

USE OF TRICARBONYLIRON COMPLEXES
IN ORGANIC SYNTHESIS

a thesis presented by

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ABSTRACT

5,6-Isopropylidenedioxycyclohexa-1,3-diene (17) has been prepared via the palladium catalysed elimination of acetic acid from 1,2-Isopropylidenedioxycyclohex-3-en-5-ol acetate (27). Reaction of 5,6-Isopropylidenedioxy-cyclohexa-1,3-diene (17) with enneacarbonyl diiron produced exo-5,6-Isopropylidenedioxycyclohexa-1,3-diene tricarbonyliron.

A number of tricarbonyliron lactone complexes have been prepared by irradiation of vinyl epoxides in the presence of pentacarbonyliron. In this manner, tricarbonyliron - (1,1¹,2-η-ethylcyclopent-1-ene-1-yl) - 2¹-oxycarbonyliron (30); Z-tricarbonyl - (1,1¹,2¹-η-1,1-propylidenecyclohexane-1-yl) - 3¹-oxycarbonyliron (33); E-tricarbonyliron- (1,1¹,2¹-η-1,1-propylidenecyclohexane-1-yl) - 3¹-oxycarbonyliron (34) and tricarbonyliron-(2,3,4-η-2,3-[tetramethylene]-2-buten-2-yl)-1-oxycarbonyliron (36) have been prepared from their respective epoxides.

Oxidation of these tricarbonyliron lactone complexes with ceric ammonium nitrate leads predominantly to β lactones. Thus, complexes (30) and (33) have been converted on oxidation to 3-(cyclopenten-1-yl) oxetanone (37) and 3-(1¹-methylenecyclohexane) oxetanone (39) respectively.

The chemistry of these novel α-vinyl β-lactones

has been further studied.

Upon thermolysis, tricarbonyliron lactone complexes have been shown to afford products of rearrangement. A number of different pathways have been shown to operate in these thermally induced rearrangements, and the factors which influence the product distribution have been discussed. This work has led to the synthesis of the naturally occurring lactone ($\pm$) Massoia lactone (99), from trans-tricarbonyliron-(1,2,3- η -1-nonen-3-yl)-4-oxycarbonyliron (49).

High field ^1H n.m.r. studies of a number of tricarbonyliron lactone complexes has enabled for the first time complete characterisation of this class of compound. It is now possible to obtain a complete structural assignment of tricarbonyliron lactone complexes from ^1H n.m.r. spectra.

ACKNOWLEDGEMENTS

I would like to thank Dr. S.V. Ley for his advice, guidance, encouragement and friendship throughout the course of this work. I thank Mr K.I. Jones and his staff for the microanalytical service, Mrs Lee for the mass spectrometry service and Mrs Day and Mrs Hamblin for their services at the stores. Thanks also to Dr. G. Hawkes and Dr. H. Rzepa for high field n.m.r. services. I would also like to thank my colleagues at the laboratory for their help, co-operation and friendship.

Finally, I would like to thank the Science Research Council for a studentship for the period of this work.

INTRODUCTION

The use of carbonyliron complexes is now an established part of the synthetic chemists' repertoire.

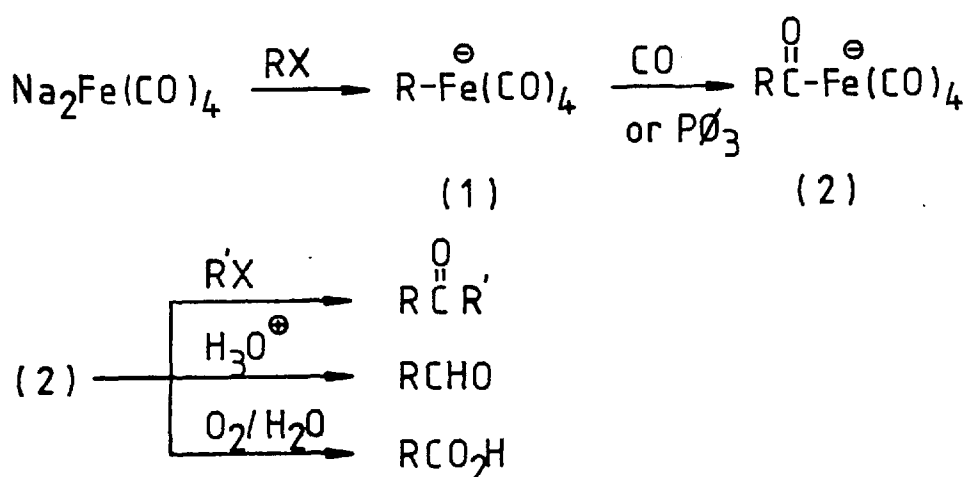
The chemistry of organoiron complexes has been the subject of many reviews,¹⁻³ however, only a few have emphasised the versatility of carbonyliron species in organic synthesis.

This review will therefore deal with recent advances in the use of carbonyliron species towards organic synthesis.

1. IRON CARBONYL ANIONS: VERSATILE SYNTHETIC REAGENTS

(a) Disodium Tetracarbonylferrate

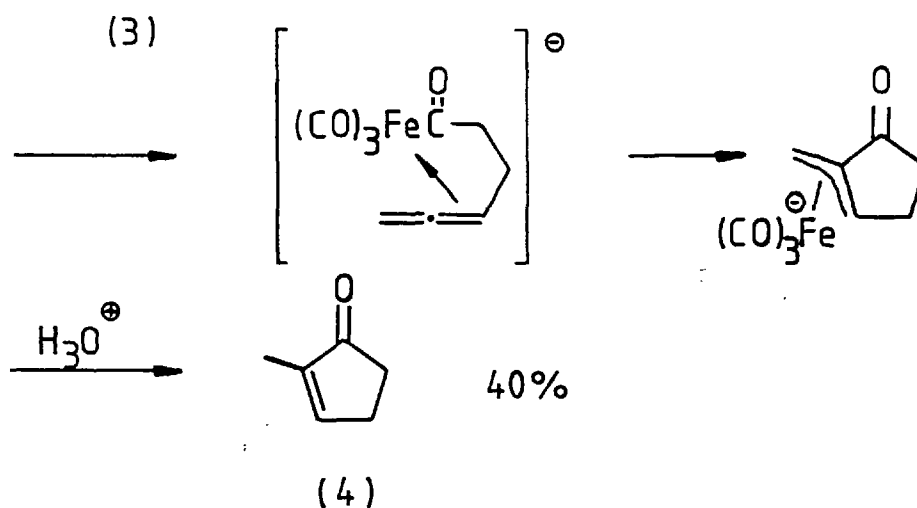
Disodium tetracarbonylferrate⁴ has found extensive use in the preparation of aldehydes, ketones, acids, esters and amides from primary halides and secondary tosylates. Initial SN_2 displacement of halide or tosylate by the highly nucleophilic tetracarbonylferrate anion leads to an intermediate ferrate complex (1), possessing an iron-carbon σ bond. In the presence of a suitable ligand (carbon monoxide or triphenylphosphine) CO insertion into the iron-carbon σ bond occurs to give an intermediate acyl metal complex (2). This complex can then be treated with various electrophiles to give the desired products, via a reductive elimination from a 6 co-ordinate



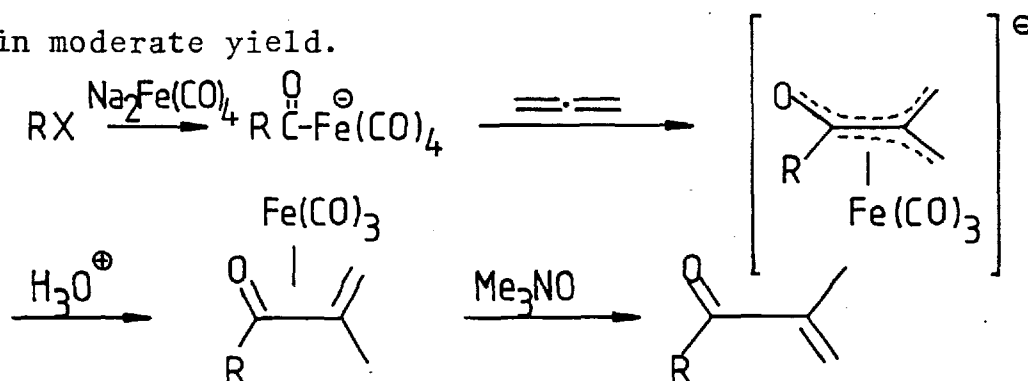
iron species.

Interestingly when the allenic bromide (3) was treated with disodium tetracarbonylferrate, the cyclopent-

enone (4) was formed in moderate yield via an intramolecular insertion reaction.⁵

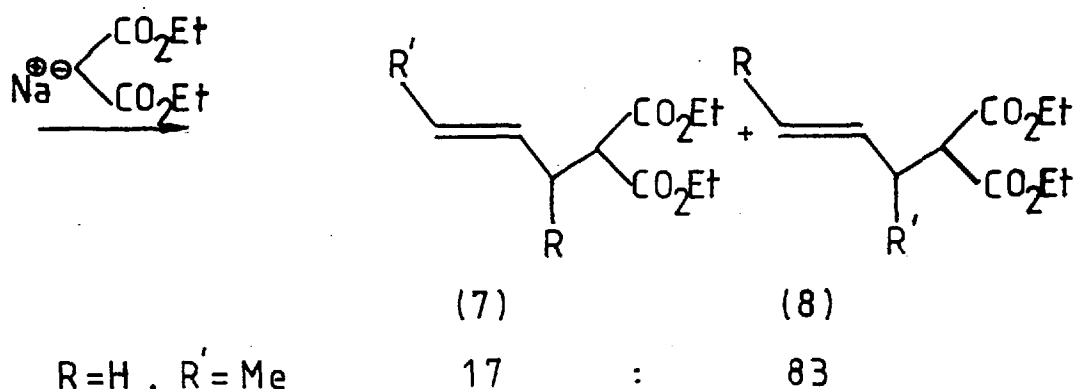
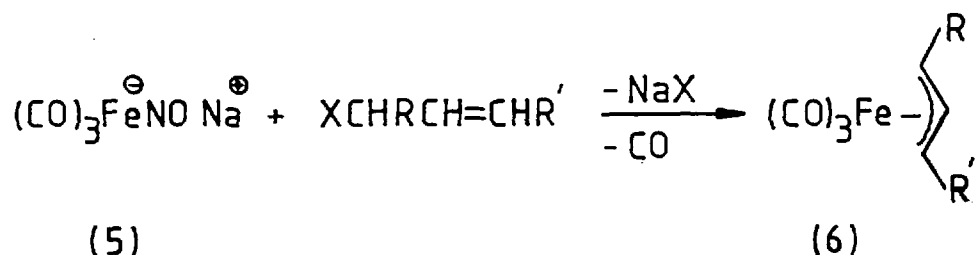


The insertion of an allene into an iron-carbon σ bond was found to be general, and therefore enabled the synthesis of α , β -unsaturated ketones from alkyl halides in moderate yield.



