVIII) in dioxane solution, the remainder being the quinone-monoxime tautomer (XLIX). However, a 40.9% yield of



4,4'-dihydroxyazobenzene (L) was obtained when a mixture of the nitrosophenol and iron pentacarbonyl were refluxed in dioxane for one day. Butyl ether could not be used as the solvent for the reaction because of the decomposition of the nitrosophenol below 140°C.[99] When the reaction was repeated in the presence of a catalytic amount of boron trifluoride etherate, essentially the same yield of azo compound was obtained. No *p*-benzoquinone (LI) formation was detected. This was unexpected since the quinone-monoxime form is the major tautomer of *p*-nitrosophenol and therefore deoximation seemed likely, particularly in the presence of boron trifluoride (p. 73).

A substituted nitrosophenol was then investigated. 5-Methyl-4-nitroso-2-isopropylphenol has been shown, by the ultraviolet spectra of its solutions in alcohol or dioxane,[100] to exist almost solely in the



quinone-monoxime form (LIII). In this case, reaction with iron pentacarbonyl in butyl ether produced a low yield of two products: 5-methyl-4-amino-2-isopropylphenol (LV) in 17.6% yield and 5-isopropyl-2-methyl-1,4-benzoquinone (LIV) in 10.7% yield. The yield of the two products changed when the reaction was repeated in the presence of boron trifluoride. Here, the yield of quinone increased to 19.4% while that of amine was reduced to 6.0%.

These results seem to indicate that the rate of deoxygenation of the nitrosophenol is much greater than the rate of deoximation of the quinone-monoxime tautomer. If the rates of the two processes were the same, a substantial amount of deoximation ~~was~~ would be expected to occur, particularly in the presence of boron trifluoride.

C. Nitro Compounds

As mentioned previously (p. 13), von Gustorf and Jun[38] reported that no thermal reaction occurred between nitrobenzene and iron pentacarbonyl. However, we have found that when nitrobenzene is treated with iron pentacarbonyl in anhydrous butyl ether, reduction takes place, the nature of the product depending upon the quantity of metal carbonyl used.

When equimolar quantities of iron pentacarbonyl and nitrobenzene were refluxed in anhydrous butyl ether for 18-24 hours, crude azoxybenzene was obtained. Chromatography on Florisil gave on elution with petroleum ether: azobenzene (XLVII) in 3.3% yield and azoxybenzene (XLVI) in 63.7%

yield. Essentially the same yield was obtained when the reaction was carried out for 36 hours. Using a 1.4/1.0 mole ratio of iron pentacarbonyl to nitrobenzene, azobenzene was obtained in 76% yield, no azoxybenzene formation being observed. Using a large excess of iron pentacarbonyl, complex XI was obtained. The latter was obtained more conveniently by stirring nitrobenzene (1.0 mole) with diiron enneacarbonyl (1.4 mole) in anhydrous tetrahydrofuran.

The scope and limitations of this deoxygenation reaction were then investigated with a series of aromatic nitro compounds. The products from the various nitrobenzenes, their yields, and their physical properties are presented in Tables VII and VIII. The mole ratio of metal carbonyl to nitro compound was 1.4 to 1.0. Use of a 1:1 mole ratio gave the azoxy rather than the azo compound. For example, 2,2'-dimethylazoxybenzene was obtained in 59.3% yield from o-nitrotoluene under the described conditions.

Reasonable yields of azo compound were obtained from para-substituted nitrobenzenes having electron-releasing groups (H,CH_3,OCH_3,F). An exception occurred in the case of the p-dimethylamino substituent, presumably because the metal carbonyl can behave as a Lewis acid towards the dimethylamino group and thus alter its electronic properties: this compound gave p-amino-N,N-dimethylaniline. A substantially lower yield of azo compound resulted when the nitrobenzene had an electron-attracting para substituent. For example, p-nitrobenzonitrile gave the azo compound in 20.1% yield and p-aminobenzonitrile in 11.3% yield. p-Nitrophenol and

TABLE VII

PRODUCTS FROM THE REACTION OF SUBSTITUTED NITROBENZENES (1.0 MOLE) WITH IRON PENTACARBONYL (1.4 MOLE)

Substituent	Products	Yield %	M.P. or B.P. (mm.) °C (OBSD.)	M.P. or B.P. (mm.) °C (LIT.)
H	Azobenzene	76.0	66.0-68.0	68.0[3]
o-CH_3	2,2'-Dimethylazobenzene	67.2	55.0-56.0	55.0-56.0[3]
	o-Toluidine	13.1	196-198(760)	199.8(760)[3]
m-CH_3	3,3'-Dimethylazobenzene	48.4	52.5-53.5	54.0-55.0[3]
	m-Toluidine	5.7	199-201(760)	203(760)[3]
p-CH_3	4,4'-Dimethylazobenzene	67.0	142.0-144.0	144[3]
o-C_2H_5	2,2'-Diethylazobenzene	38.6	47.0-48.0	46.5[101]
	o-Ethylaniline	34.9	213-216(760)	215-216(760)[3]
o-OCH_3	o-Methoxyaniline	73.9	222-224(760)	225(760)[3]
m-OCH_3	3,3'-Dimethoxyazobenzene	36.9	74.5-75.5	73-74[102]
p-OCH_3	4,4'-Dimethoxyazobenzene	43.4	161.0-163.0	161.0-162.0[103]
p-F	4,4'-Difluoroazobenzene	67.0	100.0-101.0	101.0[104]
o-C_6H_5	2-Aminobiphenyl	58.3	47.0-49.0	49.3[3]
	Carbazole	14.7	244.0-246.0	246.0[3]
m-$N(CH_3)_2$	3-Amino-N,N-dimethylaniline	60.1	265.0-267.0 (760)	268-270(760)[3]
p-$N(CH_3)_2$	4-Amino-N,N-dimethylaniline	76.6	38.0-41.0	37[3]
p-CN	4,4'-Dicyanoazobenzene	20.1	266.0-268.0	268.0-270.0[105]

TABLE VII (cont'd)

Substituent	Products	Yield %	M.P. or B.P. (mm.) °C (OBSD.)	M.P. or B.P. (mm.) °C (LIT.)
	p-Aminobenzonitrile	11.3	86.0-89.0	86.0[3]
p-OH	--	--	--	--
p-COOH	--	--	--	--
o-NO_2	2,2'-Diaminoazobenzene	11.1	118.0-120.0	123[3]

TABLE VIII

ULTRAVIOLET ABSORPTION MAXIMA (IN ETHANOL) OF AZO COMPOUNDS FORMED FROM REACTION OF NITROBENZENES WITH IRON PENTACARBONYL

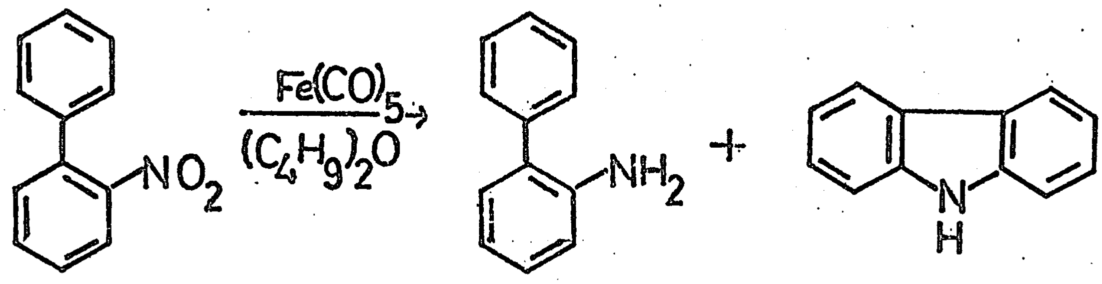
Compound	max, mμ (log ε)	max, mμ (LIT.) (log ε)
Azobenzene	317.0(4.22),442.0(2.77)	316.0(4.2),441.0(2.8)[106]
2,2'-Dimethylazobenzene	233.5(4.01),331.0(4.22),455.0(2.75)	232(4.0),332(4.2),461(2.7)[102]
3,3'-Dimethylazobenzene	232.0(4.01),322.0(4.18),441.0(2.77)	234(4.0),321(4.2),439(2.8)[102]
4,4'-Dimethylazobenzene	236.0(4.22),332.0(4.30),434(2.87)	235(4.0),340(4.3),434(2.9)[102] 235(4.2),333(4.3)[107]
2,2'-Diethylazobenzene	233.5(3.94),331.0(4.15),454.0(2.73)	235(4.05),330(4.17),460(2.75)[108] 240(4.06),336(4.15),446(2.92)[109]
3,3'-Dimethoxyazobenzene	240.0(4.04),315.0(4.11),432(2.83)	243(4.1),316(4.1),435(2.8)[102]
4,4'-Dimethoxyazobenzene	240.5(4.12),355.0(4.40),430.0(3.42)	355(4.40),430(3.34)[103]
4,4'-Difluoroazobenzene	227.0(4.07),232.0(4.07),323.0(4.19),433.0(2.73)	227(4.12),325(4.22),432(2.74)[110]
4,4'-Dicyanoazobenzene	230.0(4.13),325.0(4.37),340.0sh(4.29),441.0(2.98)	----
2,2'-Diaminoazobenzene	450.0(4.05)	----

p-nitrobenzoic acid were recovered unchanged when treated with the metal carbonyl either in the absence of a catalyst or in the presence of boron trifluoride etherate or triethylamine. This is in marked contrast to the reactivity of p-nitrosophenol, which formed the azo compound in reasonable yield.

Azo compounds were also obtained from m-nitrotoluene and m-nitroanisole, although in lower yields than the corresponding para derivatives. 3-Nitro-N,N-dimethylaniline gave the amino compound with no azo formation being observed.

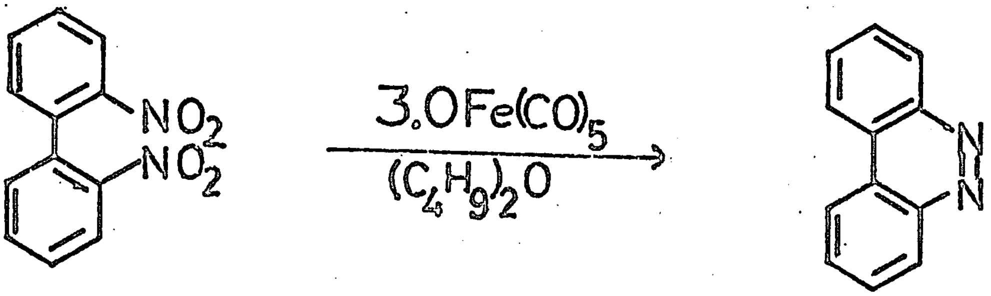
Unique behavior was exhibited by ortho substituted nitrobenzenes. When o-nitrotoluene was refluxed with iron pentacarbonyl in butyl ether for 24 hours, 2,2'-dimethylazobenzene was obtained as the major (67.2%) and o-toluidine as the minor product (13.1% yield). Essentially the same yields resulted when the reaction was carried out in the more polar solvent, butryonitrile. The sensitivity of the reaction to steric effects was shown by the reaction of o-ethylnitrobenzene, which gave approximately equal amounts of azo and amino compounds. However, o-methoxynitrobenzene gave only the amine when the reaction was conducted in either butyl ether (74%) or n-octane (58%). Since the ethyl and methoxyl groups are approximately the same size, the nature of the products is not dependent only on steric effects.

2-Aminobiphenyl (LVII) was obtained as the major product from 2-nitrobiphenyl (LVI) along with some of the insertion product, carbazole.



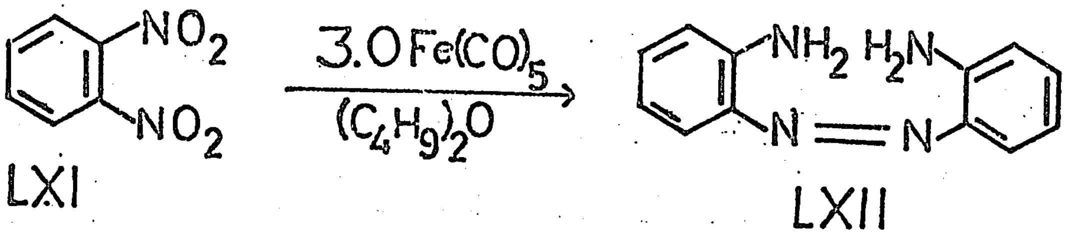
LVI LVII LVIII

2,2'-Dinitrobiphenyl (LIX) refluxed with a 3.0 mole excess of iron pentacarbonyl in butyl ether formed benzo[c]cinnoline (LX) in 64.8% yield. No amine formation was observed.



LIX LX

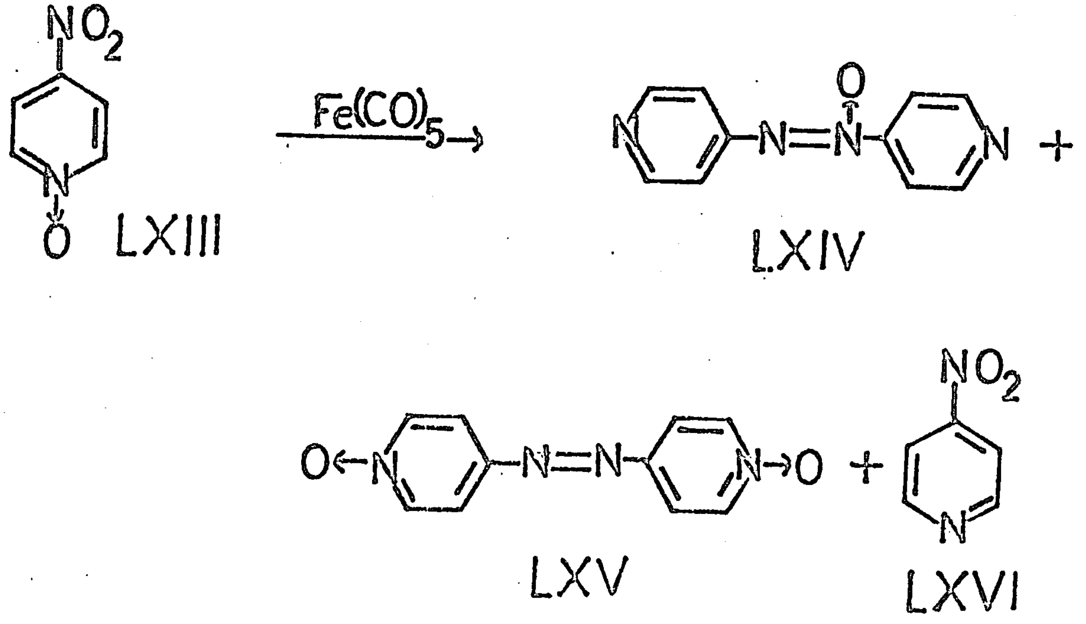
o-Dinitrobenzene underwent both reduction and coupling to give a low yield of 2,2'-diaminoazobenzene (LXII), substantial polymerization occurring.



LXI LXII

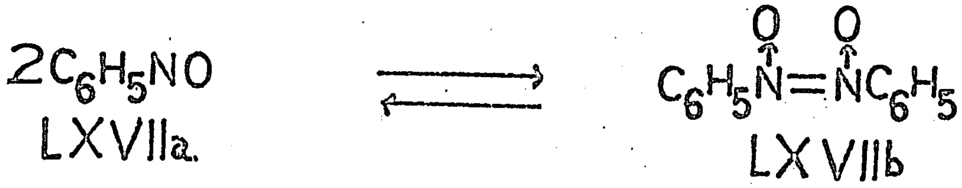
A 70.0% yield of pure 1-aminonaphthalene was obtained from the deoxygenation of 1-nitronaphthalene with iron pentacarbonyl. In contrast, 1,8-dinitronaphthalene produced only trace amounts of 1,8-diaminonaphthalene when the dinitro compound was treated with the metal carbonyl (3.0/1.0 mole ratio of iron carbonyl/dinitro compound). No other products were detected. Lowering the ratio of metal carbonyl to nitro compound used only resulted in producing a mixture of starting material and amines.

4-Nitropyridine-1-oxide gave 4,4'-azoxypyridine (LXIV) in 22% yield and traces of 4,4'-azoxypyridine-1,1-dioxide (LXV) and 4-nitropyridine (LXVI). Evidently, the metal carbonyl exhibits no great selectivity towards amine oxide or nitro groups.



LXIII LXIV LXV LXVI

The mechanism of deoxygenation of nitroso and nitro compounds is more difficult to rationalize in terms of the products observed in the reactions than the mechanism of deoxygenation of amine oxides or azoxy compounds. Nitrosobenzene monomer exists in equilibrium with its dimer (LXVIIb) in various solvents at room temperature.[111] If the dimeric



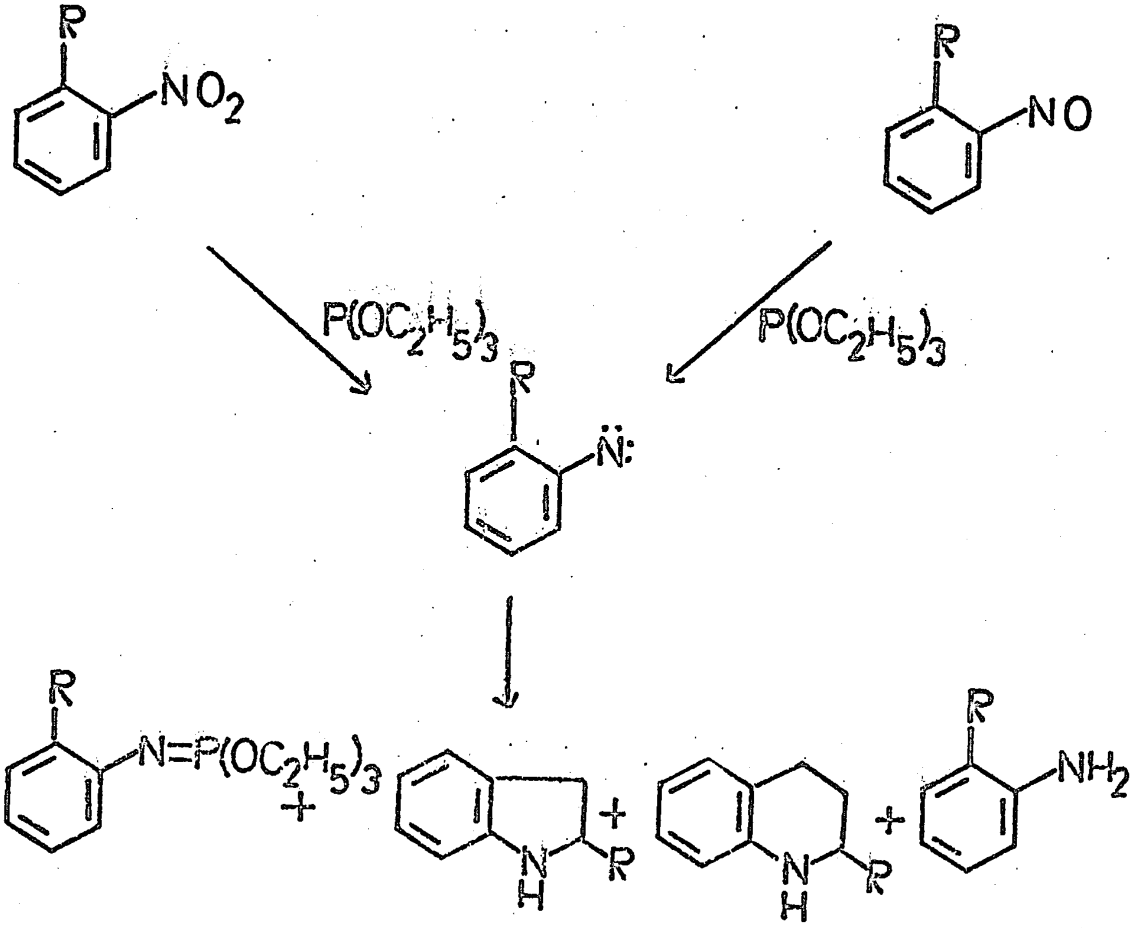
$$2C_6H_5NO \rightleftharpoons C_6H_5\overset{\overset{O}{\uparrow}}{N}=\overset{\overset{O}{\uparrow}}{N}C_6H_5$$

LXVIIa. LXVIIb

form is present to some extent at the reflux temperature of the reaction, then a mechanism analogous to that described for the deoxygenation of azoxybenzene could explain the formation of azobenzene. About two moles of carbon dioxide are evolved for each mole of azo compound formed, indicating the overall reaction:

$$2C_6H_5NO + 2Fe(CO)_5 \longrightarrow C_6H_5N=NC_6H_5 + 2CO_2 + 2Fe(CO)_4$$

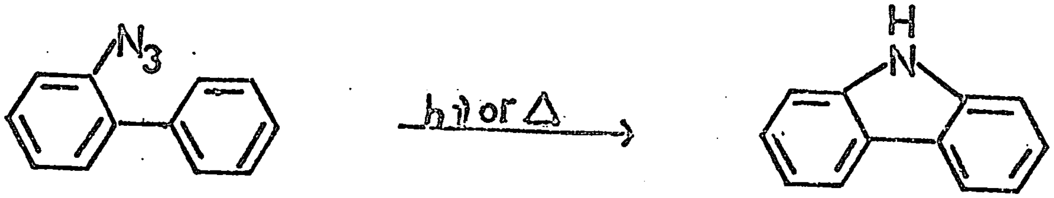
The deoxygenation of nitrobenzene to azoxybenzene and azobenzene could occur in a similar manner, assuming initial deoxygenation to nitrosobenzene. The formation of amines is most plausibly explained by a nitrene intermediate.[112] The deoxygenation of o-alkylnitrobenzenes and o-alkylnitrosobenzenes by trivalent phosphorus compounds has been postulated to proceed via a discrete nitrene intermediate, to give amines among other compounds.[113]



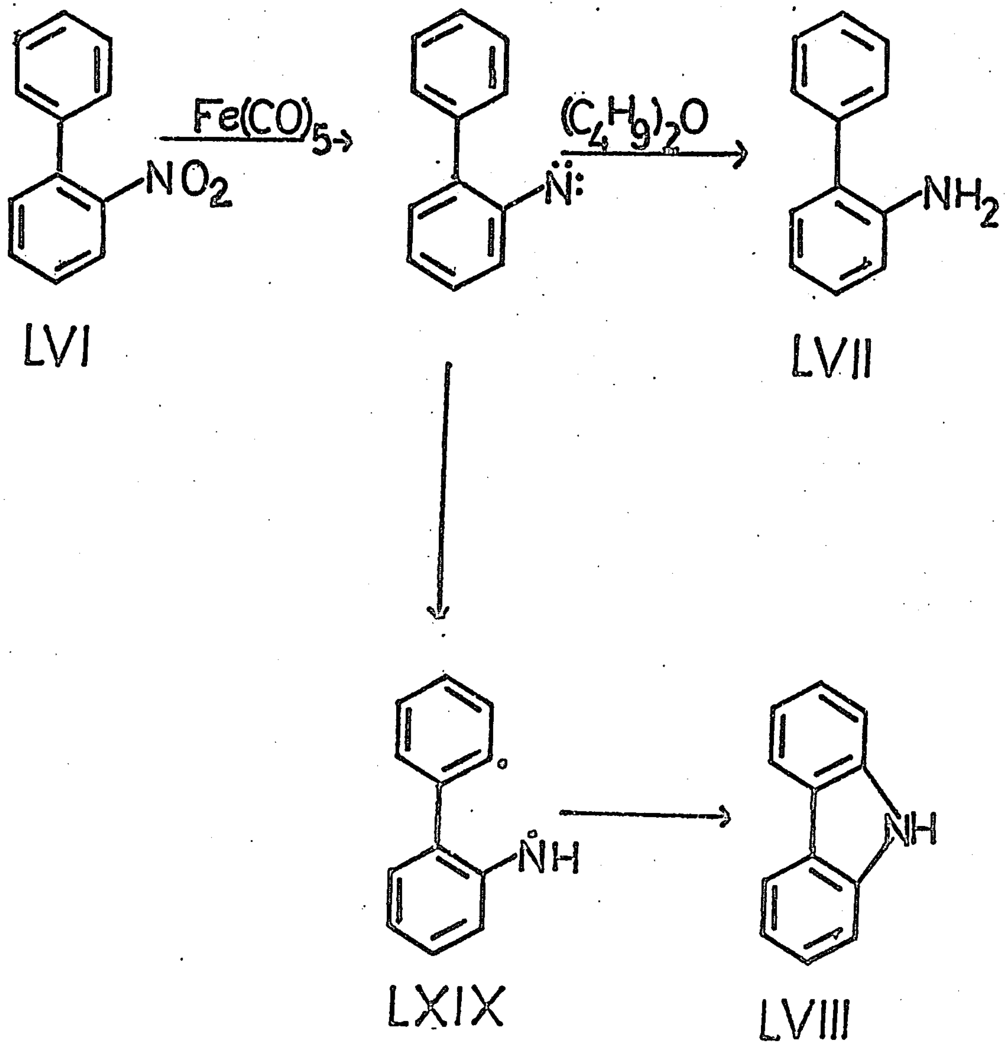
Similar intermediates were postulated by Horner and co-workers[114] for the photolysis of aryl azides to azo compounds. They noted that electron-releasing groups in the aryl ring increased the yield of azo compound. For example, phenyl azide, in dimethylsulfoxide, gave azobenzene in trace amounts, while p-tolyl azide gave the azo compound in 82.5% yield.

$$ArN_3 \xrightarrow{h\nu} ArN{=}NAr$$

o-Azidobiphenyl, on heating in 1,2,4-trichlorobenzene, or on photolysis in tetrahydronaphthalene, forms carbazole in 76-77% yield.[115] Carbazole is also obtained by deoxygenation of *o*-nitro[116] or *o*-nitrosobiphenyl[117] with triethylphosphite or triphenylphosphine. The similarity in behavior of the three reactants suggests that they all generate nitrenes, since it is known that azides on thermal decomposition form nitrenes.[112] The products obtained from the deoxygenation of 2-nitrobiphenyl with iron pentacarbonyl also suggest a nitrene mechanism. The nitrene can either abstract hydrogen from solvent to give the primary aromatic amine (LVII) or insert to form LVIII.



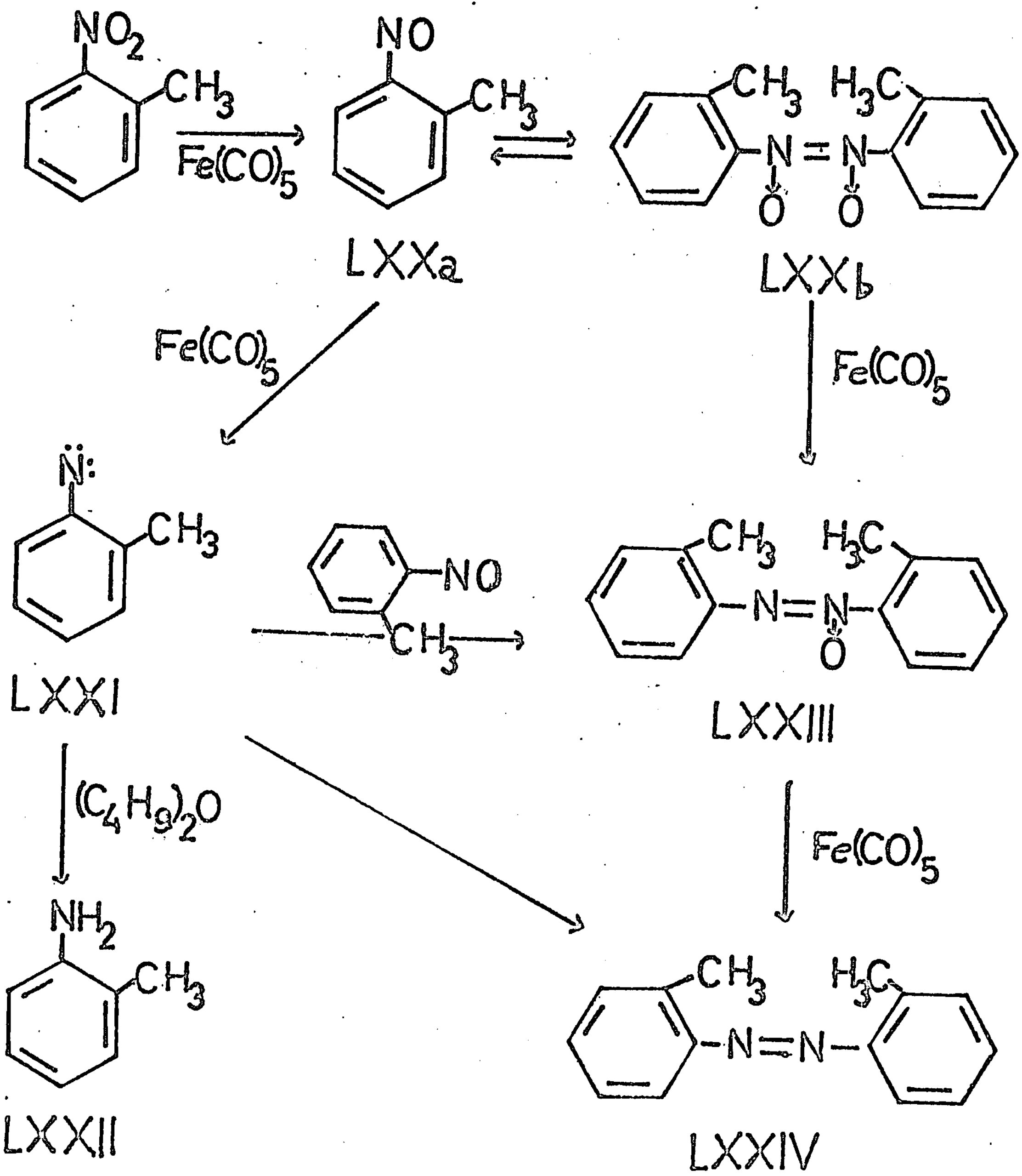
LXVIII LVIII



LVI LVII LXIX LVIII

The formation of azo compounds can be explained either by deoxygenation of the nitroso dimer, as described above, by dimerization of nitrenes, as in the photolysis of azides, or by reaction of a nitrene with a nitroso compound to give an azoxy intermediate. This is illustrated

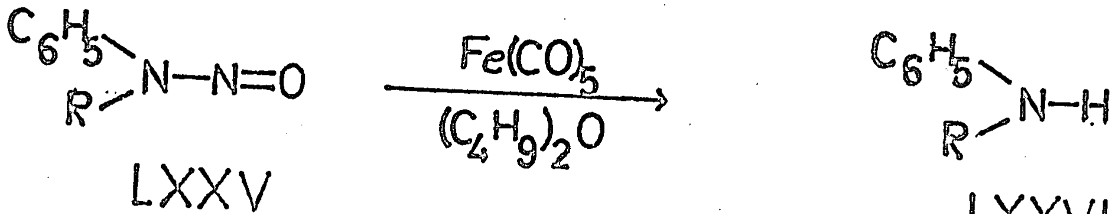
SCHEME 6


NO2
CH3
Fe(CO)5
NO
CH3
LXXa
CH3
H3C
N = N
O
O
LXXb
Fe(CO)5
Fe(CO)5
N:
CH3
LXXI
NO
CH3
CH3
H3C
N=N
O
LXXIII
(C4H9)2O
Fe(CO)5
NH2
CH3
LXXII
CH3
H3C
N=N
LXXIV

for the case of o-nitrotoluene (Scheme 6). The change in product composition with o-ethylnitrobenzene could be due to the greater steric hindrance of the nitrene, which would retard coupling to azo or azoxy compounds. The formation of some amine from p-nitrobenzonitrile may be due to the electron-withdrawing nitrile group destabilizing the electron-deficient nitrene so that it abstracts hydrogen from solvent more rapidly, and hence is less available for coupling reactions.

D. Nitrosamines

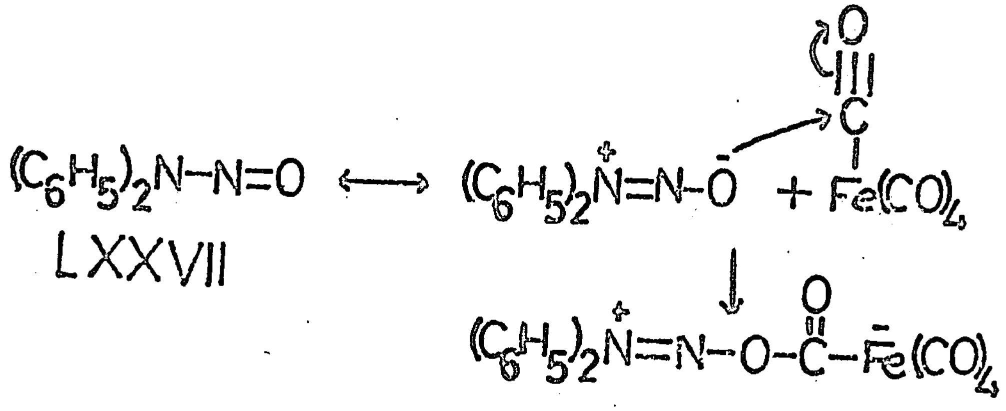
Nitrosamines can be converted to secondary amines by reduction with Raney nickel,[118] sodium amalgam in alcoholic acid[119] and by acid hydrolysis.[120] When a solution of iron pentacarbonyl (1.1 mole) and a nitrosamine (1.0 mole) having at least one phenyl group, in anhydrous butyl ether, was refluxed for two to sixteen hours, high yields (85-92%) of pure secondary amines were obtained (Table IX). The presence of a catalytic quantity of boron trifluoride etherate did not improve the yield of amine.

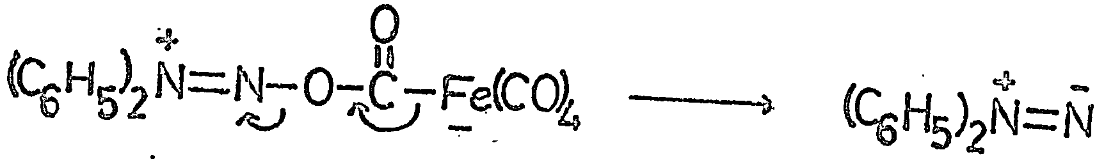


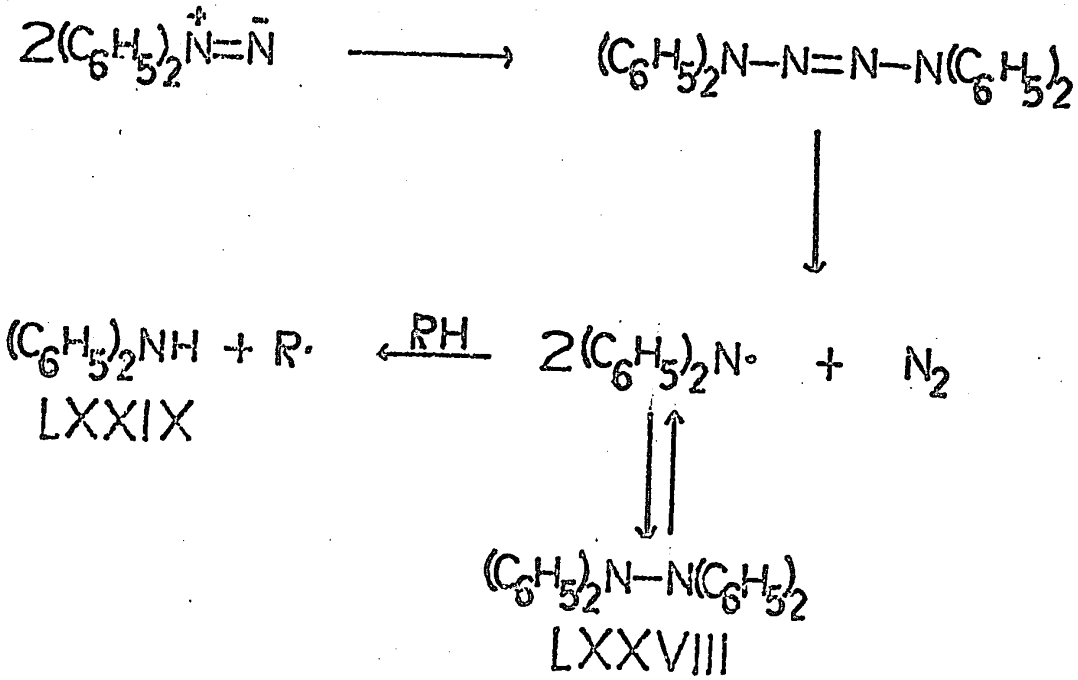
LXXV

LXXVI

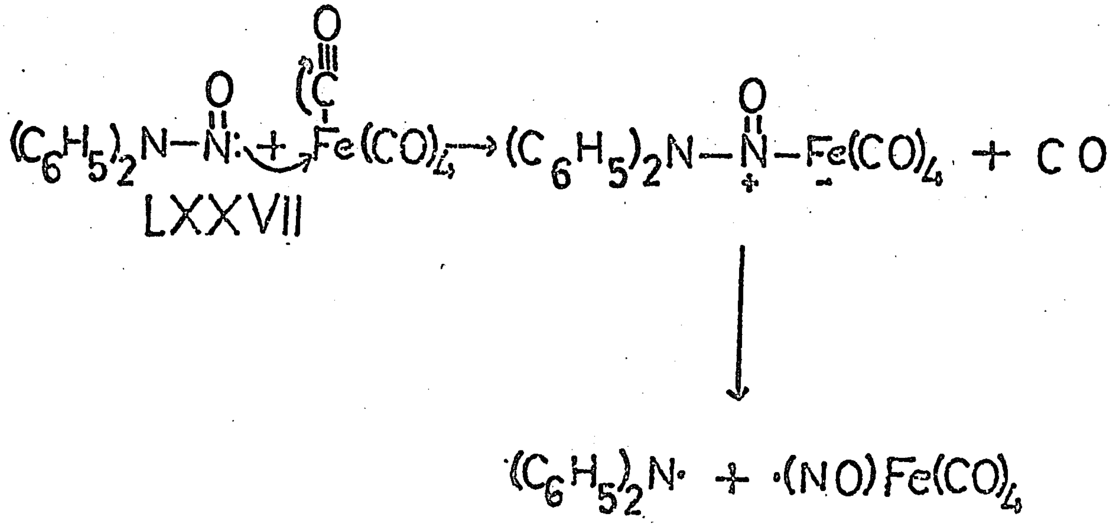
One possible mechanism for this reaction involves deoxygenation of the nitrosamine to an intermediate azamine[122] which dimerizes to a tetrazene. Since mild heating (80-120°C)[123,124] can decompose tetrazenes to nitrogen and secondary amino radicals, the reaction temperature (ca. 140°C) used for the metal carbonyl reaction is sufficient for such a process to occur. Hydrogen abstraction from solvent by the amino radicals could give rise to product. Support for this mechanism was obtained by conducting the reaction of iron pentacarbonyl and N-nitrosodiphenylamine (LXXVII) in isooctane, in which hydrogen abstraction should not occur as readily as in butyl ether.[125] In this reaction, tetraphenylhydrazine (LXXVIII) was the major product (51.6% yield), diphenylamine (LXXIX) being obtained in substantially lower yield (27.2%) than in butyl ether. Refluxing tetraphenylhydrazine in butyl ether gave diphenylamine in 87.9% yield.


LXXVII





An alternative mechanism would involve cleavage of the nitrosyl group to form the secondary amino radical and iron carbonyl nitrosyl radical, which could then form iron dicarbonyl dinitrosyl[17] by disproportionation. This mechanism would be favoured by the low N-N bond energy (39 kcal/m).[126] Analysis of the gaseous products of the reaction might distinguish between the two mechanisms.