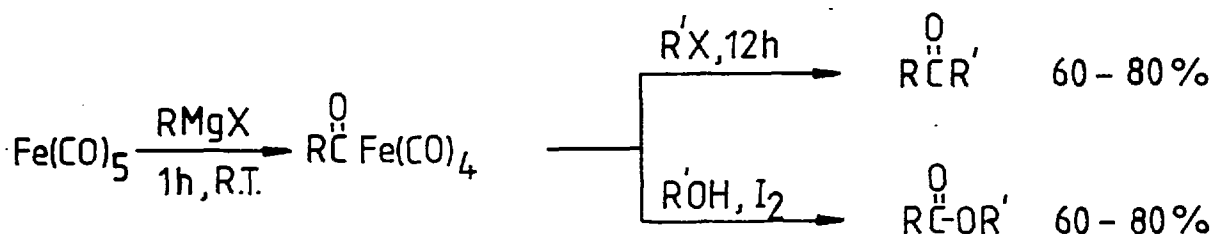
The anionic carbonyliron complex (5) has been found to catalyse the alkylation of allylic halides, acetates and formates⁶ by sodium diethylmalonate, with high regioselectivity. The reaction is presumed to proceed via the allyl complex (6). Attack by the malonate anion, at the termini of the allyl system with expulsion the iron

moiety leads to the alkenes (7) and (8). The major product of reaction even with bulky R^1 was the alkene (8).



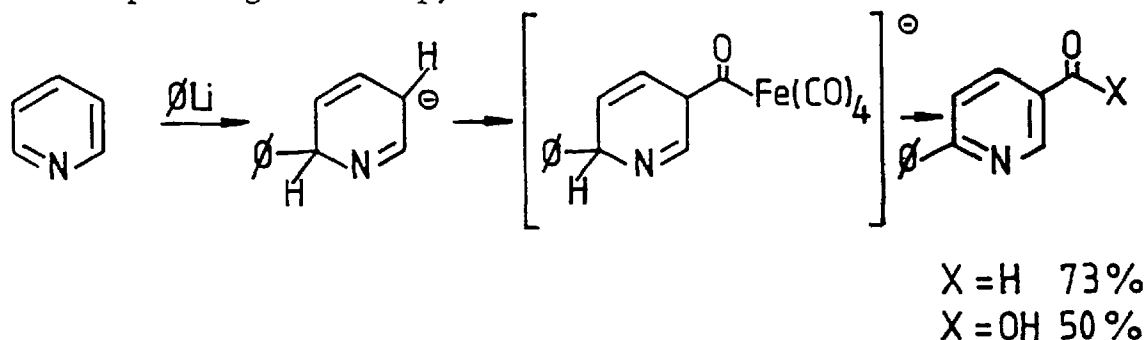
(b) Generation and Synthetic Transformation of Acyl Tetra-carboxylferrates

Treatment of pentacarbonyliron with Grignard reagents^{7, 8} has been shown to be the basis of a convenient one-pot synthesis of esters and ketones.

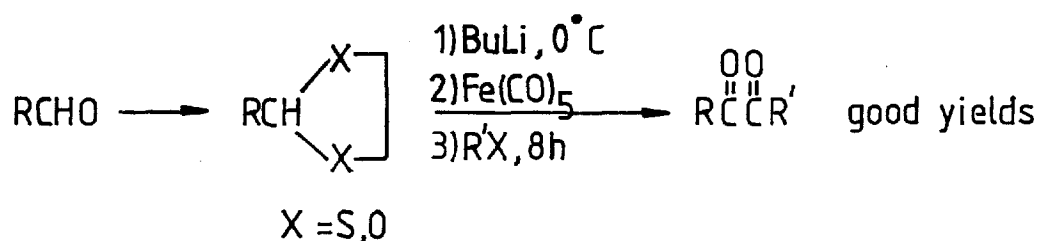


The reaction proceeding via nucleophilic attack upon co-ordinated carbon monoxide to afford an intermediate acyl

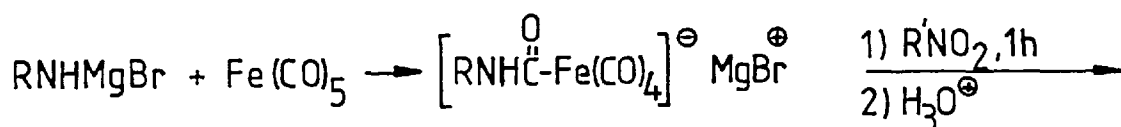
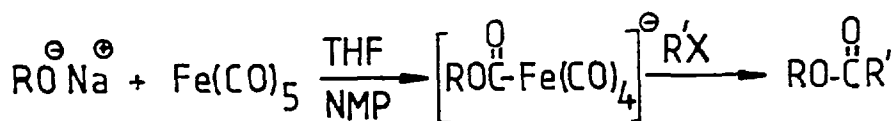
tetracarbonylferrate. In this manner 3-formyl and 3-acyl pyridines have been prepared⁹ in high yield from the corresponding lithio pyridines.



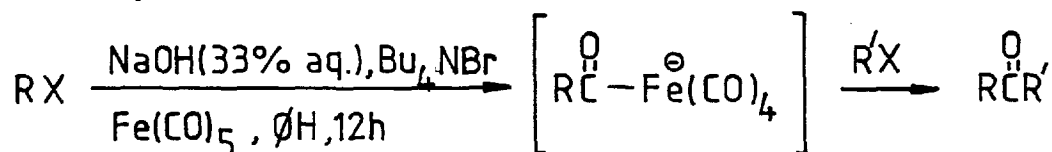
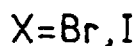
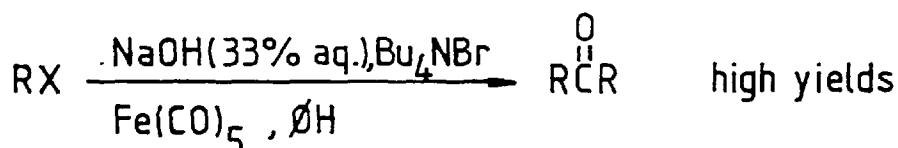
Thus a synthetically difficult transformation had been accomplished in one step via the use of an iron carbonyl reagent. Other organometallic species such as lithium thioacetals¹⁰ have been used to generate acyl tetracarbonylferrates, affording α -diketones on work-up.



Alkoxides,¹¹ and magnesium salts of primary amines¹² on treatment with pentacarbonyliron also afford acyl tetracarbonylferrates, and these have been used in the synthesis of esters and ureas respectively.



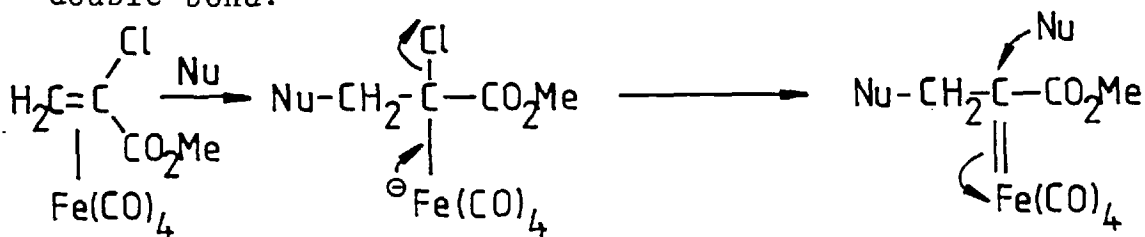
A convenient synthesis of symmetrical and unsymmetrical ketones from alkyl halides has been developed involving phase transfer catalysis.¹³ Here the tetracarbonylferrate anion is generated in situ under conditions in which it would not normally be stable.



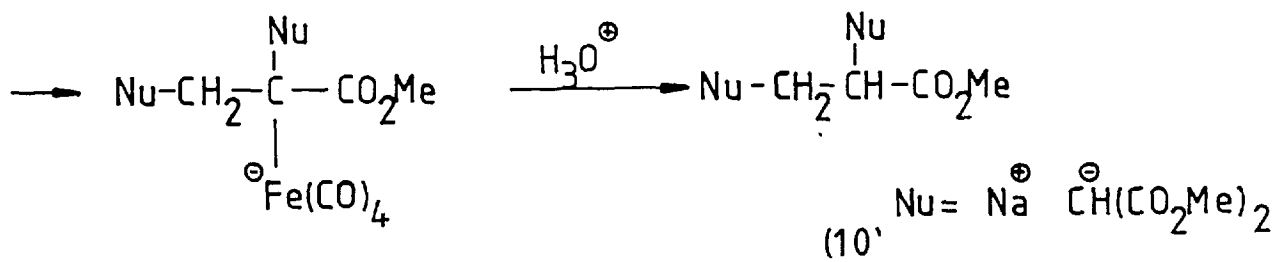
where RX is the less reactive halide

Such procedures have the advantage of avoiding the use of the toxic and pyrophoric disodium tetracarbonylferrate.

A novel reaction involving activation of an olefin via its tetracarbonyliron complex (9) towards nucleophilic attack¹⁴ has led to the product (10) derived from the addition of two moles of the nucleophile across the double bond.



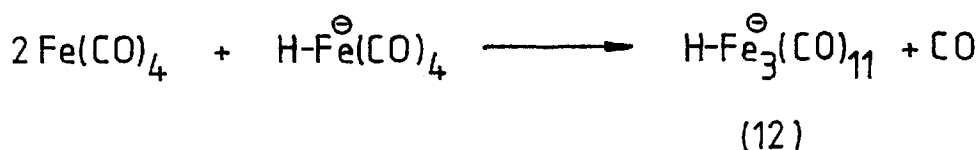
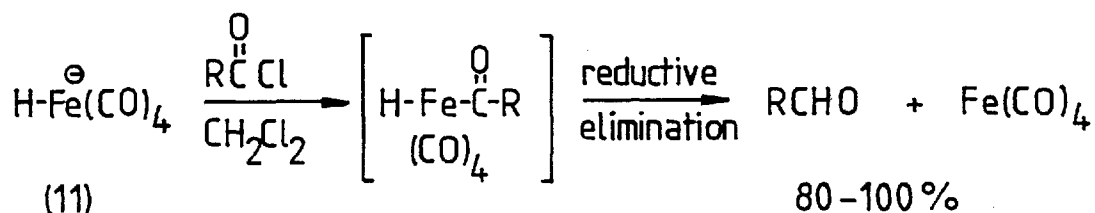
(9)



The initial tetracarbonylferrate intermediate presumably loses chloride anion to give a metal-carbene complex, which undergoes further reaction with the nucleophile.