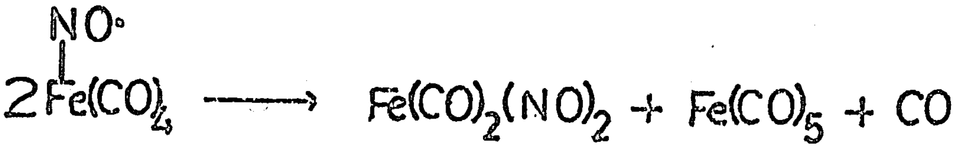


LXXVII

$$(C_6H_5)_2N-\overset{O}{\overset{\|}{N}}: + \overset{O}{\overset{\|\|\|}{C}}-Fe(CO)_4 \rightarrow (C_6H_5)_2N-\overset{O}{\overset{\|}{\underset{+}{N}}}-\underset{-}{Fe}(CO)_4 + CO$$

$$\downarrow$$

$$\cdot(C_6H_5)_2N\cdot + \cdot(NO)Fe(CO)_4$$



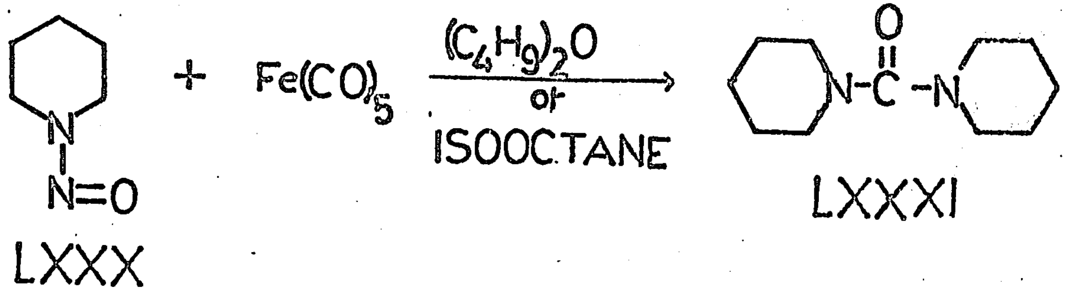
$$2\overset{NO\cdot}{\overset{|}{Fe}}(CO)_4 \longrightarrow Fe(CO)_2(NO)_2 + Fe(CO)_5 + CO$$

When the reaction was carried out on non-aromatic nitrosamines such as N-nitrosopiperidine (LXXX) and N-nitrosomorpholine no amine was obtained. Instead, the tetrasubstituted ureas, carbonyl dipiperidine (LXXXI) and carbonyl dimorpholine, were formed in yields of 48 and 57%, respectively (Table IX). The carbonyl insertion products were also obtained in slightly lower yield using isooctane as the solvent. No hydrazine formation was observed.

TABLE IX

PRODUCTS FROM THE REACTION OF NITROSAMINES WITH IRON PENTACARBONYL

Nitrosamine	Product	Yield %	M.P.orB.P. (mm) °C (OBSD.)	M.P.orB.P. (mm) °C (LIT.)
N-Nitrosodiphenylamine	Diphenylamine	91	52-54	52.8[3]
N-Nitroso-N-phenylbenzylamine	N-Phenylbenzylamine	85	36-37	36.5-36.8[3]
N-Nitroso-N-methylaniline	N-Methylaniline	90	195-197 (760)	195.2(760)[3]
N-Nitrosocarbazole	Carbazole	92	245-246	247[3]
N-Nitrosopiperidine	Carbonyl Dipiperidine	48	155-157 (15)	152-154(13)[121]
N-Nitrosomorpholine	Carbonyl Dimorpholine	57	141-143	143[121]

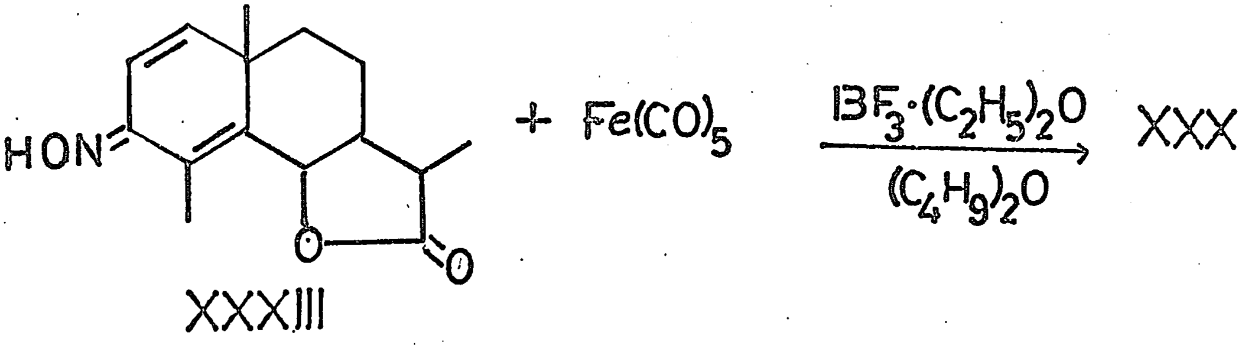


LXXX

LXXXI

E. Oximes

The parent carbonyl compound may be regenerated from an oxime by treatment of the latter in aqueous solution with sodium bisulfite,[127] levulinic or pyruvic acids,[128] or formaldehyde and concentrated hydrochloric acid.[129] However, there may be instances when it is desirable to effect this transformation under anhydrous conditions. In the previous chapter, it was shown that while the oxime of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone gave the ketone upon treatment with iron pentacarbonyl, santonin oxime reacted to form the diene-iron tricarbonyl complex (XXXII). However, treatment of santonin oxime with an approximately equimolar quantity of iron pentacarbonyl and a catalytic amount of boron trifluoride in refluxing butyl ether resulted in the formation of santonin (XXX) in 67% yield.



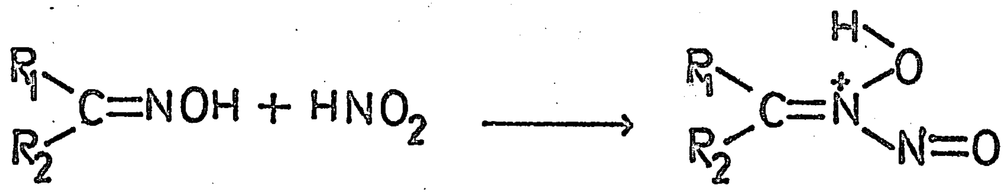
This reaction was found to be applicable to a wide variety of oximes of aldehydes and ketones of widely differing character (Table X) giving carbonyl compounds in 55-81% yield; the limitations, if any, of the reaction are not apparent. No reaction took place when the oximes were treated with a catalytic amount of boron trifluoride in butyl ether.

No carbonyl compound was regenerated by treatment of fluorenone phenylhydrazone or of N,2,6-trichloro-*p*-benzoquinoneimine with iron pentacarbonyl and boron trifluoride. Hence it seems likely that the oxygen atom of the regenerated carbonyl group comes from the oxygen atom of the oxime. These results suggest a mechanism analogous to the reaction of some oximes with nitrous acid to form carbonyl compounds and nitrous oxide.[130] Attack of nitrosonium ion upon the oximino nitrogen produces the intermediate LXXXII. Oxazirane formation and subsequent ring opening forms the products.

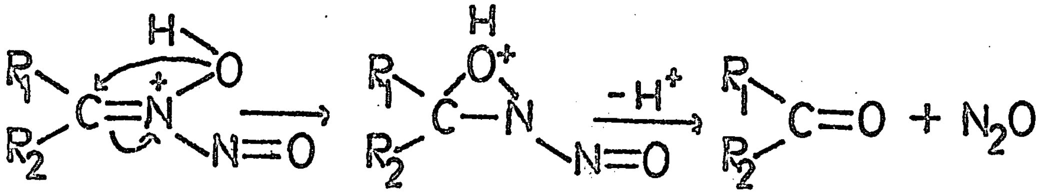
TABLE X

YIELDS OF CARBONYL COMPOUNDS FROM OXIMES

Parent Carbonyl Compound	Reflux Time (Hrs.)	Isolation Procedure	Yield %
Cyclohexanone	20	-	81
4-Methyl-4-trichloromethylcyclo-hexa-2,5-dienone	10	b	72
Fluorenone	16	a	69
Cholest-4-en-3-one	16	d	67
Santonin	18	c	67
O-Methylpodocarpinal	17	c	55



LXXXII

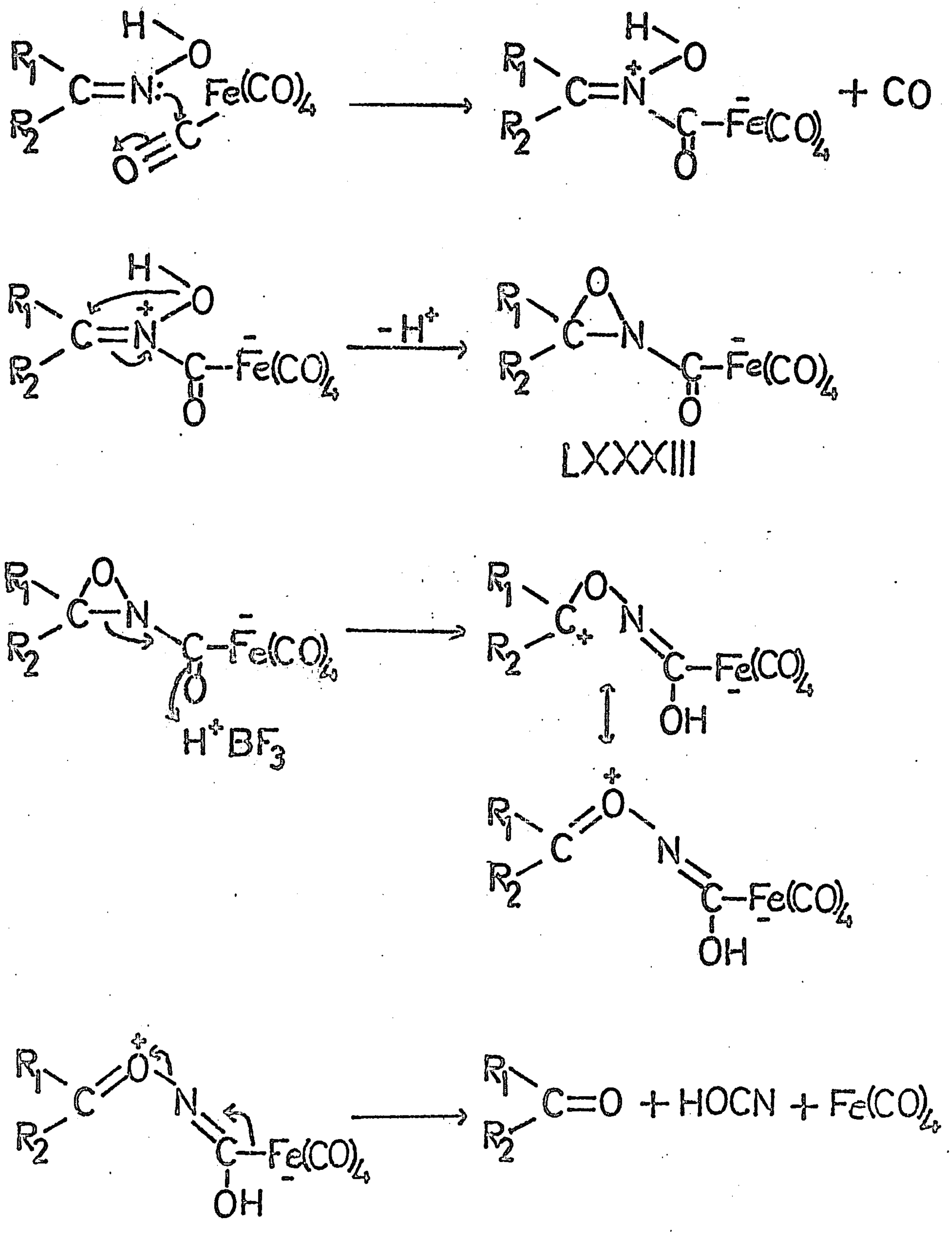


Oxazirane formation may also be postulated for the reaction of oximes with iron pentacarbonyl. Ring-opening of the oxazirane (LXXXIII) followed by cleavage of the N-O bond would give the carbonyl compound. The role of boron trifluoride etherate might be as shown (Scheme 7).

F. Amides and Thionamides.

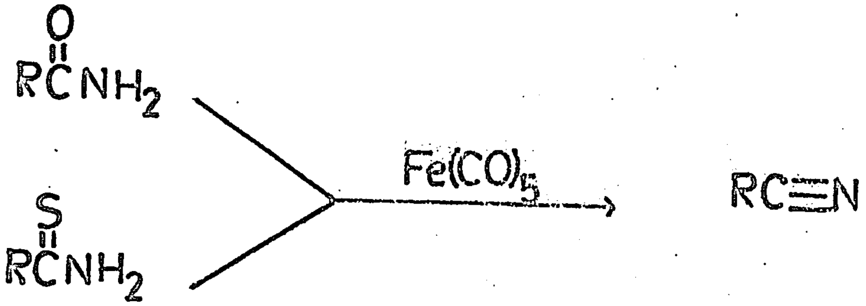
Amides and thionamides are converted by iron pentacarbonyl to nitriles. Amides have previously been converted to nitriles by phosphorus pentoxide, phosphorus pentachloride, thionyl chloride or phosphorus oxychloride[131] and thionamides by phosphorus pentoxide, phosphorus

SCHEME 7



pentasulfide or tertiary amines.[132]

When a mixture of amide or thionamide* (1.0 mole) and iron pentacarbonyl (1.6 moles) was refluxed in anhydrous butyl ether for 18 hours, the corresponding nitrile was obtained.



The yield of nitrile from a thionamide was generally about twice that from an amide (Table XI). No nitrile formation was observed when the reaction was carried out with only a catalytic amount of metal carbonyl. The yield of nitrile did not improve when the mole ratio of iron pentacarbonyl to amide was increased from 1.6/1.0 to 5.0/1.0.

The mechanism of the reaction can be rationalized as an attack of sulfur or oxygen of the reactant on the metal atom to form an imine intermediate (LXXXIV) which then, in butyl ether, can give rise to the product.

---

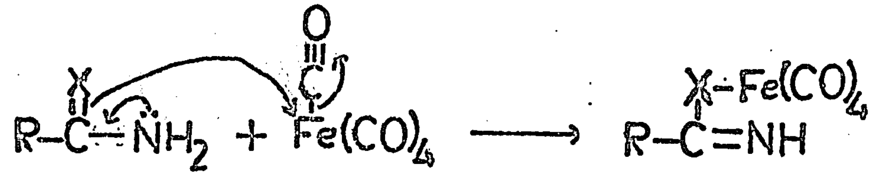
*Thionamides were kindly donated by Mr. G. Derdall.

TABLE XI

NITRILES OBTAINED FROM REACTION OF AMIDES OR THIONAMIDES WITH IRON PENTACARBONYL

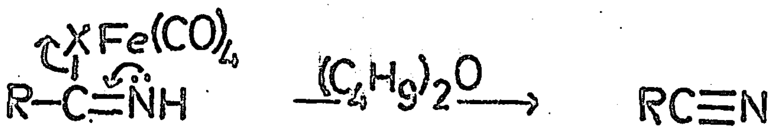
Reactant	Product	Yield %	M.P. or B.P.(mm.) °C	M.P. or B.P.(mm.)[3] °C (Lit.)
2-Phenylacetamide	Phenylacetonitrile	35.4	233-235(760)	234(760)
2-Phenylthionacetamide	Phenylacetonitrile	61.6	231-233(760)	234(760)
Benzamide	Benzonitrile	32.0	190-191(760)	191(760)
Thionbenzamide	Benzonitrile	63.9	188-190(760)	191(760)
p-Methoxybenzamide	*p*-Methoxybenzonitrile	27.5	60.0-62.0	61-62
p-Methoxythionbenzamide[a]	*p*-Methoxybenzonitrile	60.9	60.0-62.0	61-62
p-Toluamide	*p*-Tolunitrile	20.0	26.0-28.0	29.5
m-Toluthionamide	*m*-Tolunitrile	65.7	210-212(760)	212(760)

[a] N-(*p*-methoxybenzyl)-*p*-methoxythionbenzamide, m.p. 85-87°C, was obtained as a side product

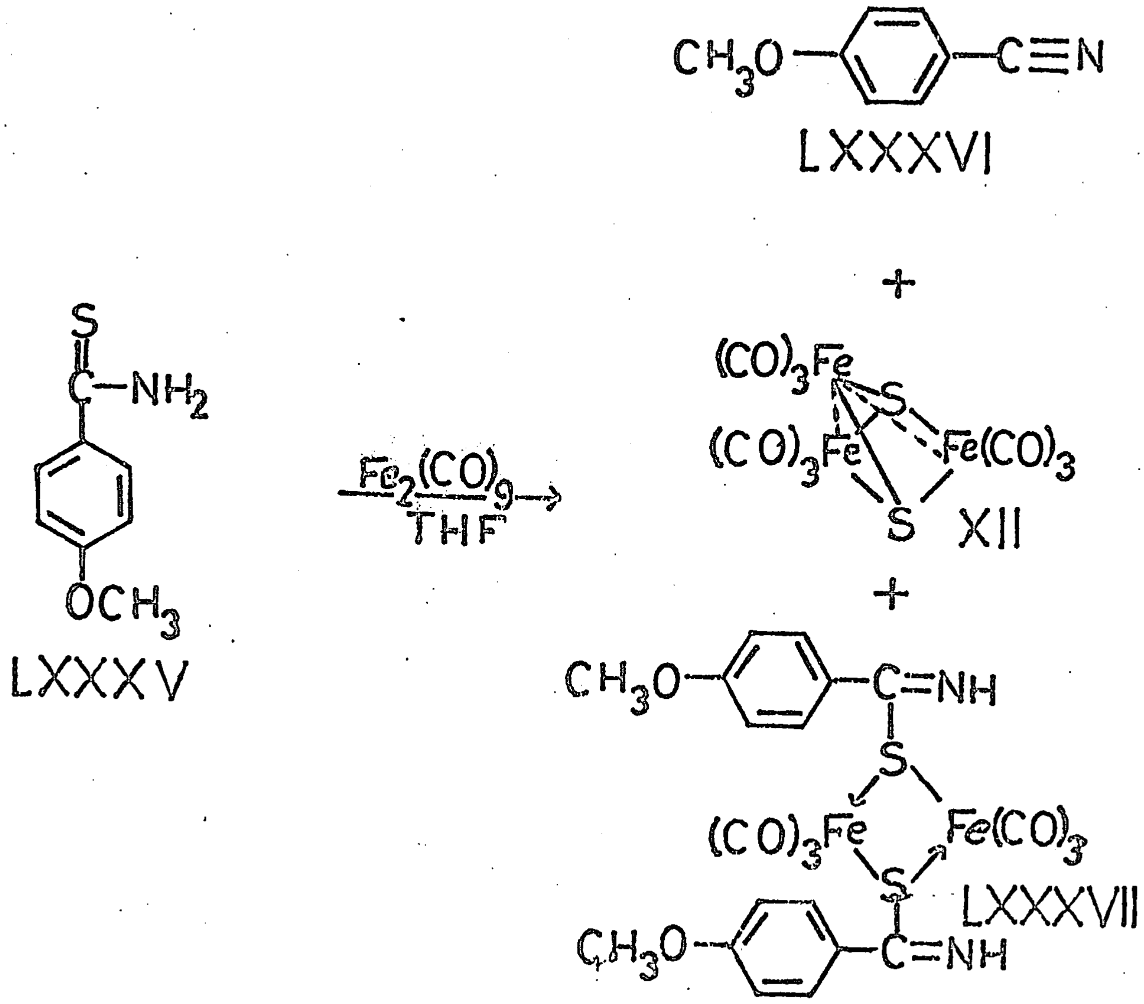


X=O,S

LXXXIV

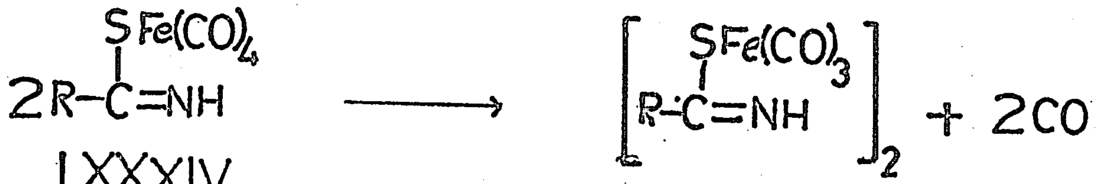


Some support for this mechanism comes from the reaction of p-methoxythionbenzamide (LXXXV) with diiron enneacarbonyl in anhydrous tetrahydrofuran (THF) at room temperature. Three products were obtained: the nitrile (LXXXVI) in 17.2% yield; complex (XII) in 2.6% yield, identified by its melting point and infrared spectrum[46]; and complex (LXXXVII). The latter complex was a black solid which showed infrared absorption (carbon tetrachloride solution) at 3330 cm.$^{-1}$ (NH stretching) and at 2070, 2030, 2000, 1985 and 1945 cm.$^{-1}$ (γ (C≡O)), but no absorption due to -NH_2-deformation (1625 cm.$^{-1}$) or to thiocarbonyl stretching (1280 cm.$^{-1}$). The infrared data, together with the analysis and molecular weight results, indicate structure (LXXXVII) for the complex. This structure is similar to the product



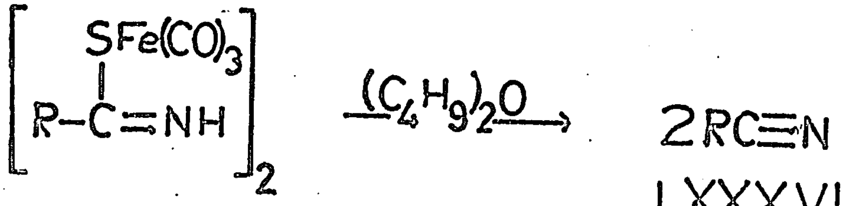
obtained by photolysis of ethyl mercaptan and the metal carbonyl (see p. 16). When LXXXVII was refluxed in butyl ether, p-methoxybenzonitrile was obtained.