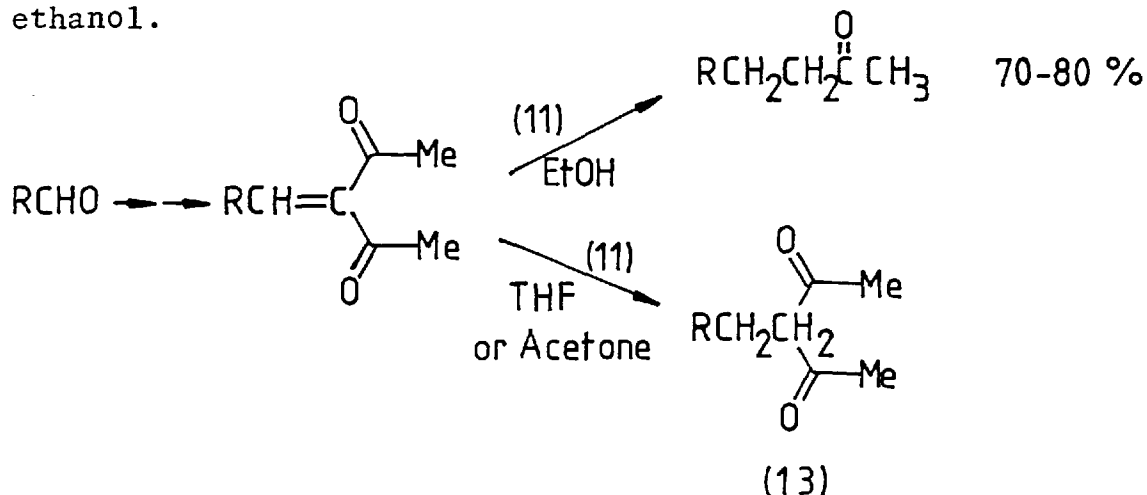
(c) Hydrido Carbonylferrates: Selective Reducing Agents

The hydrido tetracarbonyl ferrate anion (11) is an excellent reducing agent for acid chlorides¹⁵ affording the corresponding aldehydes in high yield. Excess reagent is required, as the hydrido metal cluster (12) produced



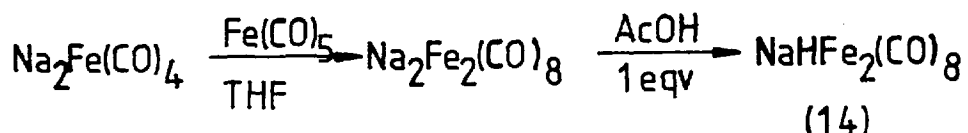
during reaction is inert under the reaction conditions.

The hydrido ferrate anion (11) on reaction with Knoevenagel condensates brought about a novel reductive elimination of an acyl group¹⁶ when the reaction was carried out in ethanol.

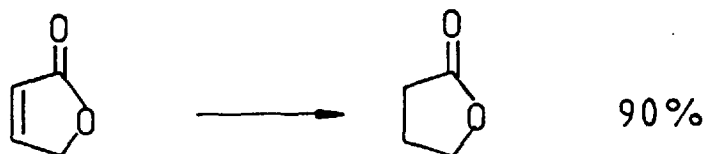
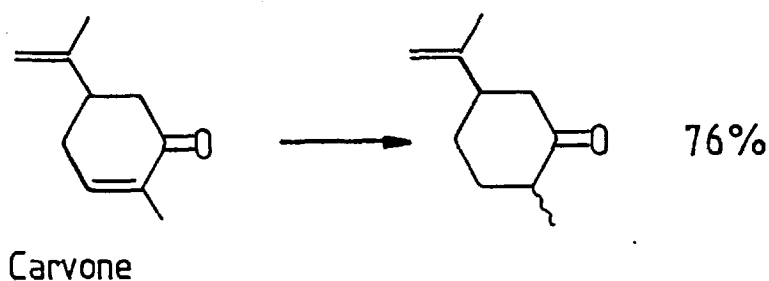


In THF or acetone the normal reduction product (13) was obtained. Further investigation revealed that acetyl groups are lost in preference to other acyl groups; and the replacement of one acyl group by an ester function afforded the product of reduction with no loss of the acyl group.

Collman has shown the dinuclear hydrido ferrate (14) to be a more selective reducing agent than hydrido tetracarbonylferrate(11).¹⁷ It will reduce the double

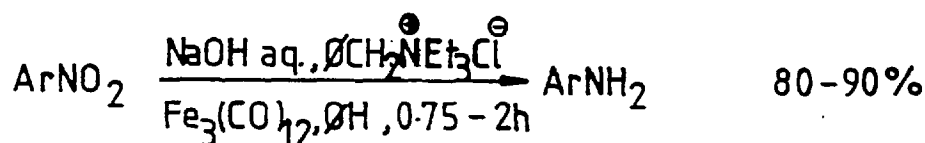


bond in α,β -unsaturated esters, ketones, aldehydes, nitriles, amides and lactones without concurrent reduction of the carbonyl moiety or reduction/isomerisation of other isolated double bonds.



Also (14) produces higher yields and reacts faster than corresponding mononuclear hydrido ferrate. (11)

Reduction of aromatic nitro groups to amino functions¹⁸ is easily accomplished by the use of the hydrido cluster complex (12) which can be generated from dodecacarbonyl triiron under phase transfer conditions. It is interesting to note that pentacarbonyliron and

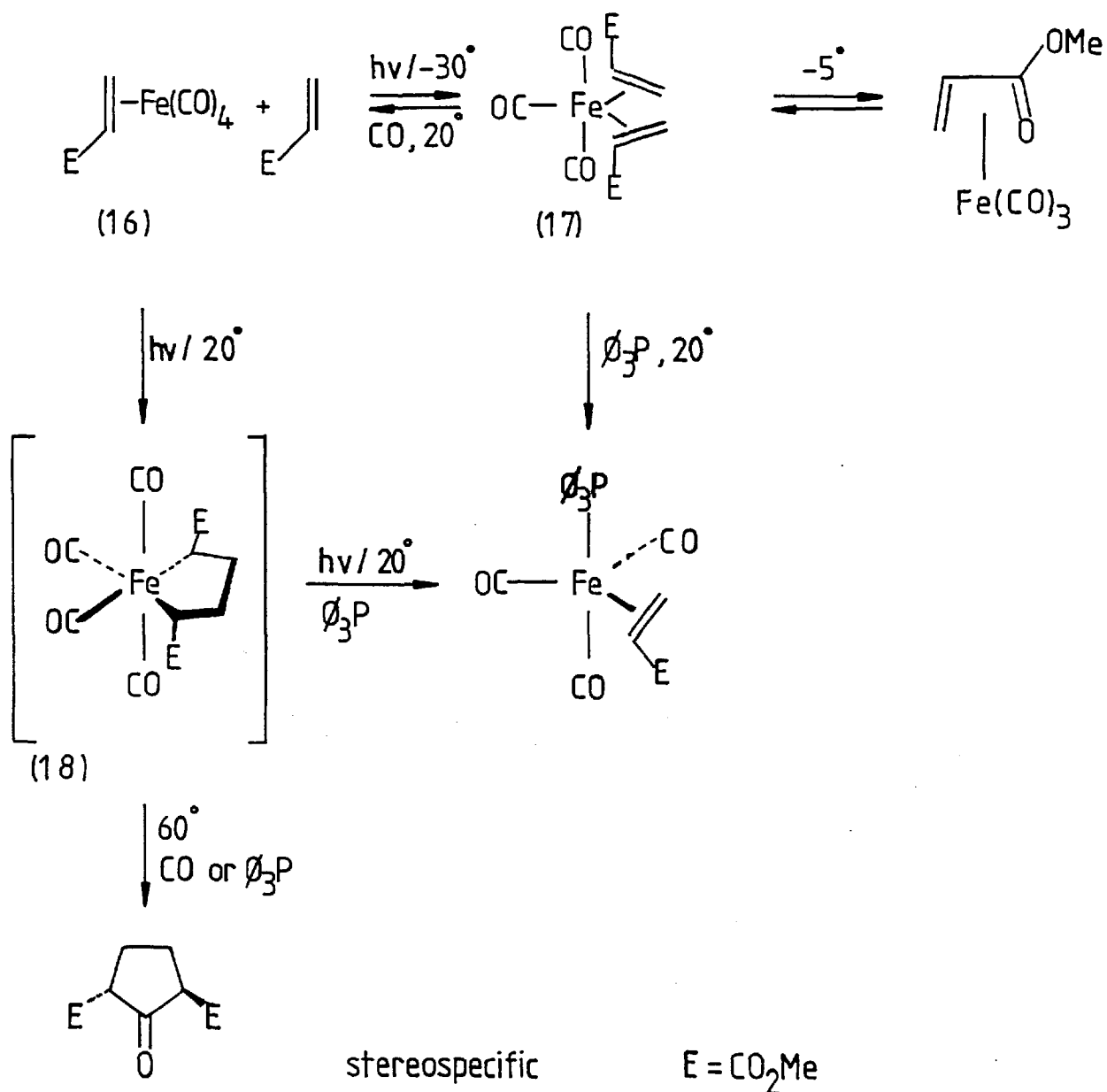


enneacarbonyl diiron will also accomplish the same transformation without the need for a phase transfer catalyst. Reaction of pentacarbonyliron with aqueous sodium hydroxide for 2 hours led to 87% recovery of pentacarbonyliron. Therefore it seems that pentacarbonyliron requires the presence of the nitro compound to induce attack of hydroxide upon itself. The mechanism for the pentacarbonyliron reduction seems quite complex, and results relating to the steric and electronic effects of substrates gave different results for pentacarbonyliron and dodecacarbonyl triiron.

2. REACTION OF IRON CARBONYLS WITH UNSATURATED SYSTEMS

(a) Coupling of Olefins using Iron Carbonyls

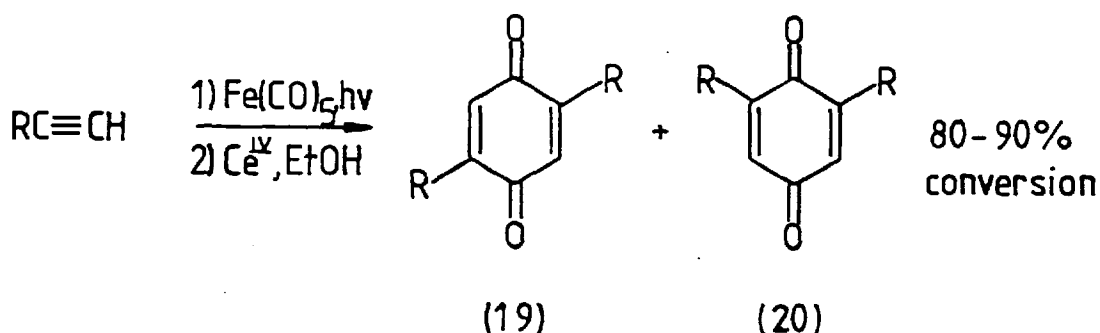
Coupling of Olefins induced by iron carbonyls can give rise to cyclopentanones¹⁹ and disubstituted benzoquinones²⁰ in good yields. The reaction of alkenes with pentacarbonyliron has been shown to proceed via initial co-ordination of the alkene with co-ordinatively unsaturated tetracarbonyliron (generated by photolytic dissociation of pentacarbonyliron), loss of carbon monoxide again leads to a co-ordinately unsaturated intermediate which can co-ordinate another molecule of alkene to give the bis-olefin complex (17). Rearrangement to the metallacycle (18), followed by insertion of carbon monoxide and extrusion of the iron moiety affords the cyclopentenone. Most of the intermediates of this reaction have been characterised at low temperature, and the structure of metallacycle (18) confirmed by X-ray crystallography. The bis-olefin complex (17) to metallacycle (18) interconversion has been the subject of a theoretical study by Hoffmann et al²¹, the reaction proceeding stereoselectively, placing the substituents so that the ethylene π^* enters reaction with its largest lobe β to the metal in the product metallacycle. There are a few examples where no selectivity is observed, and in these cases it is thought that the cycloreversion reaction (18) to (19) has a small activation energy hence the



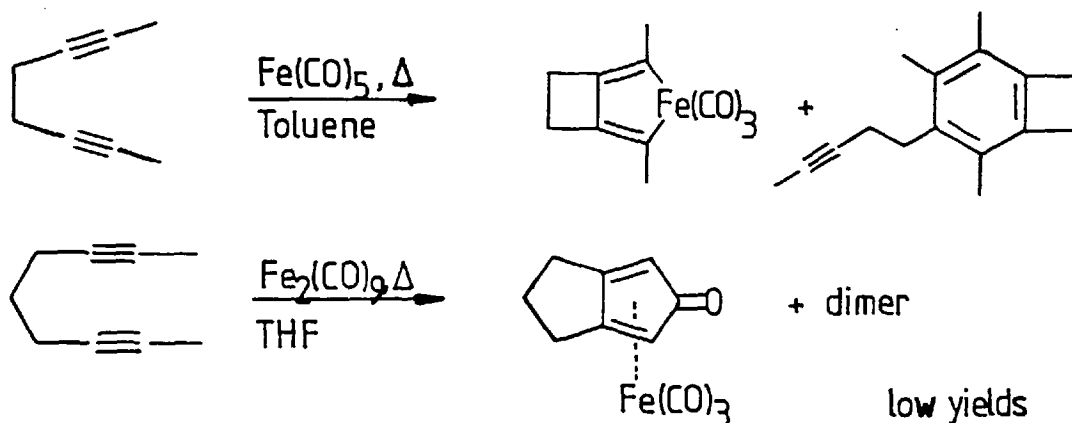
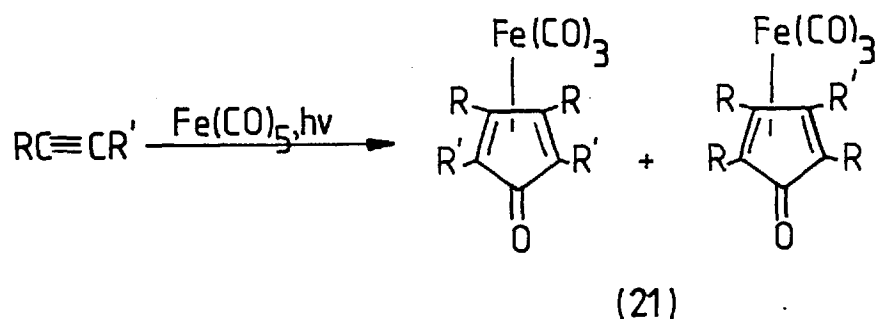
Scheme 1. Reaction of Alkenes with Iron Carbonyl

products of reaction would reflect more a thermodynamic equilibrium than the kinetic selectivity in the ring-closure reaction.

In a similar manner acetylenes²⁰ give rise to the synthetically difficult to obtain disubstituted benzoquinones. The 1,4 -isomer (19) predominating,

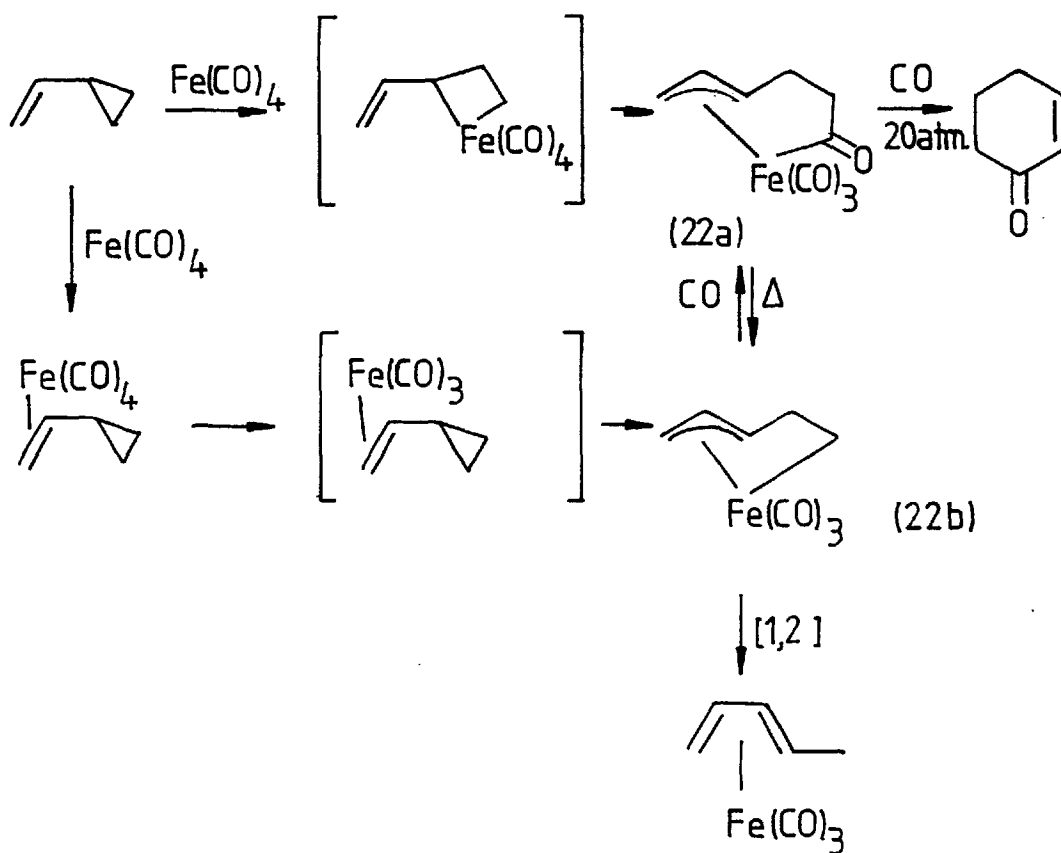


presumably steric factors dominate the reaction. Disubstituted acetylenes can lead to cyclopentadienone tricarbonyliron complexes²² (21), and with substituted dyines, intramolecular coupling can take place. A similar reaction can also be carried out using cobalt carbonyls.

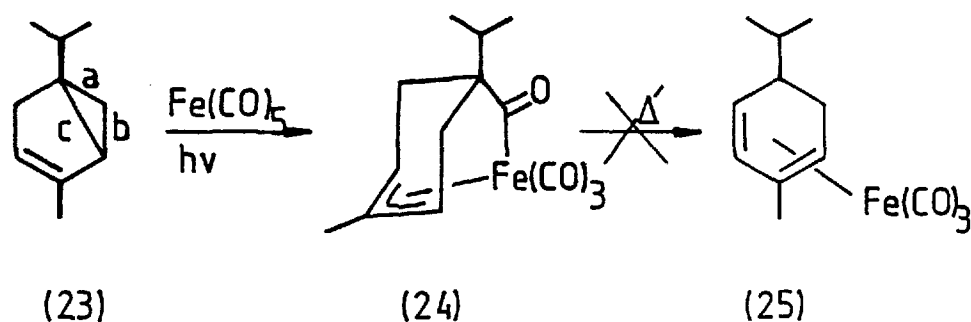


(b) Carbonyl insertion reactions

The reaction of vinyl cyclopropanes with iron carbonyls^{3, 23} is well known and has been studied extensively. Reaction proceeds to give an intermediate σ, π -allyl tricarbonyliron complex (22) in which co-ordinatively unsaturated tetracarbonyliron has become inserted into the



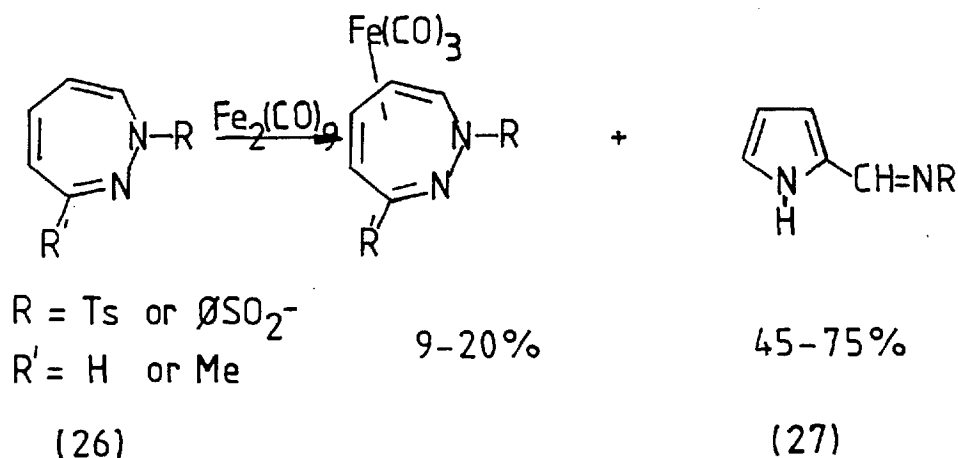
cyclopropane ring. The mechanistic pathway²⁴ of this 'insertion' reaction is dependent upon many factors, but the main feature in all of these reactions is the formation of a σ , π -allyl carbonyliron intermediate; subsequent reaction being dependent upon the original substitution pattern of the original vinyl cyclopropane.