Assuming initial formation of LXXXIV, its conversion to LXXXVI can be visualized as follows:



$$2R-\overset{SFe(CO)_4}{\overset{|}{C}}=NH \longrightarrow \left[R-\overset{SFe(CO)_3}{\overset{|}{C}}=NH\right]_2 + 2CO$$

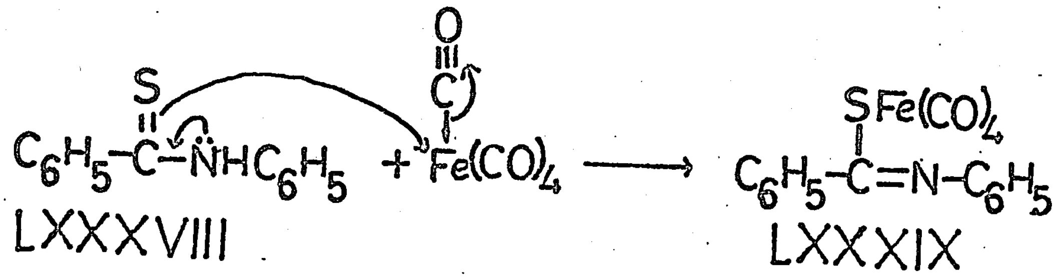
LXXXIV



$$\left[R-\overset{SFe(CO)_3}{\overset{|}{C}}=NH\right]_2 \xrightarrow{(C_4H_9)_2O} 2RC\equiv N$$

LXXXVI

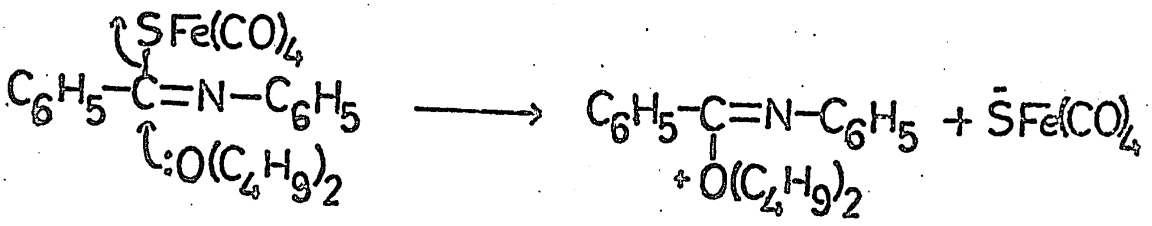
The effect of iron pentacarbonyl on a substituted thionamide, which could not form a nitrile, was investigated. Thionbenzanilide (LXXXVIII) gave a 47.1% yield of N-benzylideneaniline (XLV), previously obtained from metal carbonyl treatment of the corresponding nitrone. The same product was obtained, albeit in lower yield, from reaction of N-deuteriothionbenzanilide with iron pentacarbonyl under the same reaction conditions as for the non-deuterated compound. Clearly, the hydrogen in the product arises from the solvent. One can postulate a mechanism initially the same as for the unsubstituted thionamide. Attack of solvent on the substituted intermediate (LXXXIX) followed by <u>alpha</u> hydrogen migration can give rise to the product.



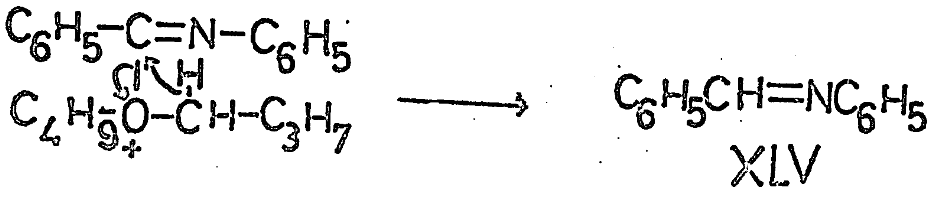
$$C_6H_5-\overset{S}{\overset{\|}{C}}-NHC_6H_5 + Fe(CO)_4 \longrightarrow C_6H_5-\overset{SFe(CO)_4}{\overset{|}{C}}=N-C_6H_5$$

LXXXVIII

LXXXIX



$$C_6H_5-\underset{:O(C_4H_9)_2}{\overset{SFe(CO)_4}{C}}=N-C_6H_5 \longrightarrow C_6H_5-\underset{+O(C_4H_9)_2}{\overset{|}{C}}=N-C_6H_5 + \bar{S}Fe(CO)_4$$



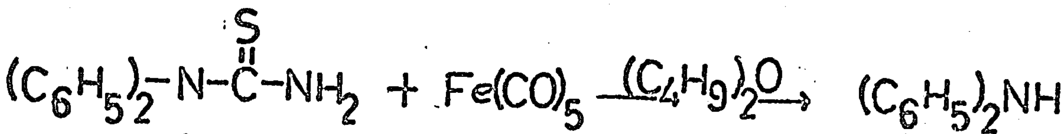
$$\begin{matrix} C_6H_5-C=N-C_6H_5 \\ C_4H_9\overset{+}{O}-\overset{H}{C}H-C_3H_7 \end{matrix} \longrightarrow C_6H_5CH=NC_6H_5$$

XLV

Benzanilide also gave N-benzylideneaniline when treated with iron pentacarbonyl. The N,N-disubstituted amide, N-methylacetanilide, failed to react with the metal carbonyl.

G. Thioureas, Thiohydantoins and Sulfonamides

Reaction of 1,1-diphenyl-2-thiourea with the metal carbonyl in butyl ether gave a 71.9% yield of diphenylamine (LXXIX). No diphenylcyanamide was obtained as would have been expected had the reaction followed the same course as for the thionamides.



$$(C_6H_5)_2-N-\overset{S}{\overset{\|}{C}}-NH_2 + Fe(CO)_5 \xrightarrow{(C_4H_9)_2O} (C_6H_5)_2NH$$

XC

LXXIX

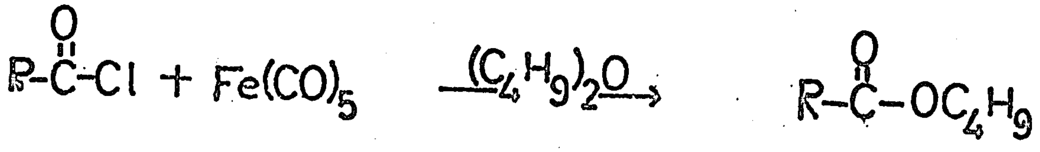
Unfortunately, other thioureas such as N,N'-diphenylthiourea, N,N'-diethylthiourea and N,N'-di-t-butylthiourea decomposed at the reaction temperature and hence could not be investigated under the usual conditions.

3,5-Diphenyl-2-thiohydantoin, failed to react with iron pentacarbonyl in butyl ether. The inability of the thiohydantoin to react may have been due to its insolubility.

Benzenesulfonamide and p-toluenesulfonamide were unreactive towards iron pentacarbonyl.

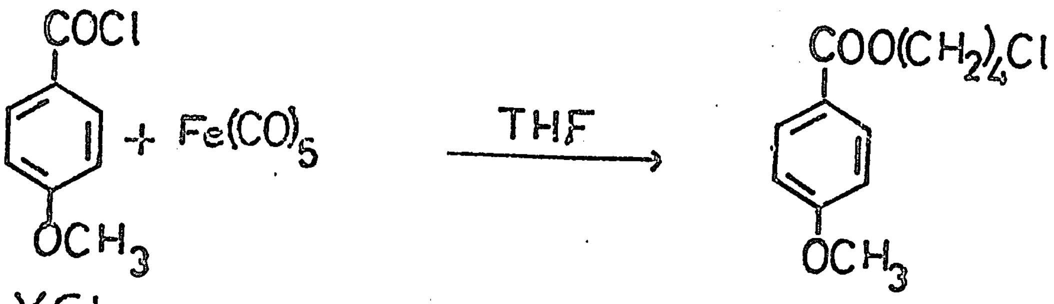
H. Acid Chlorides

Although the reaction of gem-dihalo compounds with iron pentacarbonyl has been reported (p. 21), no publication has appeared on the reaction of acid halides with the metal carbonyl. When either octanoyl, benzoyl or p-methoxybenzoyl chloride was refluxed with iron pentacarbonyl in butyl ether, the corresponding butyl ester was obtained in 66-75% yield.



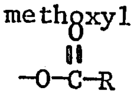
$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + Fe(CO)_5 \xrightarrow{(C_4H_9)_2O} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OC_4H_9$$

When tetrahydrofuran was used as a solvent, benzoyl chloride gave 4-chlorobutyl benzoate in 86.1% yield. The same product was obtained in 78-83% yield by Synerholm[133] upon treatment of benzoyl chloride with tetrahydrofuran in the presence of zinc chloride. Reaction of p-methoxybenzoyl chloride with iron pentacarbonyl produced a new ester, 4-chlorobutyl p-methoxybenzoate (XCII), identifiable by analysis and spectral data. Sodium fusion indicated the presence of chlorine. The infrared spectrum (neat) showed strong carbonyl stretching of an ester at 1717 cm.$^{-1}$ The N.M.R. spectrum of the compound (in CCl_4) showed, beside

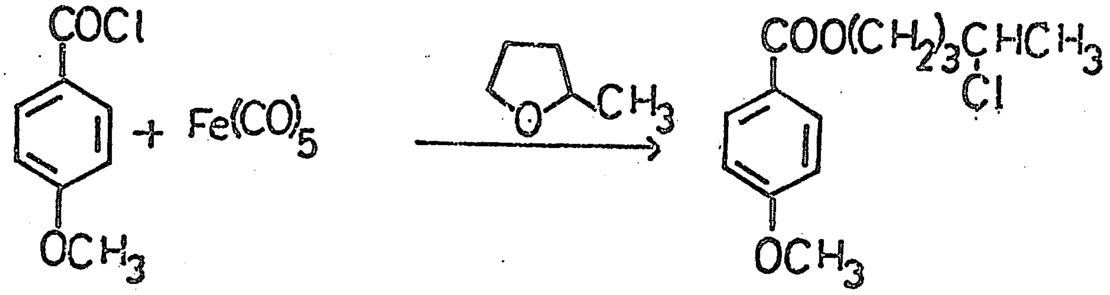


XCI

XCII

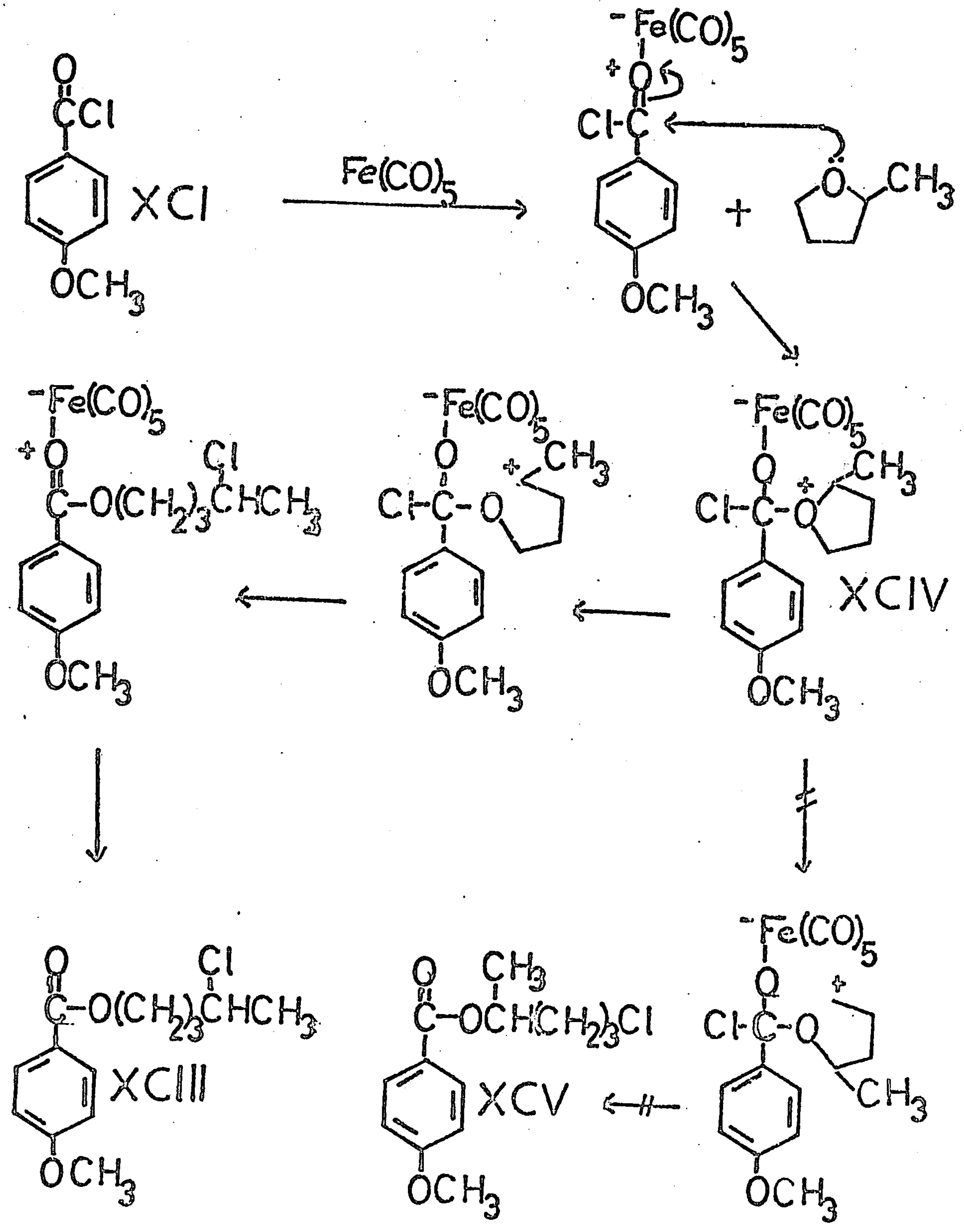
absorption for the aromatic and methoxyl protons, a triplet at 4.20 p.p.m. caused by methylene adjacent to  $-O-\overset{O}{\overset{\|}{C}}-R$; a poorly resolved triplet at 3.50 p.p.m. for the methylene protons adjacent to chlorine; and a multiplet centered at 1.82 p.p.m. for the four remaining methylene protons. When the reaction was repeated substituting anhydrous ferric chloride for iron pentacarbonyl, the same ester was not obtained. On the basis of the N.M.R. spectrum, the product seemed to be polymeric. In agreement with previously published data, no polymerization reaction occurred when tetrahydrofuran was treated with ferric chloride.[134]

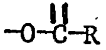
Treatment of p-methoxybenzoyl chloride with iron pentacarbonyl in 2-methyltetrahydrofuran gave a single product in 75.7% yield. The product was identified as 4-chloropentyl p-methoxybenzoate (XCIII) as follows. Sodium fusion indicated the presence of chlorine. Carbonyl stretching of an ester occurred at 1720 cm.$^{-1}$ in the infrared region (neat). The N.M.R. spectrum of the ester showed, beside absorption for the methoxyl and aromatic protons, a doublet centered at 1.43 p.p.m. caused by the protons of the methyl group adjacent to -CHCl; a multiplet at 1.77 p.p.m.



XCI XCIII

SCHEME 8



arising from the protons on the methylene groups <u>beta</u> and <u>gamma</u> to the ester function; a multiplet between 4.0 and 4.1 p.p.m. for the methine proton adjacent to chlorine and a triplet at 4.17 p.p.m. ascribed to the methylene protons adjacent to  $-O-\overset{O}{\overset{\|}{C}}-R$.

A mechanism analogous to the acylation of olefins with aluminum chloride[135] can be postulated for the latter reaction (Scheme 8). As indicated, the heterocyclic ring can cleave in two ways to give the esters XCIII and XCV. The fact that only the product arising from a secondary carbonium is obtained (the other ester would have to result from a primary carbonium ion) indicates that the cleavage of the ether must proceed by a S_N1 rather than S_N2 mechanism.

I. Triphenylphosphine Oxide

Since it was conceivable that a phosphine oxide could undergo deoxygenation with iron pentacarbonyl, the behavior of triphenylphosphine oxide towards the metal carbonyl was investigated. When the reactants were refluxed in either butyl ether or butryonitrile, only starting material was recovered. This result contrasts with the formation of an ionic complex by photolysis of the reactants in benzene at 80°C[36] (see introduction).

J. Ketones and Nitriles

Benzophenone, fluorenone, phenylacetonitrile and *p*-tolunitrile were recovered unchanged when treated with iron pentacarbonyl in butyl ether.

FIGURE 1

INFRARED SPECTRUM OF ERGOSTEROL-IRON TRICARBONYL
(XVII) IN CHLOROFORM

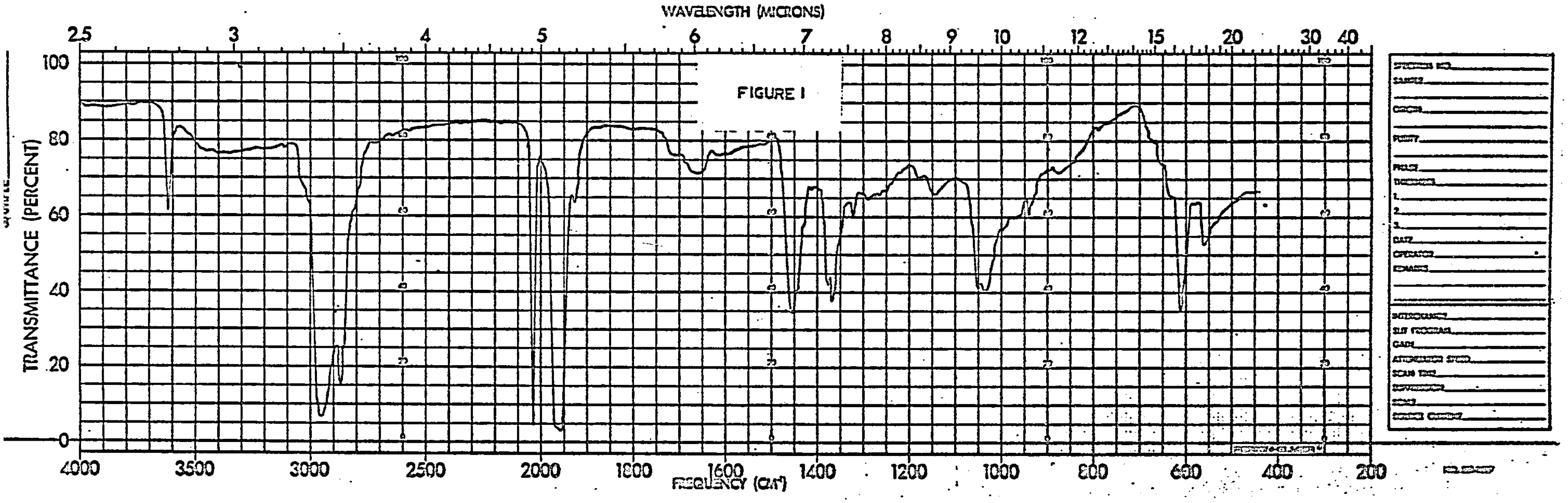


FIGURE I
WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
FREQUENCY (CM⁻¹)