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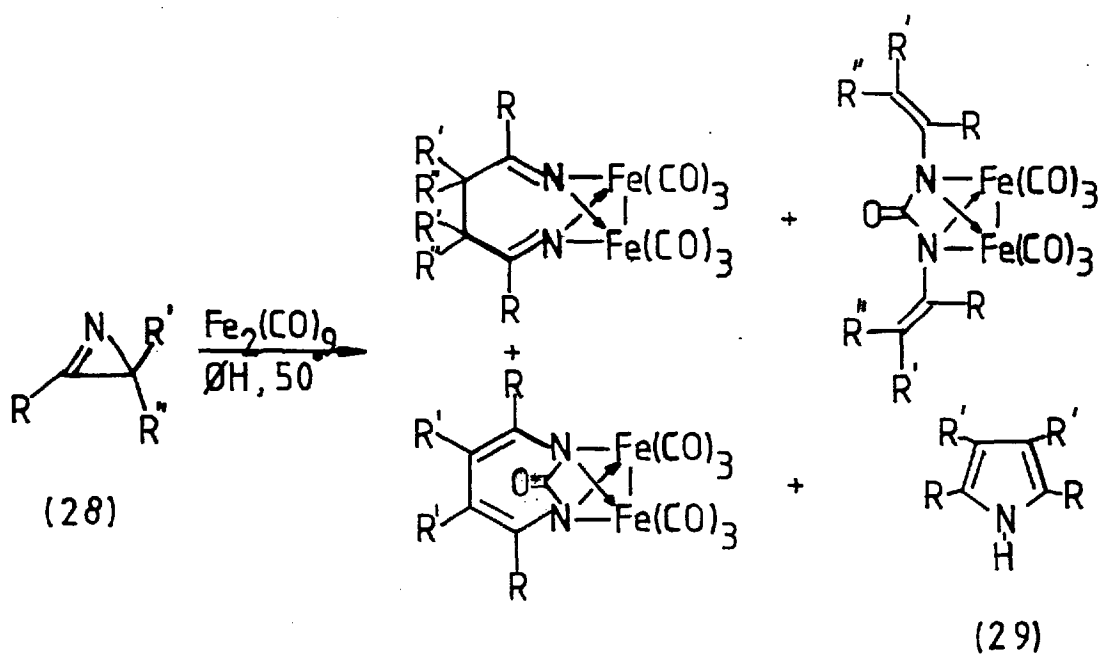
Tricyclic systems²⁵ often undergo skeletal arrangements, while (+) α thujene²⁶ (23) undergoes regio and stereospecific acyl metal insertion to afford the σ , π -allyl complex (24) as the only product. Attempts to induce further reaction gave only polymeric material and none of the expected diene tricarbonyliron complex (25).

The reaction of co-ordinatively unsaturated tetracarbonyliron (generated either by photolytic dissociation of $\text{Fe}(\text{CO})_5$ or thermolytic decomposition of $\text{Fe}_2(\text{CO})_9$ with hetero substituted olefinic systems proceeds in general via an iron carbonyl promoted cleavage of the carbon hetero atom bond. Treatment of the diazepine (26)²⁷ with enneacarbonyl diiron affords the substituted pyrrole (27) in moderate to good yields.

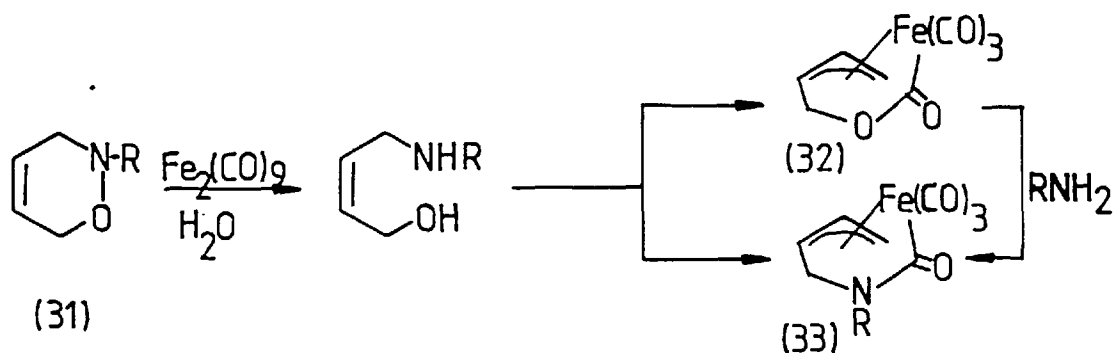


The reaction is thought to proceed via an intermediate nitrene tricarbonyliron complex, followed by insertion of the co-ordinated nitrene into the carbon-carbon double bond. Iron

carbonyl promoted cleavage of the carbon-nitrogen bond in the azirine (28)²⁸ produces a mixture of products, the pyrrole (29) being formed in 10 - 20% yields when $R = R^1 = H$.

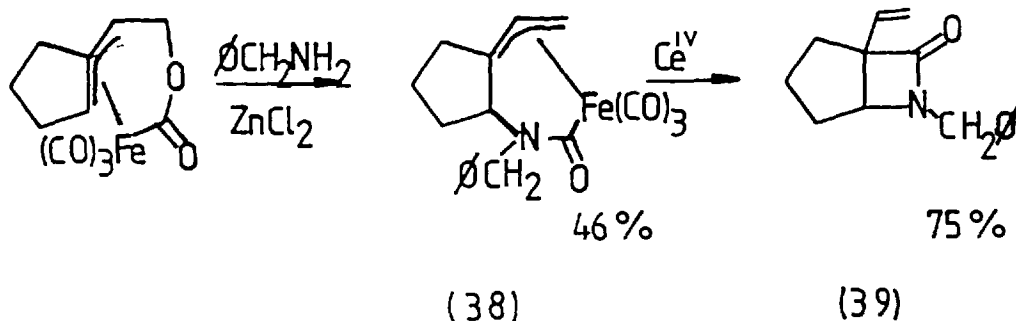
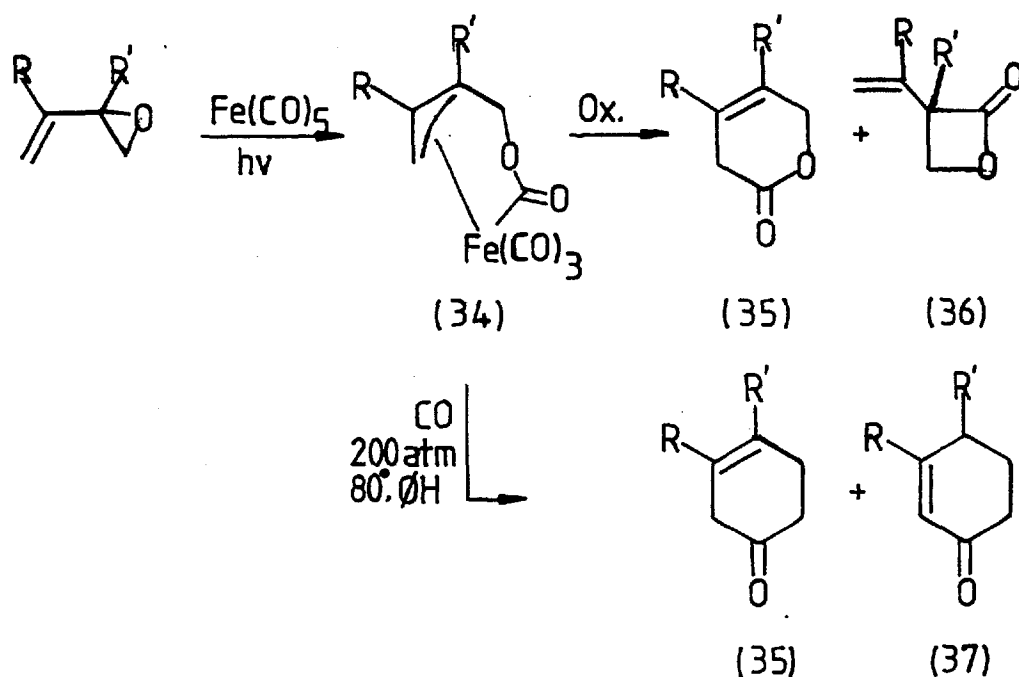


The range of products formed is consistent with the intermediacy of the nitrene complex (30). Synthetically more interesting is the iron carbonyl induced cleavage of an oxazine ring.²⁹



The tricarbonyliron lactone and lactam complexes (32) and (33) respectively have been shown to have great synthetic utility in the preparation of β and γ lactones^{30, 31} and β lactams.³² Further work on bicyclic oxazines led to isolation of a number of products, all in low yield. Therefore in these cases such a process is not of great synthetic utility.

Vinyl oxiranes, however,^{30, 31} react smoothly with the pentacarbonyliron under photolytic conditions to afford tricarbonyliron lactone complexes in high yield. These are synthetically useful intermediates which can be converted

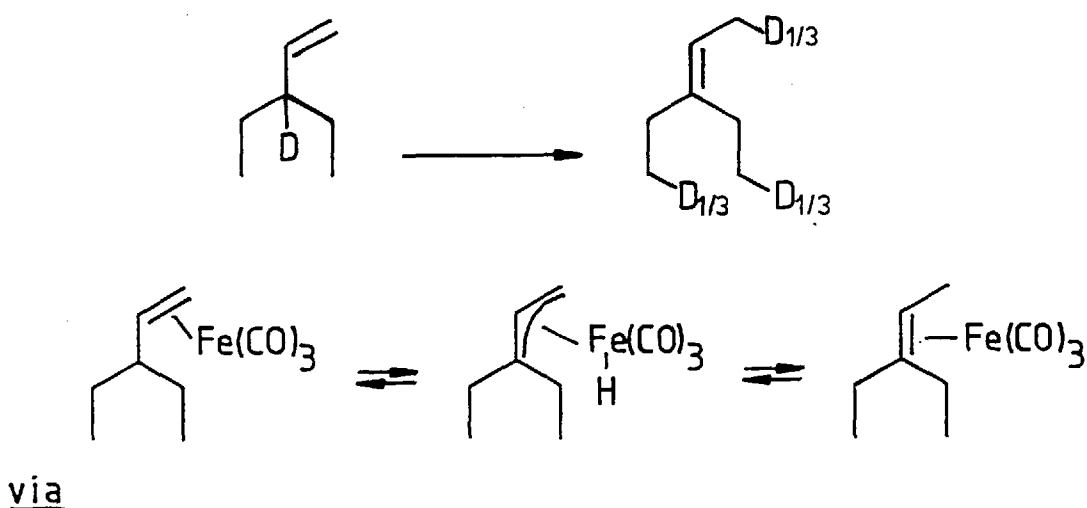


into lactones (35) and (36) upon oxidation, or exclusively to δ lactones upon carbonylation³¹ with carbon monoxide at high pressure in aprotic solvents.

Reaction with primary amines³² proceeds smoothly and in high yield to afford the tricarbonyliron lactam complex(38), which upon oxidation furnished exclusively the β lactam (39).

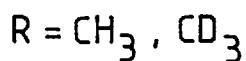
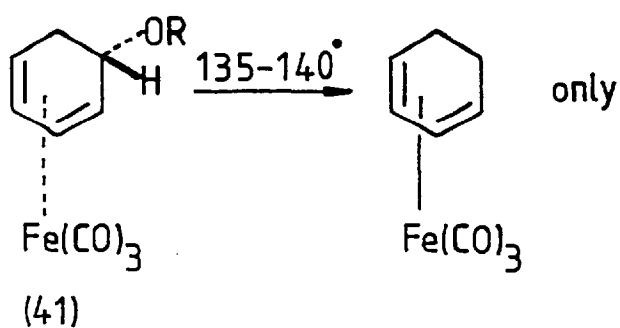
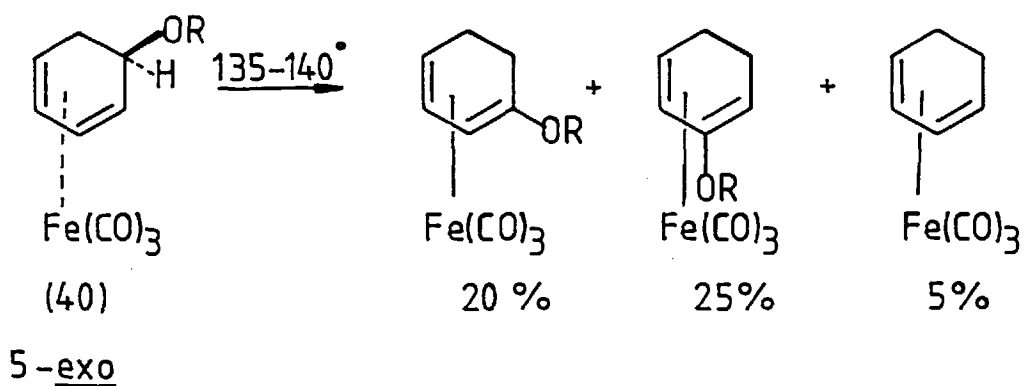
(c) Olefin Isomerisation promoted by Iron Carbonyls

The majority of evidence indicates that olefin isomerisation in the presence of iron carbonyl catalysts proceed via a sequence of 1, 3-hydrogen shifts. Numerous reports have dealt with this reaction³³ but only a few have provided convincing arguments regarding the detailed nature of the rearrangement. Casey and Cyr have established that

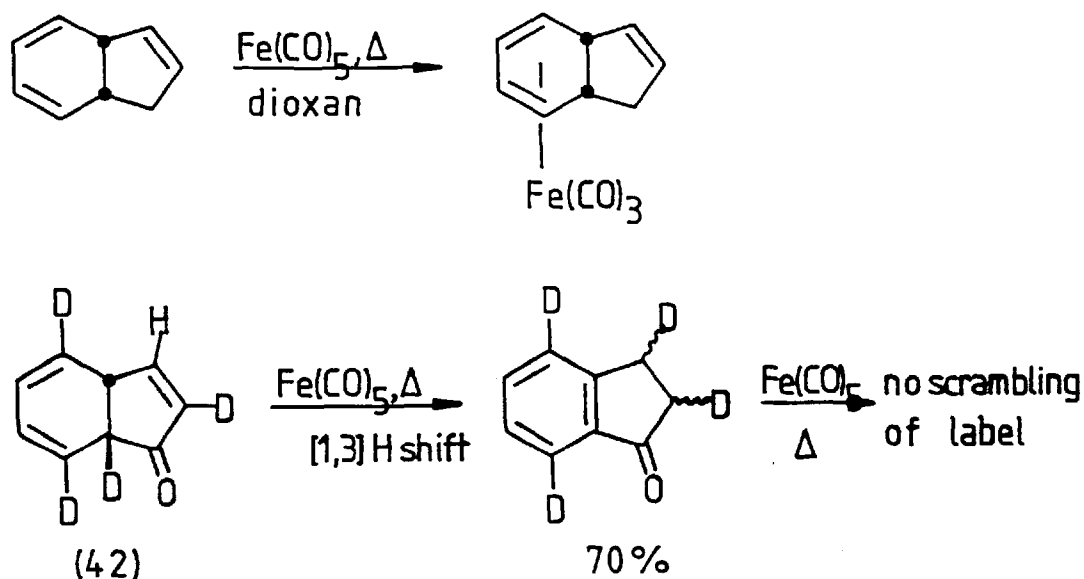


Scheme 2. π -Allyl Hydrido tricarbonyliron mechanism of Olefin Isomerisation

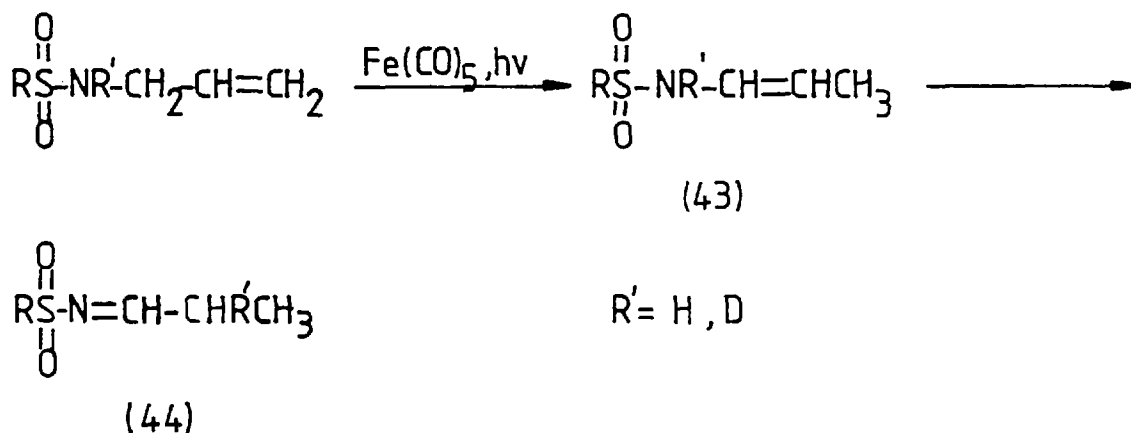
during dodecacarbonyl triiron induced rearrangement of 3-ethyl-1-pentene-3-d₁ to 3-ethyl-2 pentene the deuterium label was scrambled randomly between the terminal methyl groups.³⁴ This result is consistent with the currently accepted π -allyl hydrido tricarbonyliron mechanisms. The stereochemistry of these hydrogen shifts in purely hydrocarbon examples has recently been investigated.³⁵ A study of the isomerisation of cis and trans-bicyclo [6.2.0] dec-9-ene by enneacarbonyl diiron supports the π -allyl hydridotricarbonyliron mechanism, and since stereochemistry is maintained requires that the original iron carbonyl species, which brings about rearrangement, remain attached throughout the sequence. Rearrangements of η^2 diene tetracarbonyliron complexes³⁶ require initial loss of carbon monoxide to form a co-ordinately unsaturated species which can either collapse to a η^4 diene tricarbonyliron complex, or undergo rearrangement via hydride abstraction to yield an intermediate π -allyl hydrido tricarbonyliron complex. The thermal reactions of the 5-methoxy substituted cyclohexadiene tricarbonyliron complexes³⁷ (40) and (41) clearly shows that it is the 5-endo hydrogen which is abstracted by the tricarbonyliron moiety, and therefore illustrates the stereochemical requirements of the isomerisation sequence.



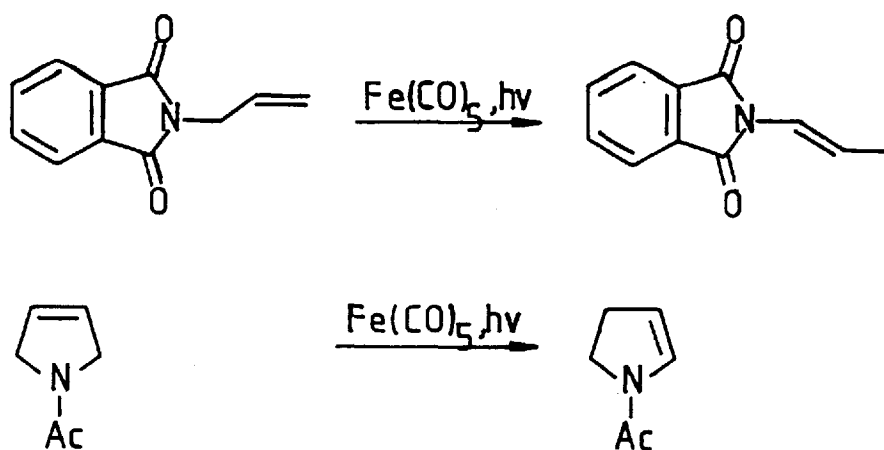
Treatment of dihydro indanones (42) with pentacarbonyliron under thermolytic conditions^{38, 39} brings about rearrangement to the indanone. This is unusual since reaction of dihydro indane under the same conditions does not lead to rearrangement. This difference in reactivity is thought to be due to the increased acidity of the ring junction protons.



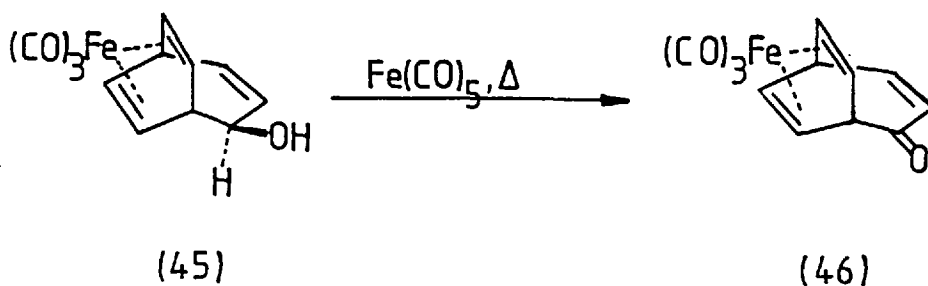
The ability of iron carbonyls to promote double bond migration has been used in the synthesis N-prop-2-enyl and N-propylidene sulphonamides.⁴⁰ N-allyl sulphonamides were treated to pentacarbonyliron under photolytic conditions, and depending upon solvent the reaction could be stopped at the intermediate N-prop-2-enyl sulphonamide (43) stage. Performing the reaction in benzene or acetone results in formation of (43) only, but in methanol (44) is



the only observed product. The mechanism was shown by labelling experiments, to be an intramolecular hydrogen transfer. This sequence has also been applied to N-allyl-amides and N-allylimides⁴¹ affording N-prop-2-enyl amides and imides in high yields.