FIGURE 2

ULTRAVIOLET SPECTRUM OF ERGOSTEROL-IRON TRICARBONYL

(XVII) IN ISOOCTANE

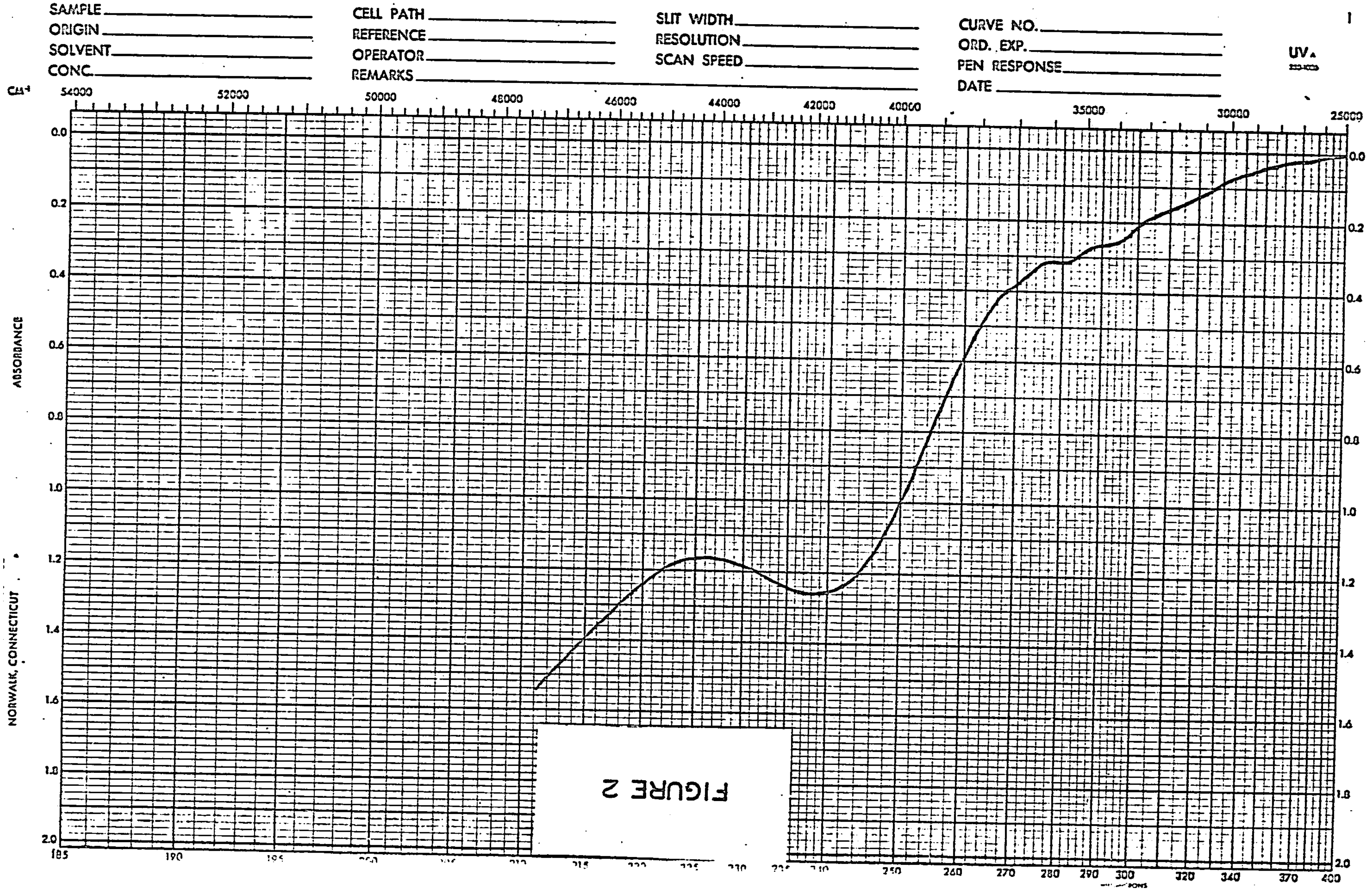

SAMPLE
ORIGIN
SOLVENT
CONC.
CELL PATH
REFERENCE
OPERATOR
REMARKS
SLIT WIDTH
RESOLUTION
SCAN SPEED
CURVE NO.
ORD. EXP.
PEN RESPONSE
DATE
1
UV
CM⁻¹
54000
52000
50000
48000
46000
44000
42000
40000
35000
30000
25000
ABSORBANCE
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
NORWALK, CONNECTICUT
185
190
215
250
260
270
280
290
300
320
340
370
400

FIGURE 2

FIGURE 3

N.M.R. SPECTRUM OF CHOLESTA-5,7-DIEN-3β-OL-IRON TRICARBONYL (XVIII) IN $CDCl_3$

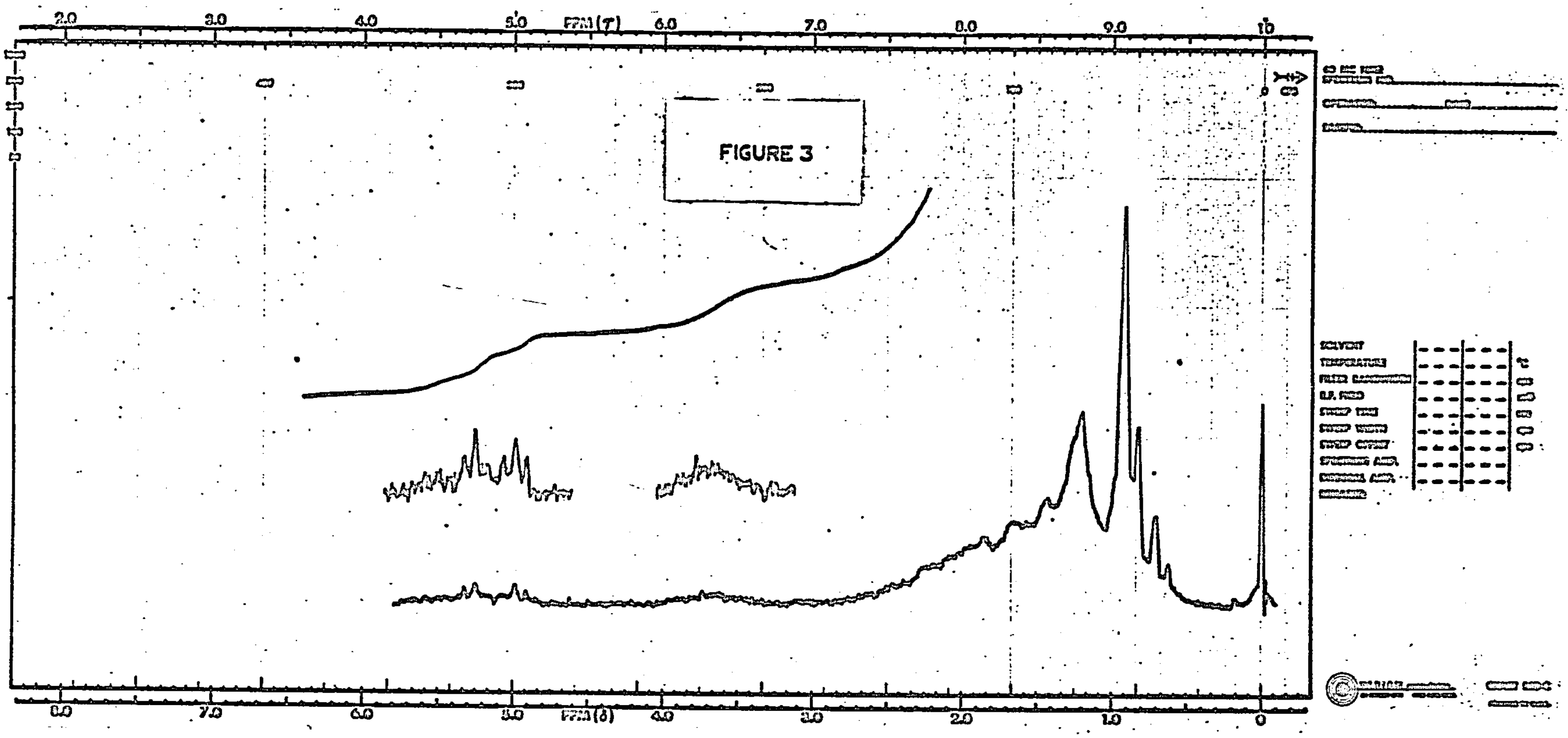


FIGURE 3

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0
SOLVENT
TEMPERATURE
FILTER BANDWIDTH
R.F. FIELD
SWEEP TIME
SWEEP WIDTH
SWEEP OFFSET
SPECTRUM AMPL.
INTEGRAL AMPL.
DECOUPLING

FIGURE 4

ULTRAVIOLET SPECTRA OF THE DIENONE-IRON TRICARBONYL COMPLEXES

Curve A: 4,4-Dimethylcyclohexa-2,5-dienone-iron tricarbonyl (XXVII)

B: Cholesta-1,4-dien-3-one-iron tricarbonyl (XXVIII)

C: Androsta-1,4-diene-3,11,17-trione-iron tricarbonyl (XXIX)

D: Santonin-iron tricarbonyl (XXXI)

SAMPLE ____ CELL PATH ____ SLIT WIDTH ____ CURVE NO. ____
ORIGIN ____ REFERENCE ____ RESOLUTION ____ ORD. EXP. ____
SOLVENT ____ OPERATOR ____ SCAN SPEED ____ PEN RESPONSE ____
CONC. ____ REMARKS ____ DATE ____

UV

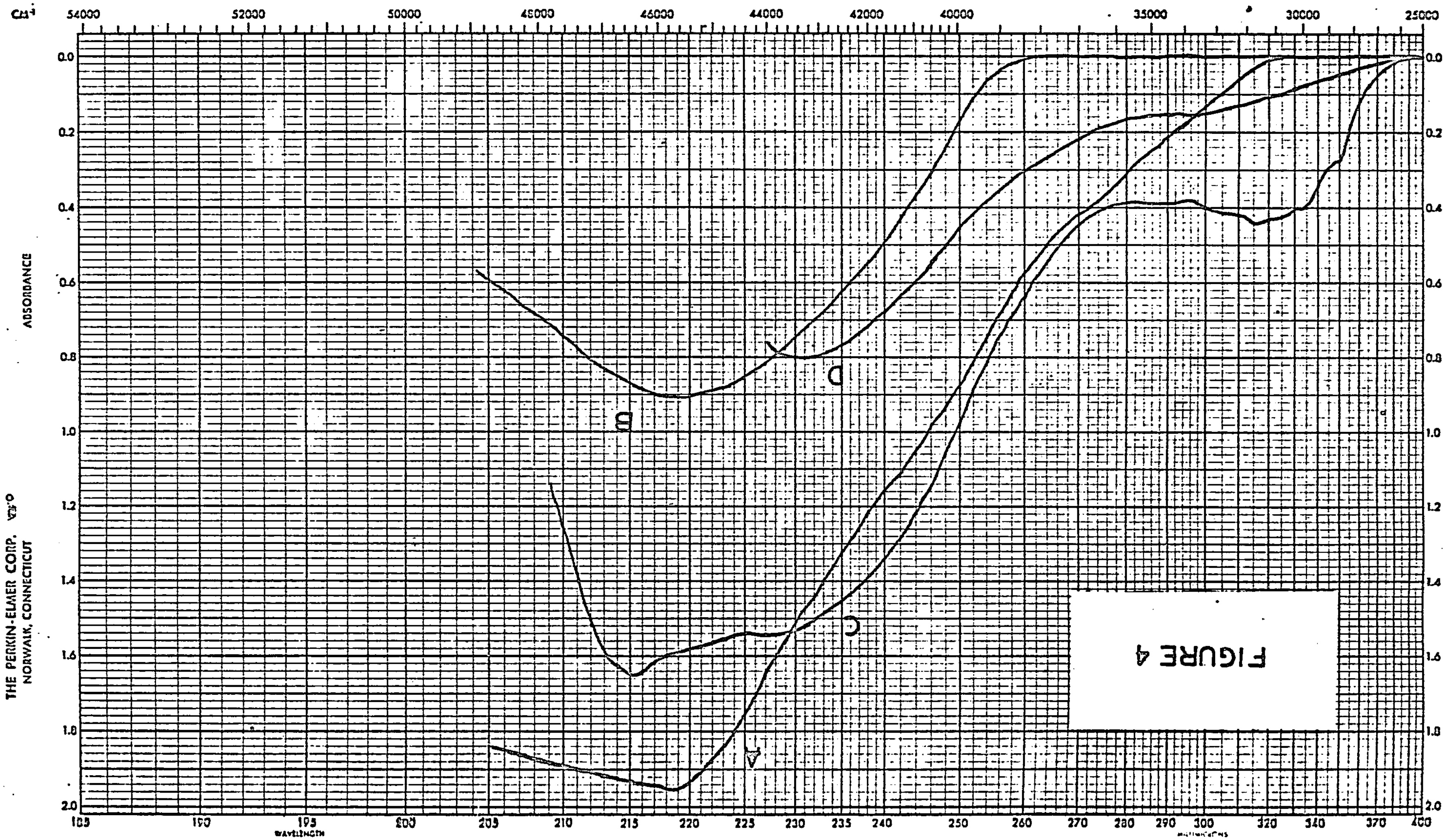


FIGURE 4

FIGURE 5

INFRARED SPECTRUM OF COMPLEX XXXIV IN A KBr DISC

FIGURE 5

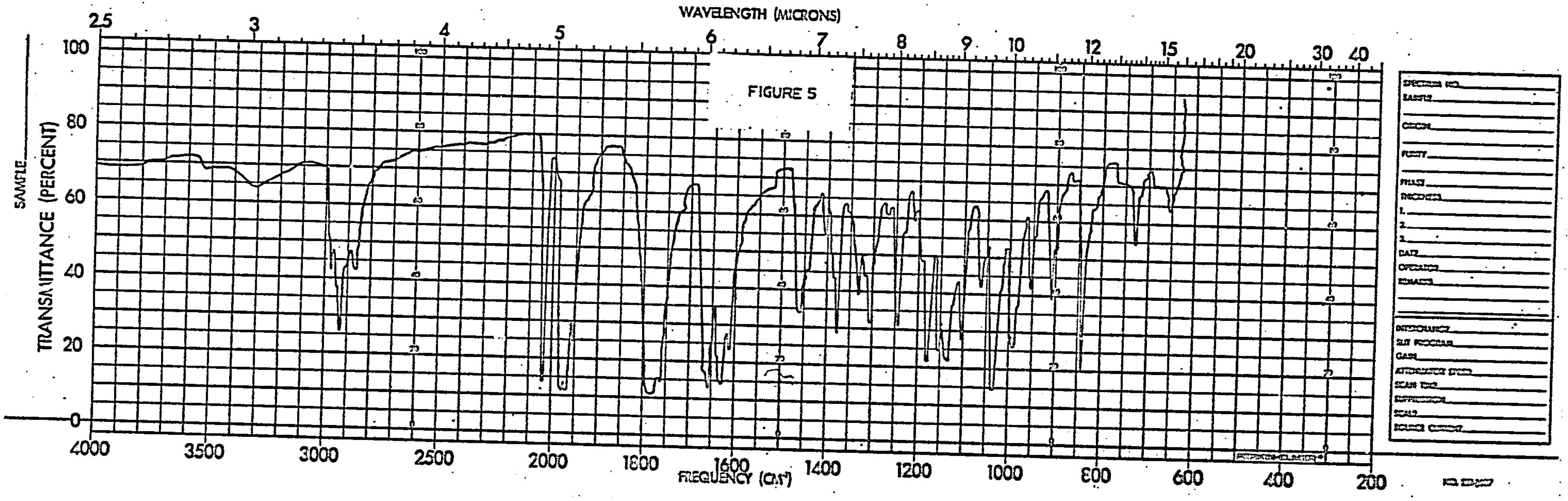

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
TRANSMITTANCE (PERCENT)
100
80
60
40
20
0
FREQUENCY (CM⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
SAMPLE

FIGURE 6

INFRARED SPECTRUM OF COMPLEX XXXV IN A KBr DISC

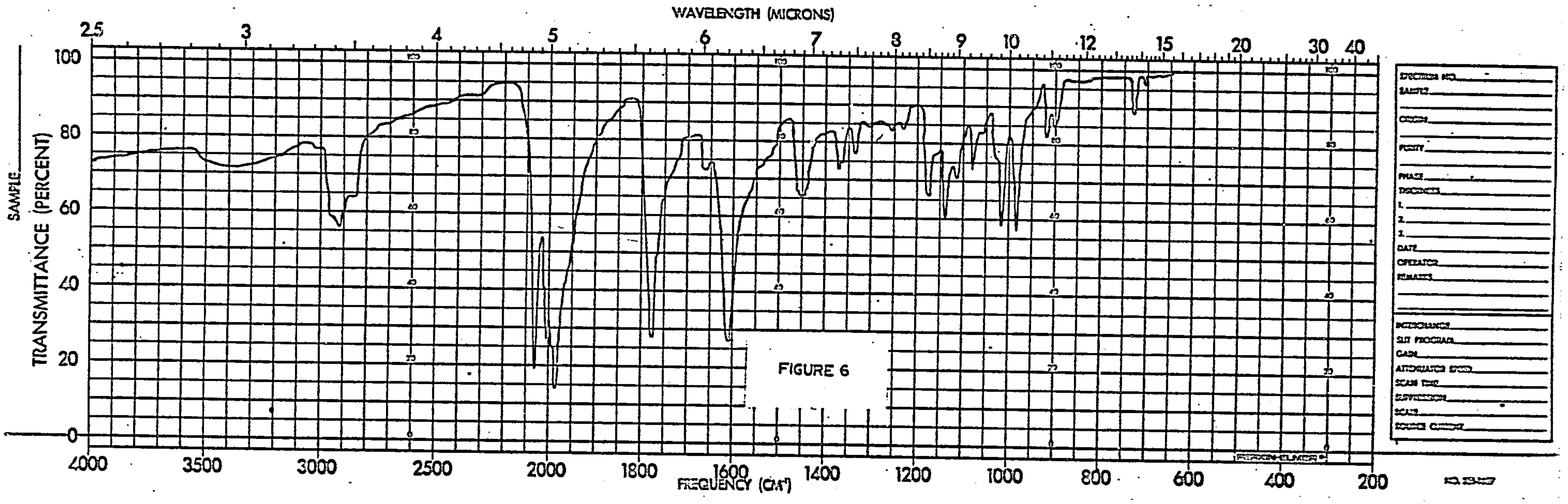


FIGURE 6

WAVELENGTH (MICRONS)
2.5
3
4
5
6
7
8
9
10
12
15
20
30
40
TRANSMITTANCE (PERCENT)
SAMPLE
100
80
60
40
20
0
FREQUENCY (CM⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
PERKIN-ELMER
SPECTRUM NO.
SAMPLE
ORIGIN
PURITY
PHASE
THICKNESS
DATE
OPERATOR
REMARKS
SLIT PROGRAM
GAIN
ATTENUATOR SPEED
SCAN TIME
SUPPRESSION
SCALE
SOURCE CURRENT

EXPERIMENTAL

General

Melting points were measured in capillary tubes in a Gallenkamp melting point apparatus and are corrected. Analyses were performed by: Bernhardt Mikroanalytisches Laboratorium, Mulheim, Germany; Schwarzkopf Microanalytical Laboratory, Woodside, New York and C. Daessele, Montreal, Canada. The infrared spectra were recorded on Perkin-Elmer model "137," "337" and "521" spectrophotometers in various solvents or as KBr-pellets as individually noted. Wavelength readings were checked with a polystyrene film. Ultraviolet spectra were recorded with Unicam SP-800 or Perkin-Elmer 350 spectrophotometers. The nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer in carbon tetrachloride or deuteriochloroform solution. Tetramethylsilane served as an internal standard.

Iron pentacarbonyl, purchased from Alfa Inorganics, Inc., was used as received. Distillation of the metal carbonyl before use gave identical results. Butyl ether (Fisher Chemical Co.) was purified by treatment with sodium followed by distillation from the metal. Tetrahydrofuran (J. T. Baker Chemical Co.) was purified in the same manner or by treatment with lithium aluminum hydride. n-Octane (J. T. Baker Chemical Co.) was purified by treatment with phosphorus pentoxide. Other solvents employed were purified by standard methods before use in reactions.

I. Diene Complexes

Steroid-Iron Tricarbonyl Complexes

(i) Preparation of Dienes

Cholesta-2,4-diene was prepared from cholesterol according to a modified procedure of Stavely and Bergmann.[136] A mixture of cholesterol (75 g.) and alumina (50 g. - Fisher chromatographic grade) was heated for two hours at 200-225°C (0.2 mm.). Instead of distillation, the mixture was cooled and extracted with ether and the ether evaporated. Chromatography of the residual oil on neutral alumina using benzene as the eluent gave cholesta-2,4-diene in 55% yield, m.p. 64.0-66.0°C (lit. m.p. 68.5°C).[68] Only a 10-15% yield of cholesta-2,4-diene was obtained by using Stavely and Bergmann's procedure. Ergosterol was purchased from Fisher Chemical Co. and cholesta-5,7-dien-3β-ol was purchased from Aldrich Chemical Co.