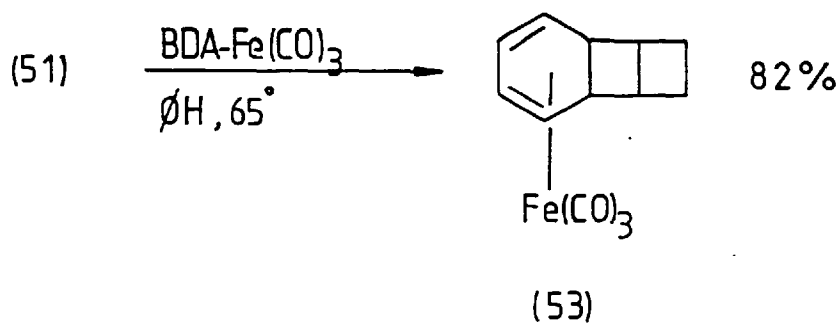
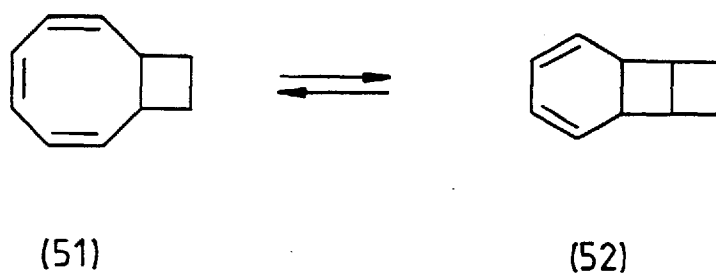
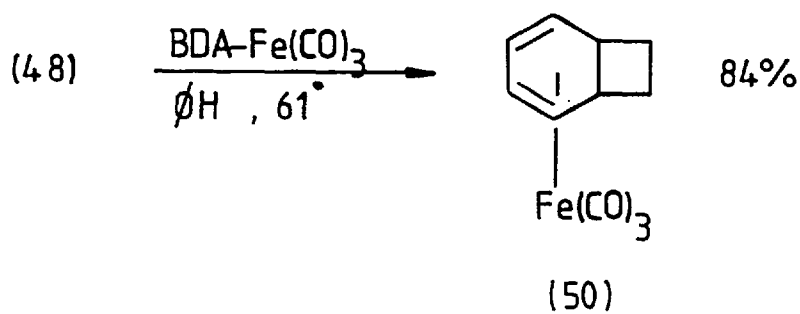
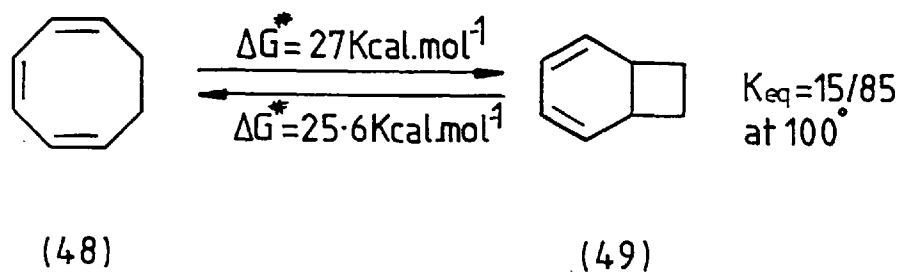
Rearrangement of allylic alcohols to aldehydes and ketones is readily accomplished by iron carbonyls. However the allylic alcohol tricarbonyliron complex (45) on

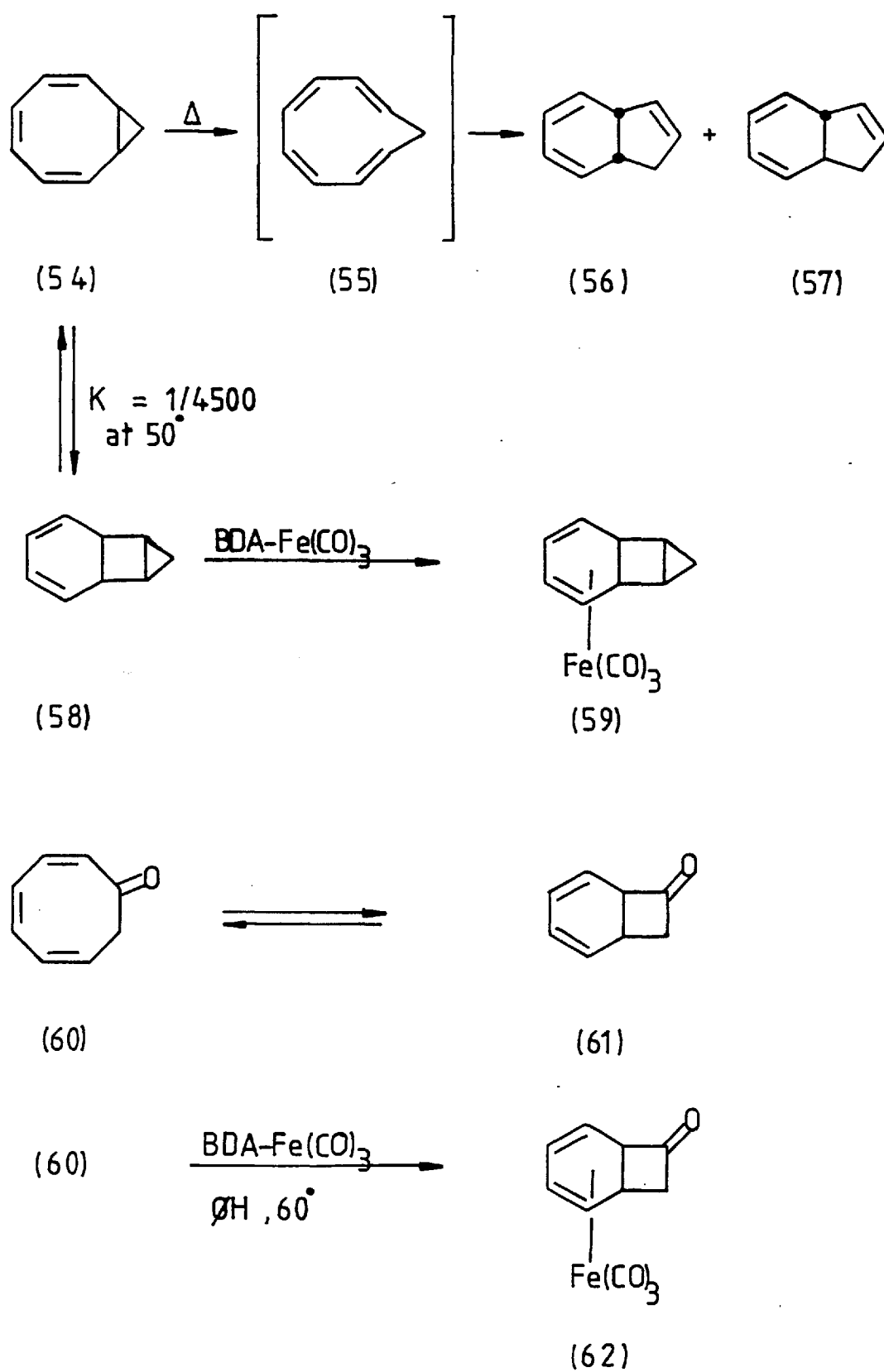


treatment with pentacarbonyliron gave the α , β -unsaturated ketone (46).⁴² This is the first time that this type of oxidative reaction has been observed.

(d) Diene Carbonyliron complexes

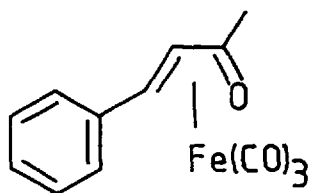
The first diene tricarbonyliron complexes were reported in 1930, and their preparation involved treatment of the parent diene with pentacarbonyliron in a bomb at 135°C for 24 hours. Since this original work numerous 1, 3 - diene complexes have been shown to react with various carbonyliron reagents to form η^4 tricarbonyliron diene complexes. Pentacarbonyliron is the least expensive reagent used but generally requires high temperatures (130°C) and therefore is not synthetically useful. Thermolytic decomposition of enneacarbonyl diiron at around 40°C provides a convenient route to 1, 3-diene complexes. The reaction proceeds via co-ordination of one double bond to co-ordinatively unsaturated tetracarbonyliron produced by decomposition of the iron reagent. Further loss of carbon monoxide from this species will produce a co-ordinatively unsaturated intermediate which collapses to the η^4 tricarbonyl diene complex. In this way the η^4 tricarbonyliron complex of ergosterol⁴³ has been prepared, complexation taking place from the α face of the steroid. More recently tricarbonyliron species in which the tricarbonyliron moiety is only weakly bound have been used to transfer the iron moiety to





Scheme 2. Reactions of Benzylidene Acetone Tricarbonyliron

1, 3-dienes, to yield the thermodynamically more stable η^4 diene tricarbonyliron complex. The most widely used of these reagents is benzylidene acetone tricarbonyliron (47).