Cholesta-3,5-diene was prepared from cholesteryl tosylate according to Chang and Wood.[137] The tosylate was in turn prepared by treatment of cholesterol with p-toluenesulfonyl chloride according to standard procedures.[138] 3-Methylcholesta-3,5-diene was prepared from cholest-4-en-3-one according to Kucherova and Ushakov.[72] 3-Methoxycholesta-3,5-diene was obtained by treatment of cholest-4-en-3-one with trimethylorthoformate in dioxane according to Just and Leznoff.[73] The melting points of the dienes obtained agreed with those reported in the literature. Cholesta-4,6-diene was kindly supplied by Dr. M. M. Frojmovic.

(ii) General Procedure

A mixture of diene (2-14 mm.) and iron pentacarbonyl (3 mole/mole of diene) in dry isooctane, cyclohexane or butyl ether (40-200 ml.) was refluxed with stirring under nitrogen. The reaction mixture was cooled and filtered to remove inorganic material, and solvent and unreacted metal carbonyl were removed at ca. 30 mm. The procedures for the isolation of the complexes from the residues differed considerably.

Reasonably pure cholesta-2,4-diene-iron tricarbonyl (XVI, R=H) was obtained by treating the residue with dry acetone, filtering, and evaporating the filtrate. Further purification was effected by chromatography on Florisil, using benzene as the eluent, to give yellow-orange crystals of XVI (R=H) which were air-stable.

Ergosterol-iron tricarbonyl (XVII) was isolated in the following way: the residue was dissolved in pentane and chromatographed on a neutral alumina column under nitrogen. Elution with methylene chloride-ether (1:1) gave a brownish-green component. Rechromatography of this material on alumina with chloroform as the eluent gave crude ergosterol-iron tricarbonyl (XVII). The crude complex was dissolved in dry acetone, filtered, and the filtrate evaporated at reduced pressure to give yellow-brown crystals of pure ergosterol-iron tricarbonyl. The complex was kept under nitrogen. If left in air for a short time, ergosterol was obtained. The reason for the instability of XVII is unknown but the failure of Nakamura and Tsutsui[65] to obtain ergosterol-iron tricarbonyl may be due to the fact that they did not carry out all operations under nitrogen.

The residue of crude cholesta-5,7-dien-3β-ol-iron tricarbonyl (XVIII) was dissolved in hexane and chromatographed on Florisil. Elution with hexane-acetone (1:1) gave beautiful golden-yellow plates of XVIII.

The procedure for the isolation of complex XVI (R=H) was applied to the 3-methyl derivative XVI ($R=CH_3$). In the case of 3-methoxycholesta-3,5-diene, the residue from solvent evaporation was treated with benzene and chromatographed on Florisil. Elution with benzene gave the complex XVI ($R=OCH_3$).

The yield, melting point and analyses of the complexes are given in Table III.

Decomposition of the Iron-Tricarbonyl Complexes

The diene-iron tricarbonyl complex (2.0-2.6mm.) in ethanol (10-15 ml.) was added dropwise to a ferric chloride solution prepared by dissolving anhydrous ferric chloride in 95% ethanol (8-10 ml.). The reaction mixture was stirred for two hours at room temperature, poured into excess water and extracted with ether. The ether extract was washed with water and dried over sodium sulfite. After solvent evaporation, the parent diene was obtained. The yields and melting points of the dienes obtained from complexes XVI-XVIII were: cholesta-2,4-diene, 90.1%, 65.0-67.0°C (lit. m.p. 68.5°C)[68]; ergosterol, 87.0%, 162.0-163.0°C (lit. m.p. 162-164°C)[3]; cholesta-5,7-dien-3β-ol, 84.2%, 148.0-150.0°C (lit. m.p. 150-151°C)[3]; and 3-methylcholesta-2,4-diene, 75.5%, 67.0-69.0°C (lit. m.p.

68-69°C).[72] The melting points were undepressed on admixture with an authentic sample.

3-Methoxycholesta-2,4-diene, m.p. 55.0-56.0°C, was obtained in 58.7% yield by reaction of the corresponding iron tricarbonyl complex with ferric chloride.

CALCULATED FOR $C_{28}H_{46}O$	:	C 84.35 ;	H 11.63
FOUND	:	C 84.01 ;	H 11.54

Reaction of Cholesta-5,7-dien-3β-ol-Iron Tricarbonyl (XVIII) with Triphenylmethyl Tetrafluoroborate

A mixture of triphenylmethyl tetrafluoroborate—prepared from triphenylmethanol and 48% tetrafluoroboric acid according to Dauben, Honnen and Harmon[139]—(0.262 g.) in methylene chloride (3 ml.) was added dropwise to a solution of the complex (0.313 g.) in methylene chloride (2 ml.) at room temperature. The solution was cooled to 0°C for ten minutes and dry ether (100 ml.) was added and the mixture was then stirred to decompose unreacted triphenylmethyl tetrafluoroborate. The solution was then evaporated in vacuo to give a gummy residue. The residue was treated with petroleum ether (b.p. 30-60°C) and black insoluble material (0.090 g.) was filtered off. Evaporation of the filtrate gave a yellow-brown solid (0.196 g.). Neither of the products showed infrared absorption ascribable to a complex and hence were not further investigated.

Reaction of Cholesta-2,4-diene-Iron Tricarbonyl (XVI, R=H) with Triphenylmethyl Tetrafluoroborate

Triphenylmethyl tetrafluoroborate (0.594 g.) in methylene chloride (5 ml.) was added dropwise to a solution of XVI (0.917 g.) in methylene chloride (2 ml.) at room temperature. The solution was cooled to 0°C and allowed to stand overnight. No carbonium ion salt precipitated out. Dry ether (100 ml.) was added and the mixture was stirred to decompose unreacted triphenylmethyl tetrafluoroborate. The solution was filtered and the filtrate evaporated to give a yellow residue. The residue was washed with acetone and then chromatographed on Florisil. Elution with petroleum ether-benzene (1:1) gave colorless needles, m.p. 130.0-132.0°C, which analyzed for 86.30% carbon and 9.61% hydrogen, and were shown to be homogenous by thin layer chromatography. The solid gave a positive ferrox test. Evaporation of acetone gave unreacted starting material.

II. Dienone Complexes

Preparation of Dienone-Iron Tricarbonyls

4,4-Dimethylcyclohexa-2,5-Dienone-Iron Tricarbonyl XXVII

(i) 4,4-Dimethylcyclohex-2-enone (XXV)

4,4-Dimethylcyclohex-2-enone was prepared from isobutyraldehyde and methyl vinyl ketone according to Bordwell and Wellmann.[84]

Isobutyraldehyde (52 g.) and methyl vinyl ketone (59.2 g.) gave 20 g. of the monoenone (XXV), b.p. 53-56°C at 4 mm. (lit. b.p. 54-56°C at 4 mm.).[84]

(ii) 4,4-Dimethylcyclohexa-2,5-dienone (XXVI)

A mixture of XXV (19.25 g., 155 mm.) and selenium dioxide (17.33 g., 157 mm.) in dry t-butanol (2890 ml.) and glacial acetic acid (29.0 ml.) was refluxed with stirring under nitrogen for 24 hours. Additional selenium dioxide was added (17.33 g.) and the reaction mixture was refluxed for one day. The solution was cooled and filtered and the filtrate was distilled at reduced pressure to remove t-butanol. The residue was dissolved in methylene chloride, washed with 0.1 N sodium hydroxide, and then treated with ammonium sulfide solution. The solution, after standing overnight, was separated from the ammonium sulfide layer. The extract was washed with water, dried, and distilled at 15 mm. Colorless 4,4-dimethylcyclohexa-2,5-dienone (5.601 g., 29.6%) was distilled at 88-92°C (lit. b.p. 86-92°C at 15 mm.).[82]

(iii) Complex (XXVII)

A mixture of 4,4-dimethylcyclohexa-2,5-dienone (1.771 g., 14.5 mm.) and iron pentacarbonyl (6.50 ml., 48.4 mm.) in dry isooctane (200 ml.) was refluxed with stirring under nitrogen for 49 hours. The solution was cooled and filtered and the solvent and unreacted metal carbonyl were removed under reduced pressure (ca. 30 mm.). The residue consisted of an oil and an inorganic solid. The oil was decanted and chromatographed on Florisil with carbon tetrachloride. Elution with carbon tetrachloride-benzene (7:1) gave first inorganic material and then 1.381 g. (36.1%) of yellow 4,4-dimethylcyclohexa-2,5-dienone-iron tricarbonyl (XXVII), b.p. 42-46°C at 0.1 mm. Further elution with carbon tetrachloride-benzene gave starting material. Elution with acetone gave an additional small amount of dienone.

CALCULATED FOR $C_{11}H_{10}O_4Fe$: C, 50.42 ; H, 3.85
FOUND : C, 50.09 ; H, 3.87

Cholesta-1,4-dien-3-one-Iron Tricarbonyl (XXVIII)

(i) With Iron Pentacarbonyl

A mixture of cholesta-1,4-dien-3-one* (3.700 g., 9.64 mm.) and iron pentacarbonyl (1.97 ml., 14.6 mm.) in dry isooctane (65 ml.) was refluxed with stirring under nitrogen for 66 hours. The solution was cooled, a solid was removed by filtration, and the filtrate was evaporated to dryness at 30 mm. Both the solid and the residue from the filtrate were triturated with chloroform. The chloroform solutions were filtered and the filtrate chromatographed on a neutral alumina column. Elution with chloroform-methanol (10:1) gave 2.57 g. (51.0%) of brownish-green crystals of cholesta-1,4-dien-3-one-iron tricarbonyl (XXVIII), m.p. 80.0-81.0°C.

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*Kindly supplied by Dr. M. J. Davis.

The complex was stored under nitrogen.

CALCULATED FOR $C_{30}H_{42}O_4Fe$: C, 68.96 ; H, 8.10
FOUND : C, 68.79 ; H, 8.27

(ii) With Diiron Enneacarbonyl

A mixture of cholesta-1,4-dien-3-one (1.011 g., 2.63 mm.) and diiron enneacarbonyl (0.956 g., 2.63 mm.) in dry benzene (30 ml.) was stirred under nitrogen at 40-50°C for four hours. The mixture was filtered to remove inorganic impurities and the solvent was removed at ca. 30 mm. Crystallization of the residue from hexane gave 0.601 g. (43.7%) of XXVIII, m.p. 79.0-81.0°C. The yield of complex did not change substantially (48.3%) and no new products were isolated when the reaction was repeated using a 2:1 mole ratio of metal carbonyl to dienone.

Androsta-1,4-diene-3,11,17-trione-Iron Tricarbonyl (XXIX)

A mixture of androsta-1,4-diene-3,11,17-trione* (6.60 g., 22.1 mm.) and iron pentacarbonyl (10.0 ml., 75.0 mm.) in dry dioxane (200 ml.) was refluxed with stirring under nitrogen for 82 hours. The reaction mixture was then distilled at 1 mm. to remove solvent and unreacted metal carbonyl. The residue was dissolved in chloroform and chromatographed on a neutral alumina column under nitrogen. Elution with chloroform-methanol (5:1) gave

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*The receipt of a generous quantity of this steroid from the Upjohn Company is gratefully acknowledged.

2.14 g. (22.1%) of a brown microcrystalline powder (XXIX), m.p. 167.0-171.0°C (dec.).

CALCULATED FOR $C_{22}H_{22}O_6Fe$: C, 60.29 ; H, 5.06
FOUND : C, 60.35 ; H, 5.01

Santonin-Iron Tricarbonyl (XXXI)

A mixture of santonin (6.84 g., 27.7 mm.) and iron pentacarbonyl (12.4 ml., 92.2 mm.) in dry dioxane (250 ml.) was refluxed with stirring under nitrogen for at least 40 hours. During this time, the color of the solution changed from amber to green and finally to brown. The solution was filtered hot to remove inorganic impurities and then the filtrate was distilled at 30 mm., b.p. 76-78°C, to remove solvent and unreacted metal carbonyl. The brown residue was dissolved in methylene chloride and chromatographed on a neutral alumina column. Elution with methylene chloride-methanol (15:1) gave 4.47 g. (41.8%) of pure pale-brown santonin-iron tricarbonyl (XXXI), m.p. 190.0-192.0°C (dec.). The product was stored under nitrogen. An attempt to purify the complex by sublimation rather than chromatography resulted in decomposition.

CALCULATED FOR $C_{18}H_{18}O_6Fe$: C, 55.98 ; H, 4.70
FOUND : C, 55.90 ; H, 4.73

Decomposition of the Dienone-Iron Tricarbonyl Complexes

Complex XXVII was decomposed with ferric chloride in an identical manner to that described for the steroid diene-iron tricarbonyl complexes. The product, obtained in 86.0% yield, was distilled at 15 mm., b.p. 88-91°C (lit. b.p. 86-92°C).[82] Ferric chloride treatment of complex XXVIII gave cholesta-1,4-dien-3-one, m.p. 111.0-112.0°C (lit. m.p. 108-111°C)[140] in 88.7% yield. The same procedure was applied to complex XXIX except that the product dienone was extracted with chloroform-methylene chloride (2:1) instead of ether. A 94.2% yield of androsta-1,4-diene-3,11,17-trione was obtained, m.p. and mixed m.p. 198.0-200.0°C (lit. m.p. 196-199°C).[86] Treatment of santonin-iron tricarbonyl with ferric chloride according to the standard procedure gave a tar.

Santonin Oxime-Iron Tricarbonyl (XXXII)

(i) From Santonin-Iron Tricarbonyl (XXXI)

Santonin-iron tricarbonyl was heated with hydroxylamine hydrochloride in pyridine-ethanol according to standard procedures.[141] The oxime complex was obtained as orange crystals, m.p. 53.0-55.0°C, in 78% yield.

CALCULATED FOR $C_{18}H_{19}NO_6Fe$	:	C, 53.89 ;	H, 4.77
FOUND	:	C, 54.19 ;	H, 4.69

Treatment of the oxime complex (XXXII) with ferric chloride by the standard method gave santonin oxime, m.p. and mixed m.p. 216.0-218.0°C (lit. m.p. 218°C)[142] in 72% yield.

(ii) From Santonin Oxime

A mixture of santonin oxime* (2.331g., 8.92 mm.) and iron pentacarbonyl (3.70 ml., 27.5 mm.) in dry dioxane or butyl ether (60-100 ml.) was refluxed with stirring under nitrogen for at least 20 hours. The solution was cooled and filtered, and the solvent and unreacted metal carbonyl were removed at ca. 30 mm. to give 1.50 g. of a crude red residue. The residue was dissolved in methylene chloride and chromatographed on Florisil. Elution with methylene chloride gave santonin oxime. Elution with methylene chloride-ethanol (10:1) gave 275 mg. (7.7%) of orange crystals of santonin oxime-iron tricarbonyl (XXXII), m.p. 53.0-55.0°C.

Reaction of 4-Methyl-4-Trichloromethylcyclohexa-2,5-dienone (XXXVIII) with Iron Pentacarbonyl

A mixture of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone* (6.520 g., 29.00 mm.) and iron pentacarbonyl (10.0 ml., 75.0 mm.) in dry dioxane or methylcyclohexane (100-160 ml.) was refluxed with stirring under nitrogen for 40-65 hours. The solution was filtered and the brown solid obtained was dissolved in methanol-methylene chloride (10:1),

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*Kindly supplied by Dr. M. J. Davis.

filtered to remove some inorganic particles, and then chromatographed rapidly on a neutral alumina column. Elution with methanol-methylene chloride (10:1) gave a brown solid. The brown solid was further purified by dissolving in boiling acetone and clarifying the solution by filtration. On cooling the solution deposited a brown powder (5.28 g.), m.p. 220°C. Analysis of two different preparations by two different laboratories (Schwarzkopf Microanalytical Laboratories, New York and A. Bernhardt, Germany) showed:

ANALYSIS: C, 24.90 ; H, 3.41 ; Cl, 33.07 ; Fe, 20.47
C, 24.74 ; H, 3.37 ; Cl, 32.98 ; Fe, 20.42

Removal of solvent from the filtrate obtained above gave traces of a deep green solid which was not further investigated.

Reaction of 4-Methyl-4-Trichloromethylcyclohexa-2,5-dienone Oxime (XXXVII) with Iron Pentacarbonyl

A mixture of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone oxime* (1.002 g., 4.16 mm.) and iron pentacarbonyl (0.61 ml., 4.6 mm.) in dry butyl ether (100 ml.) was refluxed with stirring under nitrogen for 10 hours. The solution was cooled and filtered, and the solvent removed at ca. 30 mm. The residue of crude carbonyl compound was triturated with hexane to give 0.676 g. (72.0%) of XXXVIII, m.p. and mixed m.p. 102.0-103.0°C (lit. m.p. 103.0-104.0°C).[143]

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*Kindly supplied by Dr. M. J. Davis.

Reaction of Santonin with Diiron Enneacarbonyl

A mixture of santonin (1.171 g., 4.75 mm.) and diiron enneacarbonyl (3.454 g., 9.50 mm.) in dry benzene (40 ml.) was stirred under nitrogen at 40°C for four hours. The solution was filtered to remove inorganic impurities and the solvent was evaporated at ca. 30 mm. The residue (0.80 g., 68%) was crystallized from hexane, and then dissolved in chloroform and chromatographed on Florisil. Elution with chloroform gave a light brown solid (fraction A) which thin layer chromatography (petroleum ether-ether (7:3)) indicated to be a mixture of santonin and product. Further elution with chloroform or with chloroform-methylene chloride (1:1) gave santonin (0.45 g., 38%). Elution with methylenechloride-ethanol gave 4 mg. (0.022%) of the cyclopentadienone complex XXXV, m.p. 121.0-123.0°C (dec.). Repetition of the experiment gave 3-5 mg. of XXXV.

CALCULATED FOR $C_{18}H_{18}O_6Fe$: C, 55.98 ; H, 4.70
FOUND : C, 56.00 ; H, 4.93

Fraction A (0.30 g.) was rechromatographed on Florisil. Elution with petroleum ether-ether (7:3) gave 0.265 g. (7.8%) of the almost colorless complex XXXIV, m.p. 135.0-138.0°C (under nitrogen).

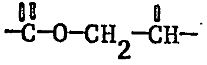
CALCULATED FOR $C_{35}H_{36}O_{11}Fe_2$: C, 56.48 ; H, 4.88
FOUND : C, 56.66 ; H, 5.20

Further elution with petroleum ether-ether (7:3) gave santonin (0.020 g.).

Repetition of the experiment for shorter or longer periods of time and/or with variations in the amount of metal carbonyl used gave poorer yields of products.

Bis-(2-ethylhexyl)-o-phthalate (XXXVI)

(i) From Santonin

A mixture of santonin (3.577 g., 15.90 mm.) and iron pentacarbonyl (6.90 ml., 51.3 mm.) in dry butyl ether (250 ml.) was refluxed with stirring under nitrogen for 12 hours. The solution was cooled, filtered to remove inorganic material, and the filtrate evaporated at ca. 30 mm. The residue was triturated with hexane to give 3.05 g. of the oil, bis-(2-ethylhexyl)-o-phthalate, b.p. 185-7°C at 0.5 mm. (lit. b.p. 183°C at 0.3 mm.).[144] It showed an A_2B_2 spectrum for the aromatic protons centered at 7.54 p.p.m., a doublet for the methylene protons of  $-\overset{\overset{O}{\|}}{C}-O-CH_2-\overset{|}{C}H-$ at 4.10 p.p.m. and signals for the remaining alkyl protons at 0.8-1.6 p.p.m.

(ii) From Santonin-Iron Tricarbonyl

Santonin-iron tricarbonyl (0.50 g.) in dry butyl ether (40 ml.) was refluxed with stirring under nitrogen for 10 hours. The reaction, worked-up in an identical manner as above, gave 0.25 g. of bis-(2-ethylhexyl)-o-phthalate.

III. Reactions of Iron Pentacarbonyl With Different Functional Groups

A. N-Oxides, Azoxy Compounds and Nitrones

(i) N-Oxides—General Procedure

A mixture of N-oxide (20-60 mm.—commercially available) and iron pentacarbonyl (1.1/1.0 mole of metal carbonyl to N-oxide) in dry butyl ether (35-60 ml.) was refluxed with stirring under nitrogen for 17 hours. The solution was cooled and filtered to remove inorganic material. The ultraviolet spectrum of the filtrate indicated absorption due solely to the product amine (by comparison with authentic samples). If the boiling point of the product was close to that of the solvent (e.g. 4-picoline), the amine was isolated as the hydrochloride by bubbling dry HCl gas into the filtrate. The amine was then obtained from the hydrochloride by dissolving the latter in water and basifying with sodium bicarbonate. Distillation gave a pure product (Table VI). If the boiling point of the product was substantially different from that of butyl ether (e.g. quinoline), then the amine was isolated simply by fractional distillation. The evolution of one equivalent amount of carbon dioxide in the deoxygenation of pyridine-N-oxide was detected by bubbling the evolved gas through a solution of barium hydroxide.

(ii) Azoxy Compounds—General Procedure

A mixture of the azoxy compound (30-65 mm.) and iron pentacarbonyl

(0.8-1.0 mole/mole of azoxy compound) in dry butyl ether (50-60 ml.) was refluxed with stirring under nitrogen for 24 hours. The solution was cooled and filtered, and the solvent removed at 30 mm. The residue was dissolved in petroleum ether (b.p. 38-54°C) and chromatographed on Florisil. Elution with petroleum ether gave the azo compound.

The evolution of an equivalent amount of carbon dioxide in the azoxybenzene reaction was detected by bubbling the evolved gas through a solution of barium hydroxide.

(iii) α-Phenyl-N-phenylnitrone (XLIV)

A mixture of the nitrone (1.524 g., 7.73 mm.) and iron pentacarbonyl (1.14 ml., 8.50 mm.) in dry butyl ether (40 ml.) was refluxed with stirring under nitrogen for 24 hours. The solution was cooled and filtered, and the solvent removed at ca. 30 mm. The residual oil was treated with petroleum ether, filtered, and the filtrate evaporated to give an oil crystallizable from carbon disulfide, giving 0.850 g. (60.7%) of pale yellow needles of N-benzylideneaniline (XLV), m.p. 50.0-52.0°C (lit. m.p. 51-52°C).[3] The infrared spectrum was identical to that reported by Nakanishi.[145]

The residual oil could also be purified by chromatography on Florisil. Elution with petroleum ether-benzene (1:1) gave XLV, m.p. 51.0-52.0°C.

B. Nitroso Compounds

(i) Reaction of Nitrosobenzene with Iron Carbonyls

(a) With Iron Pentacarbonyl

A mixture of nitrosobenzene (3.133 g., 29.25 mm.) and iron pentacarbonyl (3.93 ml., 29.25 mm.) in dry butyl ether (55 ml.) was refluxed with stirring under nitrogen for 24 hours. The solution was cooled and filtered, and the solvent removed at ca. 30 mm. Two recrystallizations of the residue from 95% ethanol gave 2.01 g. (75%) of azobenzene (XLVII), m.p. and mixed m.p. 66.0-68.0°C.

By bubbling the carbon dioxide evolved during the reaction through a solution of barium hydroxide, it was found that two moles of carbon dioxide were evolved per mole of azobenzene formed.

(b) With Diiron Enneacarbonyl

A mixture of nitrosobenzene (1.488 g., 13.9 mm.) and diiron enneacarbonyl (5.053 g., 13.9 mm.) in dry tetrahydrofuran (55 ml.) was vigorously stirred under nitrogen for 12 hours at room temperature. The solution was filtered and the solvent removed at 30 mm. The residue was treated with petroleum ether, filtered and the filtrate chromatographed on Florisil. Elution with petroleum ether gave 0.351 g. (11.0%) of complex XI, m.p. 58.5-59.0°C. XI shows infrared absorption bands (KBr pellet) at: 3375 cm.$^{-1}$ (γ NH); 2070, 2035, 1996, 1971, 1956 cm.$^{-1}$ (γ ($C\equiv O$)); 774 and 687 cm.$^{-1}$ (out-of-plane bending of five adjacent hydrogen atoms on a phenyl ring); and 743 cm.$^{-1}$ (four adjacent hydrogen atoms on a phenyl group). Further elution with petroleum ether gave traces of azobenzene (XLVII).

(ii) p-Nitrosophenol (XLVIII)

A mixture of p-nitrosophenol (2.427 g., 19.71 mm.) and iron pentacarbonyl (2.72 ml., 19.71 mm.) in anhydrous dioxane (65 ml.) was refluxed with stirring under nitrogen for 24 hours. The solution was cooled and filtered, and the solvent removed at 30 mm. Both the residue and the solid filtered were treated with ether, filtered, and the filtrate chromatographed on Florisil. Elution with ether gave 0.863 g. (40.9%) of green crystals of 4,4'-dihydroxyazobenzene (L), m.p. 212.0-214.0°C (lit. m.p. 216°C).[3] Further elution with ether gave recovered starting material. The yield of azo compound was not improved by altering either the reflux time, reagent concentration, or the presence of a catalytic quantity of boron trifluoride etherate. In all cases, no p-benzoquinone formation was observed.

(iii) 5-Methyl-4-nitroso-2-isopropylphenol (LII)

(a) With No Catalyst

A mixture of 5-methyl-4-nitroso-2-isopropylphenol (3.114 g., 17.38 mm.) and iron pentacarbonyl (2.34 ml., 17.38 mm.) in dry butyl ether (50 ml.) was refluxed with stirring under nitrogen for 22 hours. The solution was cooled and filtered, and the solvent was removed at ca. 30 mm. The residue from the filtrate was treated with petroleum ether and filtered. The petroleum ether-insoluble solid, which exhibited amino absorption in the infrared at 3455 and 3390 cm.$^{-1}$, was crystallized from benzene to give 0.503 g. (17.6%) of white needles of 5-methyl-4-amino-2-isopropylphenol (LV), m.p. 177.0-179.0^{o}C (lit. m.p. 178-179^{o}C).[142] The petroleum ether filtrate was evaporated to give 5-isopropyl-2-methyl-1,4-benzoquinone (LIV) as yellow plates. In addition, treatment of the solid filtered above with petroleum ether as described gave additional quinone. The total yield of LIV was 0.307 g. (10.7%), m.p. 42.0-44.0^{o}C (lit. m.p. 45.5^{o}C).[3]

(b) With a Catalytic Quantity of Boron Trifluoride

When the reaction between the nitrosophenol and metal carbonyl was repeated in the presence of a catalytic amount of boron trifluoride etherate (5% W/W of nitrosophenol), LV was obtained in 6.0% yield while LIV was obtained in 19.4% yield.

C. Nitro Compounds

(i) Reaction of Equimolar Quantities of Nitrobenzene and Iron Pentacarbonyl in Butyl Ether

A mixture of nitrobenzene (3.270 g., 26.56 mm.) and iron pentacarbonyl (3.57 ml., 26.56 mm.) in dry butyl ether (50 ml.) was refluxed with stirring under nitrogen for 18-24 hours. The solution was cooled and filtered, and the solvent removed at 30 mm. The residue was dissolved in petroleum ether (b.p. 38-54°C) and chromatographed on Florisil. Elution with petroleum ether gave: (1) 0.080 g. (3.3%) of azobenzene (XLVII), m.p. and mixed m.p. 66.0-68.0°C and (2) 1.677 g. (63.7%) of azoxybenzene (XLVI), m.p. and mixed m.p. 35.0-36.0°C (lit. m.p. 36.0°C).[3]

(ii) Reaction of a 1.4/1.0 Mole Ratio of Iron Pentacarbonyl to Nitrobenzene in Butyl Ether

A 1.4/1.0 mole ratio of iron pentacarbonyl to nitrobenzene was reacted as above. Chromatography on Florisil gave azobenzene in 76.0% yield, no azoxybenzene formation being detected. As an alternative to chromatography, purification of azobenzene could be effected by treating the residue from solvent evaporation with 95% ethanol. In repeating the reaction several times, it was noted, that in some cases, a small amount of azo compound was present in the solid filtered on cooling the reaction mixture after reflux. Treating this solid with petroleum ether, filtering, and evaporating the filtrate gave reasonably pure azobenzene. From 95% ethanol, analytically pure azobenzene (XLVII) was obtained.

(iii) The Generation of Complex XI

The same procedure (except for the use of a 1.4/1.0 mole ratio of diiron enneacarbonyl to nitrobenzene) as that for the reaction of nitrosobenzene with diiron enneacarbonyl to give complex XI can be used.

Approximately the same yield of XI (11.4%) was obtained as for the nitroso reaction.

(iv) Reactions of Para-Substituted Nitrobenzenes with Iron Pentacarbonyl

The general procedure used for the para-substituted nitrobenzenes (H, CH_3, OCH_3, F) follows the reaction conditions described for the reaction of a 1.4/1.0 mole ratio of iron pentacarbonyl to nitrobenzene. The melting points and yields are given in Table VII. When the para-substituent was dimethylamino, the product was eluted off the Florisil column with benzene-acetone (1:1).

The products from the reaction of p-nitrobenzonitrile with iron pentacarbonyl were isolated in the following manner: infrared absorption indicated the residue from solvent evaporation to be almost entirely starting material with traces of amino and azo compound. The solid filtered on cooling the reaction mixture after reflux was treated with boiling benzene, filtered, and the filtrate cooled and then chromatographed on Florisil. Elution with benzene gave p-aminobenzonitrile. Elution with benzene-ether (1:1) gave 4,4'-dicyanoazobenzene (Table VII). The small amounts of the two products present in the residue from solvent evaporation could be separated and isolated from the starting material in a similar manner.

p-Nitrophenol and p-nitrobenzoic acid were recovered unchanged when reacted with iron pentacarbonyl under the general conditions. Addition of either boron trifluoride etherate or triethylamine (~5% W/W of nitro compound) failed to catalyze any reaction.

(v) Reactions of Meta-Substituted Nitrobenzenes With Iron Pentacarbonyl

The general procedure was used for m-nitroanisole. For m-nitrotoluene, chromatography on Florisil gave 3,3'-dimethylazobenzene on elution with petroleum ether and m-toluidine on elution with acetone. The amine was further purified by distillation. 3-Amino-N,N-dimethylaniline, obtained from the reaction of 3-nitro-N,N-dimethylaniline with iron pentacarbonyl, was purified by distilling the residue obtained after solvent evaporation.

(vi) Reactions of Ortho-Substituted Nitrobenzenes with Iron Pentacarbonyl

(a) o-Nitrotoluene

The same general procedure as for m-nitrotoluene was used for the reaction of the corresponding ortho isomer with iron pentacarbonyl in butyl ether. With butryonitrile, essentially the same yields of azo and amino compounds were obtained.

(b) o-Ethylnitrobenzene

The procedure for the reaction of a 1.4/1.0 mole ratio of iron pentacarbonyl to nitrobenzene was applied to o-ethylnitrobenzene with the following modification: chromatography on Florisil gave 2,2'-diethylazobenzene on elution with petroleum ether and o-ethylaniline on elution with petroleum ether-acetone (1:1).

(c) o-Nitroanisole

A mixture of o-nitroanisole (5.115 g., 33.40 mm.) and iron pentacarbonyl (6.28 ml., 46.76 mm.) in dry butyl ether (40 ml.) was refluxed with stirring under nitrogen for twenty-four hours. The solution was cooled and filtered, and the filtrate carefully evaporated to dryness at 30 mm. Distillation of the residue gave 3.04 g. (73.9%) of colorless o-methoxyaniline, b.p. 222-224°C (Table VII). Alternatively, the amine could be isolated by fractional distillation of the filtrate.

The solid filtered from the reaction mixture ignited on drying, presumably due to the presence of pyrophoric iron.

Utilizing otherwise identical conditions, o-methoxyaniline was obtained from the nitro compound in 58% yield by using n-octane in place of butyl ether as solvent.

(d) 2-Nitrobiphenyl (LVI)

A mixture of 2-nitrobiphenyl (3.254 g., 16.34 mm.) and iron pentacarbonyl (3.08 ml., 22.88 mm.) in anhydrous butyl ether (75 ml.) was refluxed with stirring under nitrogen for 27 hours. The solution was cooled and filtered and the solvent removed at ca. 30 mm. The crude semi-solid residue was treated with large quantities of petroleum ether, filtered, and the filtrate concentrated. Chromatography on Florisil of the concentrated filtrate gave 0.142 g. of carbazole (LVIII), m.p. 244.0-246.0°C (undepressed on admixture with an authentic sample) on elution with petroleum ether, and 1.608 g. (58.3%) of 2-aminobiphenyl (LVII), m.p. 47.0-49.0°C (undepressed on admixture with an authentic sample) on elution with petroleum ether-acetone (9:1).

The petroleum ether-insoluble solid was recrystallized from benzene to give a further 0.259 g. of carbazole. Total yield of carbazole (LVIII) was 0.401 g. (14.7%).

(e) 2,2'-Dinitrobiphenyl (LIX)

A mixture of LIX (3.555 g., 14.56 mm.) and iron pentacarbonyl (5.87 ml., 43.68 mm.) in dry butyl ether (55 ml.) was refluxed with stirring under nitrogen for 20 hours. The solution was cooled and filtered, and the filtrate evaporated to give 0.457 g. of beautiful yellow blades of benzo [c] cinnoline (LX), m.p. 155.0-156.0°C (lit. m.p. 155-157°C).[146] The solid removed from the solution above was recrystallized from benzene to give an additional 1.240 g. of the cinnoline. The total yield of benzo [c] cinnoline (LX) was 1.70 g. (64.8%). The ultraviolet spectrum of the product (in ethanol) showed absorption maxima at 252.0 mμ (log ε = 4.58), 308.0 mμ (log ε = 3.98) and 355.0 mμ (log ε = 3.28) in agreement with the spectrum reported in the literature.[146]

(f) o-Dinitrobenzene (LXI)

The procedure for the reaction of a 1.4/1.0 mole ratio of iron pentacarbonyl to nitrobenzene was applied to o-dinitrobenzene with the following modifications: (a) a 3.0/1.0 mole ratio of metal carbonyl to dinitro compound was used and; (b) benzene was the eluent used in the column chromatography step.

(vii) 1-Nitronaphthalene

A mixture of 1-nitronaphthalene (3.202 g., 18.49 mm.) and iron pentacarbonyl (3.48 ml., 25.89 mm.) in dry butyl ether (50 ml.) was refluxed with stirring under nitrogen for 23 hours. The solution was cooled and filtered, and the solvent removed at 30 mm. Both the residue and the solid filtered were treated with acetone, filtered to remove inorganic material, and the filtrate was chromatographed rapidly through Florisil using acetone as the eluent to give 2.052 g. (77.0%) of crude 1-aminonaphthalene, m.p. 44.0-46.0°C. Purification was effected by treatment first with decolorizing charcoal and then recrystallization from dilute ethanol to give 1.85 g. (70.0%) of 1-aminonaphthalene, m.p. 49.0-50.0°C (lit. m.p. 49.0-50.0°C).[3]

(viii) 1,8-Dinitronaphthalene

A mixture of 1,8-dinitronaphthalene (3.022 g., 13.85 mm.) and iron pentacarbonyl (5.59 ml., 41.55 mm.) in dry butyl ether (60 ml.) was refluxed with stirring under nitrogen for 20 hours. The solution was cooled and filtered, and the solvent removed from the filtrate at ca. 30 mm. The residue from the filtrate (0.010 g.) showed absorption in the infrared region (3500-3300 $cm.^{-1}$) indicative of an amine. Treatment with petroleum ether-acetone (1:1) of the solid filtered from the original cooled solution removed an additional small amount (0.010 g.) of 1,8-diaminonaphthalene, m.p. 63.0-65.0°C (lit. m.p. 66.5°C).[3] The insoluble solid was largely inorganic with some initial nitro compound present.

Lowering the ratio of iron carbonyl to dinitro compound used to either 2.5/1.0 or 2.0/1.0 only resulted in producing a larger recovery of starting material with trace amounts of product formed once more. More satisfactory results were not obtained when the reflux time was either decreased to 10 hours or increased to 48 hours.

(ix) 4-Nitropyridine-1-Oxide (LXIII)

A mixture of 4-nitropyridine-1-oxide (3.004 g., 21.44 mm.) and iron pentacarbonyl (3.17 ml., 23.58 mm.) in dry butyl ether (40 ml.) was refluxed with stirring under nitrogen for 17 hours. The solution was cooled and filtered, and the solvent removed at ca. 30 mm. The crude residue, m.p. 120.0-122.0°C, showed only weak absorption in the infrared region due to a nitro group. Both the residue from the filtrate and the solid filtered originally from the reaction were dissolved in benzene and chromatographed on Florisil. Elution with benzene gave 0.472 g (22.0%) of orange-yellow needles of 4,4'-azoxypyridine (LXIV), m.p. 123.0-125.0°C (lit. m.p. 125-126°C);[147] ultraviolet absorption at 291.0 mu (log ε = 4.20 in ethanol). Elution with benzene-ether (1:1) gave a mixture of trace amounts of 4,4'-azoxypyridine-1,1-dioxide (LXV) and 4-nitropyridine (LXVI), identified by comparison of ultraviolet spectra with those reported by den Hertog, Henkens and van Roon.[147]

D. Nitrosamines

(i) Preparation of Nitrosamines

N-Nitrosodiphenylamine (m.p. 66.5-67.0°C), N-nitroso-N-phenylbenzylamine (m.p. 57.0-58.0°C), N-nitroso-N-methylaniline (b.p. 128-130°C at 20 mm.) were prepared according to standard procedures.[148] N-Nitrosomorpholine (m.p. 28.5-29.0°C), was prepared according to Zimmer and co-workers.[149] N-Nitrosopiperidine was purchased from Fisher Chemical Co. and N-nitrosocarbazole was purchased from K and K Laboratories, Inc.

(ii) General Procedure for Reaction of Aromatic Nitrosamines with Iron Pentacarbonyl

A mixture of nitrosamine (5-60 mm.) and iron pentacarbonyl (1.1 mole/mole of nitrosamine) in dry butyl ether (40-70 ml.) was refluxed with stirring under nitrogen for 2-16 hours. The solution was cooled and filtered to remove inorganic impurities and then the solvent was removed at 30 mm. Recrystallization from alcohol or other suitable solvents gave the amine in 85-92% yield (Table IX). The melting points of the solid amines were undepressed by admixture with authentic samples. N-Methylaniline was purified by fractional distillation of the filtrate.

(iii) Reaction of N-Nitrosodiphenylamine (LXXVII) With Iron Pentacarbonyl in Isooctane

Except for the use of isooctane instead of butyl ether, the same procedure was followed as in the general method described above. Recrystallization from aqueous ethanol gave diphenylamine (LXXIX), m.p. 52.0-54.0°C (lit. m.p. 52.8°C),[3] in 27.2% yield. The infrared spectrum of the solid filtered originally from the reaction indicated that it was organic rather than inorganic and hence work-up was necessary. Treatment of the solid with benzene, filtering, and evaporating the filtrate gave tetraphenylhydrazine (LXXVIII), m.p. 147°C (dec.) (lit. m.p. 147-149°C, dec.)[3] in 56.1% yield. The benzene-insoluble material was found to be inorganic.

(iv) Reduction of Tetraphenylhydrazine (LXXVIII) by Hot Butyl Ether

Tetraphenylhydrazine (1.776 g., 5.28 mm.) in dry butyl ether (40 ml.) was refluxed with stirring under nitrogen for 18 hours. The solution was cooled, a small amount of insoluble impurity was removed by filtration, and the solvent was evaporated from the filtrate at 30 mm. The residue was treated with petroleum ether, filtered, and the filtrate evaporated to give 1.57 g. (87.9%) of diphenylamine (LXXIX), m.p. 52.0-54.0°C.

(v) Reaction of Aliphatic Nitrosamines With Iron Pentacarbonyl

A mixture of aliphatic nitrosamine (20-40 mm.) and iron pentacarbonyl (1.1 mole/mole of nitrosamine) in dry butyl ether (30-50 ml.) was refluxed with stirring under nitrogen for 2 to 3 hours. (CAUTION: Attempts to carry out the reaction in the absence of a solvent resulted in an explosion.) The solution was cooled and filtered, and the solvent removed at ca. 30 mm. The residue was dissolved in petroleum ether-benzene (1:1) and chromatographed on Florisil. Elution with petroleum ether-benzene (1:1) gave trace quantities of unidentifiable material. Elution with benzene-acetone (5:1) gave the tetrasubstituted urea (Table IX). In the case of N-nitrosomorpholine, the solid filtered after reflux consisted largely of the urea which was isolated by chromatography as above. The ureas exhibited carbonyl stretching in the infrared region at 1645-1660 cm.^{-1}

The yield of carbonyl dimorpholine decreased slightly (from 57 to 51%) when the reaction was carried out in isooctane.

E. Oximes

(i) Preparation of Oximes

Cholest-4-en-3-one oxime, m.p. 152.0-152.5°C, was prepared according to Shoppee, Kreiger and Merrington.[150] Fluorenone and cyclohexanone oximes were purchased from Fisher Scientific Co. The gifts of santonin and 4-methyl-4-trichloromethylcyclohexa-2,5-dienone oximes by Dr. M. J. Davis and of O-methylpodocarpinaldoxime by Mr. W. Zehetner are gratefully acknowledged.

(ii) General Procedure for the Regeneration of Carbonyl Compounds from Oximes

A mixture of the oxime (2-35 mmole) and iron pentacarbonyl (1.1 mole/mole of oxime) in dry butyl ether (50-100 ml.) containing boron trifluoride etherate (about 5% W/W of oxime) was refluxed with stirring under nitrogen. The solution was cooled and filtered, and the solvent removed at 30 mm. (except when the volatile cyclohexanone was formed: this was isolated as the 2,4-dinitrophenylhydrazone by treating the filtrate with 2,4-dinitrophenylhydrazine in the usual manner). The residue of crude carbonyl compound was purified by trituration with petroleum ether, hexane, or methylene chloride (procedures a, b or c respectively) or by chromatography on Florisil using acetone as the eluant (procedure d). The purity of the products recorded in Table X was indicated by melting points agreeing with values in the literature, and by the absence of more than one spot on thin layer chromatograms.

(iii) Attempted Reaction of Fluorenone Phenylhydrazone with Iron Pentacarbonyl and Boron Trifluoride

A mixture of fluorenone phenylhydrazone (m.p. 150.0-152.0°C, prepared from fluorenone and phenylhydrazine according to standard procedures[151]) (2.251 g., 8.33 mm.) and iron pentacarbonyl (1.23 ml., 9.16 mm.) in dry butyl ether (65 ml.) containing boron trifluoride etherate (0.115 g., ca. 5% by wt. of phenylhydrazone) was refluxed with stirring under nitrogen for 12.5 hours. The solution was cooled and filtered, and the solvent removed at 30 mm. to give quantitative recovery of starting material.

(iv) Attempted Reaction of N,2,6-Trichloro-1,4-benzoquinoneimine with Iron Pentacarbonyl and Boron Trifluoride

To a mixture of N,2,6-trichloro-1,4-benzoquinoneimine (3.049 g., 14.49 mm.) and iron pentacarbonyl (2.14 ml., 15.94 mm.) was added boron trifluoride etherate (0.150 g., ~5% W/W of oxime). The reaction mixture was refluxed with stirring under nitrogen for 12 hours. The solution was cooled and filtered and the solvent removed at 30 mm. Yellow needles of starting material (3.01 g., 99%), m.p. 67.0-68.0°C, were recovered by crystallization from ethanol.

F. Amides and Thionamides

(i) General Procedure for the Conversion of Amides and Thionamides to Nitriles with Iron Pentacarbonyl

A mixture of amide or thionamide (10-50 mm.) and iron pentacarbonyl (1.6/1.0 mole ratio of metal carbonyl to amide or thionamide) in anhydrous butyl ether (40-50 ml.) was refluxed with stirring under nitrogen for 12-18 hours. The solution was cooled, filtered to remove starting material, and the solvent removed at ca. 30 mm. The nitrile was extracted from the residue with petroleum ether (b.p. 38-60°C) and the extract evaporated to give pure nitrile (distilled if liquid). The melting points of the solid nitriles (Table XI) were undepressed by admixture with authentic samples. The purity of the liquid nitriles was shown by comparison of boiling points, infrared spectra, and thin layer chromatograms with authentic samples.

The yield of nitrile was not improved by increasing the mole ratio of metal carbonyl to amide from 1.6/1.0 to 5.0/1.0. When the above general procedure was repeated either in the presence of a catalytic quantity of iron pentacarbonyl or with no metal carbonyl at all, no reaction was observed.

In the case of p-methoxythionbenzamide, a 5.4% yield of a second product was obtained as a petroleum ether-insoluble solid, m.p. 85.0-87.0°C, N-(p-methoxybenzyl)-p-methoxythionbenzamide. The infrared spectrum of the new material (KBr disc) exhibited strong -NH absorption at 3290 cm.$^{-1}$ and thiocarbonyl stretching at 1260 cm.$^{-1}$ (-OCH_3 at 1240 cm.$^{-1}$). The N.M.R. spectrum ($CDCl_3$) shows, besides signals for the aromatic and methoxyl protons, a doublet at 4.92 p.p.m. for the methylene protons coupled to -NH-, which appears as a broad peak in the region of 7.8-8.0 p.p.m. Upon deuterium oxide exchange, the methylene doublet collapsed to a singlet and the NH absorption disappeared.

CALCULATED FOR $C_{16}H_{17}NSO_2$: C, 66.88 ; H, 5.96 ; N, 4.89 ; S, 11.12

FOUND : C, 67.25 ; H, 5.85 ; N, 5.08 ; S, 11.07

(ii) Reaction of p-Methoxythionbenzamide (LXXXV) with Diiron Enneacarbonyl in Tetrahydrofuran

A mixture of p-methoxythionbenzamide (0.803 g., 4.80 mm.) and diiron enneacarbonyl (2.794 g., 7.68 mm.) in dry tetrahydrofuran (30 ml.) was stirred under nitrogen for 24 hours. The solution was filtered to remove inorganic material and the filtrate evaporated at ca. 30 mm. to give a crude residue showing infrared absorption bands for an iron carbonyl complex and for a nitrile. The residue was treated with 2-3 ml. of petroleum ether, filtered, and the filtrate evaporated to give 0.110 g. (17.2%) of p-methoxybenzonitrile (LXXXVI), m.p. and mixed m.p. 60.0-62.0°C (lit. m.p. 61-62°C).[3] The petroleum ether-insoluble solid was dissolved in benzene and chromatographed on Florisil. Elution with benzene gave 64 mg. (2.6% yield based on diiron enneacarbonyl) of $S_2Fe_3(CO)_9$ (XII), m.p. 112°C (lit. m.p. 114°C).[46] Further elution with benzene gave 0.558 g. (38.0%) of the black complex LXXXVII, which decomposed without melting above 250°C.

CALCULATED FOR $C_{22}H_{16}N_2S_2O_8Fe_2$: C, 42.83; H, 2.63; N, 4.58; S, 10.47

FOUND : C, 42.67; H, 2.58; N, 4.84; S, 10.77.

Molecular weight calculated: 612.2. Found (Osmometry): 606.

(iii) Reaction of Complex LXXXVII in Butyl Ether

Complex LXXXVII (0.385 g., 0.630 mm.) in dry butyl ether (30 ml.) was refluxed with stirring under nitrogen for 15 hours. The solution was cooled and filtered, and the product was worked-up according to the general procedure to give p-methoxybenzonitrile (LXXXVI) in 77% yield.

(iv) Reaction of Thionbenzanilide (LXXXVIII) with Iron Pentacarbonyl

A mixture of thionbenzanilide (4.079 g., 19.12 mm.) and iron pentacarbonyl (4.11 ml., 30.59 mm.) in dry butyl ether (50 ml.) was refluxed with stirring under nitrogen for 18 hours. Utilizing identical work-up conditions to the α-phenyl-N-phenylnitrone (XLIV)--iron pentacarbonyl reaction, 1.642 g. (47.1%) of N-benzylideneaniline (XLV), m.p. 50.0-51.0°C, was obtained.

(v) Reaction of N-Deuteriothionbenzanilide with Iron Pentacarbonyl

N-Deuteriothionbenzanilide was prepared by dissolving thionbenzanilide in ether and shaking with deuterium oxide for 4 hours. The layers were separated and the ether removed to give the deuterated compound, m.p. 102.0-102.5°C. Nuclear magnetic resonance ($CDCl_3$) indicated less than 10% N-protiumthionbenzanilide. Reacting the deuterated compound under previously described conditions resulted in the formation of the Schiff base XLV in 38.6% yield. The N.M.R. and infrared spectra indicated the absence of deuterium in the product.

(vi) Reaction of Benzanilide with Iron Pentacarbonyl

The procedure for thionbenzanilide was applied to benzanilide to give N-benzylideneaniline in 14.8% yield.

(vii) Attempted Reaction of N-Methylacetanilide with Iron Pentacarbonyl

The procedure for thionbenzanilide was applied to N-methylacetanilide to give recovered starting material.

G. Thioureas, Thiohydantoins and Sulfonamides

(i) 1,1-Diphenyl-2-Thiourea (XC)

A mixture of 1,1-diphenyl-2-thiourea (3.590 g., 15.73 mm.) and iron pentacarbonyl (3.39 ml., 25.17 mm.) in dry butyl ether (65 ml.) was refluxed with stirring under nitrogen for 17 hours. The solution was cooled and filtered and the solvent removed at ca. 30 mm. Recrystallization of the residue from aqueous ethanol gave 1.913 g. (71.9%) of diphenylamine (LXXIX), m.p. 52.0-53.0°C (lit. m.p. 52.8°C).[3]

(ii) Attempted Reactions of 3,5-Diphenyl-2-Thiohydantoin, Benzenesulfonamide and *p*-Toluenesulfonamide with Iron Pentacarbonyl

The general procedure for the conversion of amides and thionamides to nitriles was applied to the titled compounds. Only starting material was recovered in all cases.

H. Acid Chlorides

(i) General Procedure for the Reaction of Acid Chlorides and Iron Pentacarbonyl in Butyl Ether.

A mixture of the acid chloride (20-40 mm.) and iron pentacarbonyl (1.1 mole/mole of acid chloride) in dry butyl ether (40 ml.) was refluxed with stirring under nitrogen for 17 hours. The solution was cooled, filtered to remove inorganic material (shown to be ferrous chloride by its aqueous solution giving a Turnbull blue coloration with potassium ferricyanide), and the solvent removed at 30 mm. Distillation of the crude residue gave the butyl ester. The ester, yield, and boiling point of the acid chlorides reacted are: butyl octanoate, 75.0%, b.p. 243-245°C (lit. b.p. 245°C),[3] butyl benzoate, 66.6%, b.p. 248-250°C (lit. b.p. 247°C),[3] butyl *p*-methoxybenzoate, 66.0%, b.p. 165-167°C at 20 mm. (lit. b.p. 186-187°C at 40 mm.).[152]

(ii) Reaction of Benzoyl Chloride with Iron Pentacarbonyl in Tetrahydrofuran

A mixture of benzoyl chloride (5.250 g., 37.34 mm.) and iron pentacarbonyl (5.52 ml., 41.07 mm.) in dry tetrahydrofuran (40 ml.) was refluxed with stirring under nitrogen for 40 hours. The solution was cooled and filtered and the solvent removed at 30 mm. The residue was distilled to give 7.977 g. (86.1%) of 4-chlorobutyl benzoate, b.p. 142-144°C at 5 mm. (lit. b.p. 140-143°C at 5 mm.).[133]

(iii) Reaction of p-Methoxybenzoyl Chloride (XCI) with Iron Pentacarbonyl in Tetrahydrofuran

A mixture of p-methoxybenzoyl chloride (7.486 g., 43.88 mm.) and iron pentacarbonyl (6.48 ml., 48.27 mm.) in dry tetrahydrofuran (40 ml.) was refluxed with stirring under nitrogen for 40 hours. The solution was cooled and filtered and the solvent removed at 30 mm. Distillation of the residue at 1.0 mm. gave 8.349 g. (78.4%) of 4-chlorobutyl p-methoxybenzoate (XCII), b.p. 160-162°C.

CALCULATED FOR $C_{12}H_{15}O_3Cl$: C, 59.40 ; H, 6.23

FOUND : C, 59.84 ; H, 6.39

(iv) Reaction of p-Methoxybenzoyl Chloride with Anhydrous Ferric Chloride in Tetrahydrofuran

Utilizing identical reaction conditions as the last reaction, with the exception of the substitution of ferric chloride for iron pentacarbonyl, a liquid boiling at 295-298°C at 0.4 mm. was obtained. N.M.R. (CCl_4) indicated the product ester was polymeric. When the reaction was repeated in the absence of p-methoxybenzoyl chloride, no polymerization product was obtained.

(v) Reaction of p-Methoxybenzoyl Chloride (XCI) with Iron Pentacarbonyl in 2-Methyltetrahydrofuran

A mixture of p-methoxybenzoyl chloride (5.396 g., 31.63 mm.)

and iron pentacarbonyl (4.67 ml., 34.79 mm.) in anhydrous 2-methyltetrahydrofuran (40 ml.) was refluxed with stirring under nitrogen for 40 hours. The solution was cooled and filtered and the solvent removed at 30 mm. Distillation of the residue at 0.55 mm. gave 6.145 g. (75.7%) of 4-chloropentyl *p*-methoxybenzoate (XCIII), b.p. 147-149°C.

CALCULATED FOR $C_{13}H_{17}O_3Cl$:	C,	60.82	;	H,	6.68
FOUND :	C,	61.14	;	H,	6.76

I. Triphenylphosphine Oxide

A mixture of triphenylphosphine oxide (2.215 g., 7.96 mm.) and iron pentacarbonyl (1.17 ml., 8.66 mm.) in dry butyl ether (35 ml.) was refluxed with stirring under nitrogen for 18 hours. The solution was cooled and filtered and the solvent removed at 30 mm. to give quantitative recovery of triphenylphosphine oxide.

J. Ketones and Nitriles

The general procedure for the reaction of aromatic nitrosamines with iron pentacarbonyl was applied to benzophenone, fluorenone, phenylacetonitrile and *p*-tolunitrile. Only starting material was recovered in all cases.

SUMMARY AND CLAIMS TO ORIGINAL RESEARCH

The iron-tricarbonyl complexes of cholesta-2,4-diene, ergosterol and cholesta-5,7-dien-3β-ol were prepared by reaction of the parent diene with iron pentacarbonyl in isooctane, cyclohexane, or butyl ether. The isomerization of heteroannular dienes to homoannular diene-iron tricarbonyl complexes was achieved by refluxing the diene with iron pentacarbonyl in butyl ether. In this way, both cholesta-3,5-diene and cholesta-4,6-diene gave cholesta-2,4-diene-iron tricarbonyl; 3-methylcholesta-3,5-diene and 3-methoxycholesta-3,5-diene formed the corresponding cholesta-2,4-diene-iron tricarbonyl complexes.

The spectral properties of the complexes were determined. In the infrared spectrum, the complexes exhibited metal carbonyl stretching bands of strong intensity in the regions 2029-2040 cm.$^{-1}$ and 1938-1970 cm.$^{-1}$. The ultraviolet absorption maximum of the complexes appeared at a much shorter wavelength than that of the parent dienes. The N.M.R. properties were similar to those reported for diene-iron tricarbonyl complexes of simpler systems.

The parent dienes were regenerated from the complexes by the use of ferric chloride.

A number of dienone-iron tricarbonyl complexes were prepared. 4,4-Dimethylcyclohexa-2,5-dienone was synthesized simply by reaction of isobutyraldehyde with methyl vinyl ketone to give 4,4-dimethylcyclohex-2-enone followed by dehydrogenation of the latter with selenium dioxide to give the desired dienone. Reaction of the dienone with iron pentacarbonyl in isooctane gave the dienone-iron tricarbonyl complex. Cholesta-1,4-dien-3-one-iron tricarbonyl was obtained in a similar manner or by stirring a mixture of the dienone and diiron enneacarbonyl in dry benzene at 40-50°C for four hours. Androsta-1,4-diene-3,11,17-trione-iron tricarbonyl and santonin-iron tricarbonyl were obtained by refluxing the corresponding dienone with iron pentacarbonyl in dioxane.

The spectral properties of the dienone complexes were recorded. There is little difference between the positions of the metal carbonyl stretching frequencies for the dienone and diene-iron tricarbonyl complexes. Only a small hypsochromic shift of the ultraviolet absorption maxima of the dienones upon complex formation is observed. The N.M.R. signals for the olefinic protons of the dienones are only slightly shifted upon complex formation.

All of the dienone-iron tricarbonyl complexes, except santonin-iron tricarbonyl, were readily decomposed to the corresponding dienones with ferric chloride. Santonin-iron tricarbonyl was decomposed via its oxime.

4-Methyl-4-trichloromethylcyclohexa-2,5-dienone failed to form an iron-tricarbonyl complex, and its oxime regenerated the carbonyl compound upon treatment with iron pentacarbonyl.

Santonin reacted with diiron enneacarbonyl in benzene to give two products: a dimeric complex with bridging carbonyl groups and a cyclopentadienone-iron tricarbonyl complex. Bis-(2-ethylhexyl)-*o*-phthalate was obtained from reaction of either santonin and iron pentacarbonyl in butyl ether or santonin-iron tricarbonyl in butyl ether.

An investigation of the behavior of iron pentacarbonyl towards various functional groups was undertaken. The following results were obtained:

(a) N-Oxides gave the corresponding amines on deoxygenation with the metal carbonyl. The deoxygenation of pyridine-N-oxide (and presumably other N-oxides investigated) was accompanied by evolution of one equivalent amount of carbon dioxide. This method is competitive with and in some instances superior to others reported in the literature.

(b) Azoxy compounds also underwent deoxygenation giving azo compounds in good yields. Deoxygenation of azoxybenzene was accompanied by evolution of one equivalent amount of carbon dioxide.

(c) α-Phenyl-N-phenylnitrone gave N-benzylideneaniline.

(d) Nitrosobenzene gave either azobenzene on treatment with iron pentacarbonyl or a complex on reaction with diiron enneacarbonyl. p-Nitrosophenol gave 4,4'-dihydroxyazobenzene by reaction with iron pentacarbonyl either in the presence of absence of boron trifluoride etherate. 5-Methyl-4-nitroso-2-isopropylphenol gave 5-methyl-4-amino-2-isopropylphenol as the major product and 5-isopropyl-2-methyl-1,4-benzoquinone as the minor product. In the presence of a catalytic quantity of boron trifluoride etherate, the product composition was reversed.

(e) Nitrobenzene gave azoxybenzene, azobenzene or a complex depending upon reagent concentration. Azo compounds were obtained in reasonably good yields from reaction of iron pentacarbonyl (1.4 moles) with para-substituted nitrobenzenes (1.0 mole) having electron-releasing groups (H, CH_3, OCH_3, F). A substantially lower yield of azo compound resulted when the nitrobenzene had an electron-attracting para substituent. Azo compounds were also obtained from meta-substituted nitrobenzenes although in lower yields than the corresponding para derivatives.

o-Nitrotoluene gave 2,2'-dimethylazobenzene in 67.2% yield and o-toluidine in 13.1% yield. o-Ethylnitrobenzene gave approximately equal amounts of azo and amino compounds. o-Methoxynitrobenzene gave the corresponding amine as the sole product. 2-Aminobiphenyl and carbazole were obtained from 2-nitrobiphenyl. o-Dinitrobenzene gave 2,2'-diaminoazobenzene. 2,2'-Dinitrobiphenyl gave benzo [c] cinnoline.

Reaction of the metal carbonyl with 4-nitropyridine-1-oxide gave 4,4'-azoxypyridine as the major product with 4-nitropyridine and 4,4'-azoxypyridine-1,1-dioxide formed in trace amounts.

(f) Reaction of a nitrosamine (1.0 mole) having at least one phenyl group and iron pentacarbonyl (1.1 moles) in dry butyl ether gave high yields of pure secondary amines. Non-aromatic nitrosamines gave tetrasubstituted ureas.

(g) Oximes regenerated the corresponding carbonyl compounds upon treatment with the metal carbonyl in the presence of a catalytic quantity of boron trifluoride etherate.

(h) Amides and thionamides gave nitriles. Thionbenzanilide and N-deuteriothionbenzanilide gave N-benzylideneaniline. The latter compound was also obtained from benzanilide.

(i) 1,1-Diphenyl-2-thiourea gave diphenylamine.

(j) Acid chlorides reacted with the metal carbonyl in butyl ether to give the corresponding butyl ester. Esters were also obtained using tetrahydrofuran or its 2-methyl derivative as solvents.

(k) Thiohydantoins, sulfonamides, ketones, nitriles and triphenylphosphine oxide failed to react with the metal carbonyl under the described conditions.

Mechanisms were postulated for many of the above reactions.

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