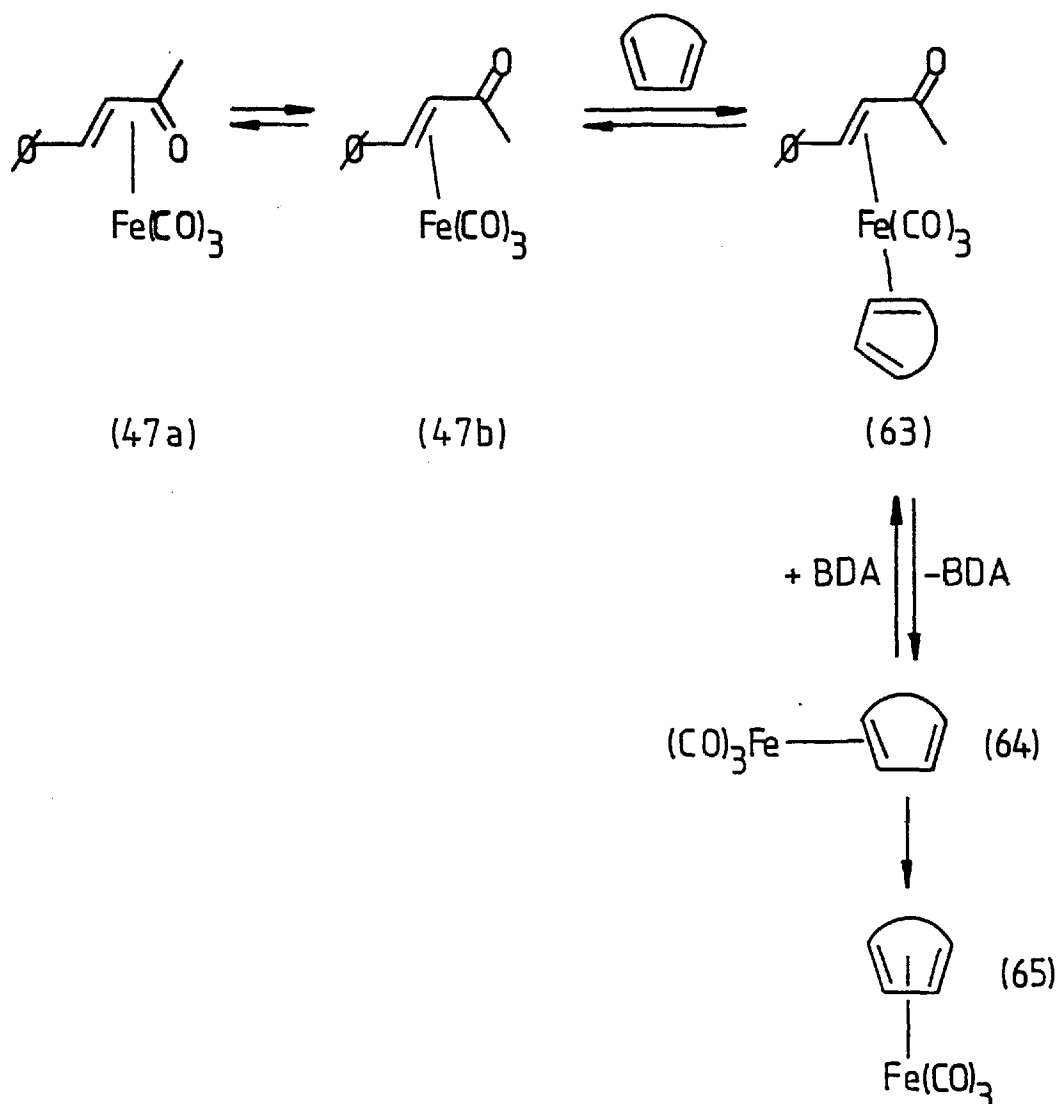
BDA-Fe(CO)₃

(47)

This reagent is a mild, synthetically useful reagent for the trapping of acyclic dienes. It shows a remarkable selectivity with planar 1, 3-cyclohexadienes,^{44, 45, 46} enabling trapping out of thermodynamically unstable tautomers (Scheme 2). The tautomeric isomers (49), (52), (58) and (61) of the corresponding cyclooctatrienes are only present in low concentration, but upon reaction with BDA - Fe(CO)₃ the corresponding η^4 tricarbonyliron complexes (50), (53), (59) and (62) are obtained as the only product in high yield.

It is interesting to note that (59) is obtained as the sole product from (58) upon treatment with BDA-Fe(CO)₃ even though it is present in very low concentration. Oxidation of the complexes (50), (53), (59) and (62) at low temperature (-30°C) with cerium (IV) allows spectroscopic observation of the free diene tautomers (49), (52), (58) and (61); which upon warming up revert back to an equilibrium mixture of tautomers. Thus it has been possible to

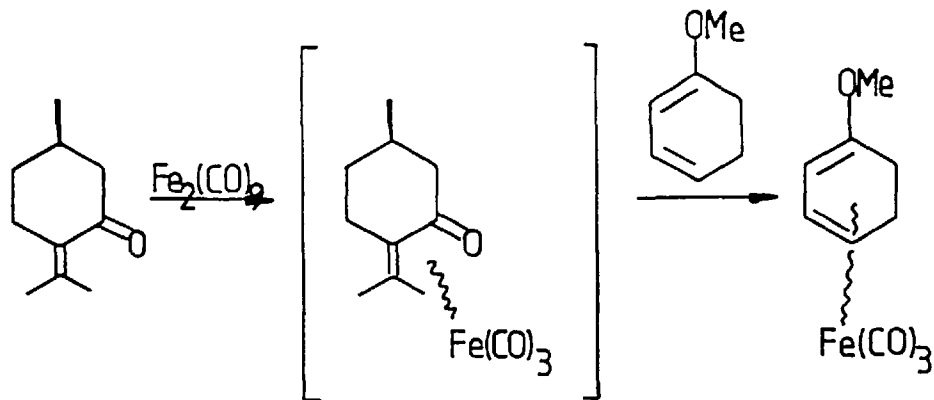
measure the rates of the back reactions. The remarkable kinetic selectivity for the diene relative to the triene tautomers of BDA-Fe(CO)₃ can be explained by considering Scheme 3. Initial formation of the co-ordinatively unsaturated isomer of BDA-Fe(CO)₃ (47b) and reaction of this with an olefin to give intermediate (63) is relatively straightforward.⁴⁶ However the triene tautomers are not planar, they exist as tub shaped conformers; and for such a species to form a η^4 triene complex, dissociation of BDA must occur in addition to distortion of the tub shaped



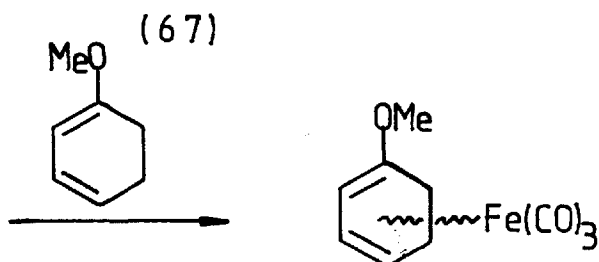
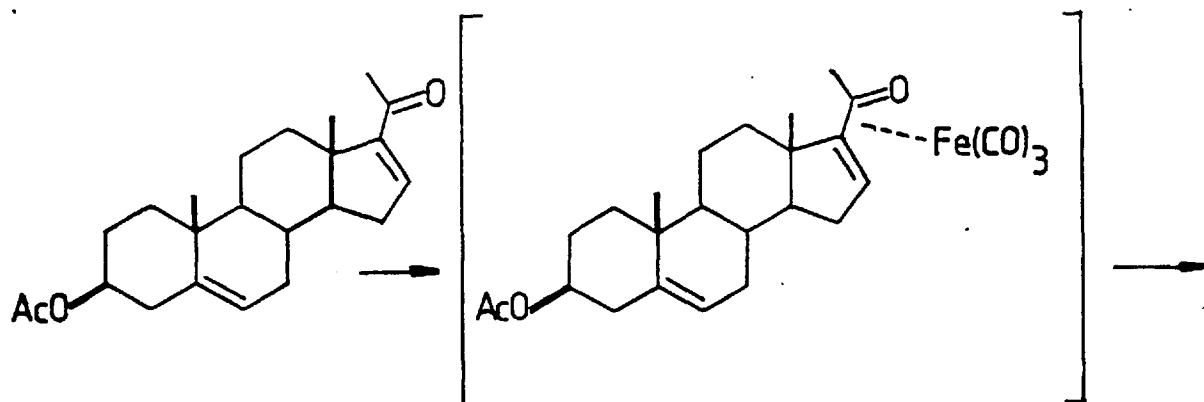
Scheme 3. Mechanism of BDA-Fe(CO)₃ transfer of the Tricarbonyliron moiety to Dienes

bound triene to a relatively planar conformation in order to co-ordinate the second double bond to iron. The diene tautomers however require no distortion (by virtue of their planar cyclohexadiene structures); therefore there will be a higher activation energy required to form the η^4 triene complex, than the corresponding barrier for conversion of the analogous η^2 diene tautomers to η^4 diene complex. Such an increased activation barrier would account for the much lower rate of reaction of BDA-Fe(CO)_3 with cyclooctatetraenes relative to diene tautomers, and the resulting high selectivity displayed in reactions. The η^4 triene complex of (48) is easily obtained by irradiation in the presence of pentacarbonyliron, and this on heating with benzyldiene acetone does not yield any of the η^4 diene complex. (50).

Co-ordination of a prochiral 1, 3-diene to iron produces a chiral molecule with one face of the diene distinguished by the metal. In an attempt to synthesise optically active diene tricarbonyliron complexes by asymmetric induction, the enone (+) Pulegone (66) and (-) acetoxy pregna-5, 16-diene-20-one (67) were heated with methoxy cyclohexadiene and enneacarbonyl diiron in benzene.⁴⁷ However, optical yields were poor ($\leq 20\%$ e.e.). Pulegone might be expected to form two η^4 tricarbonyliron complexes, and thus lead to poor optical yields, but only one η^4 tricarbonyliron complex can be formed with (67). Resolution of η^4 tricarbonyliron cyclohexadiene carboxylic acid has been achieved by classical methods,⁴⁸ but this approach



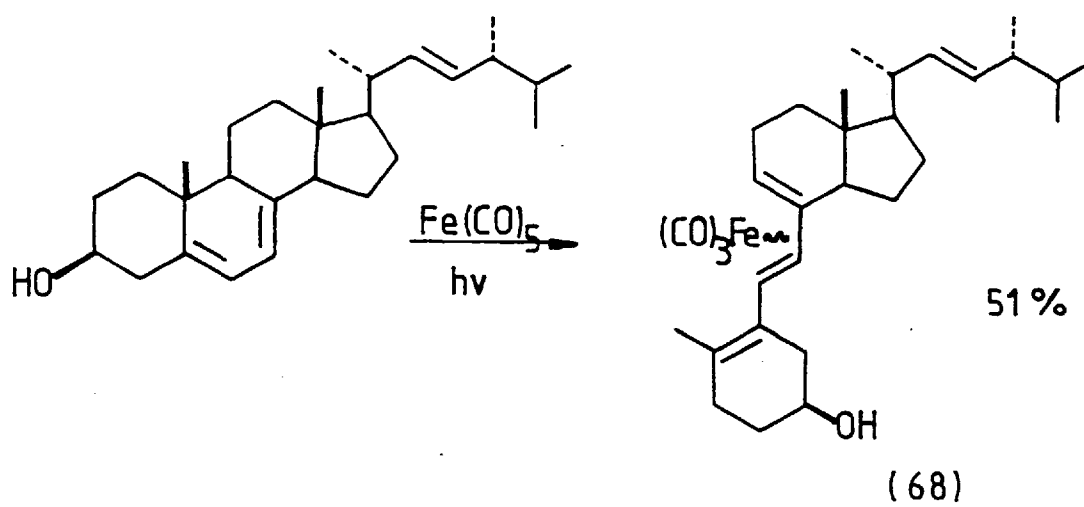
(66)



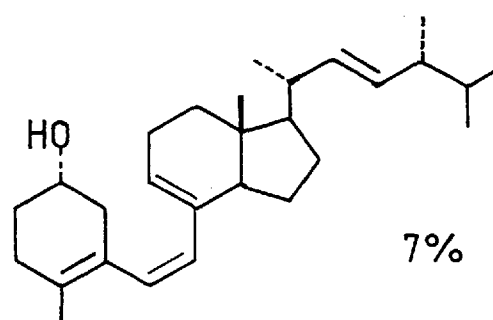
(67)

is rather limited, and of no practical use.

In an attempt to protect the 1, 3-diene unit of ergosterol by forming the η^4 tricarbonyliron complex under photolytic conditions from pentacarbonyliron, a mixture of the η^4 tricarbonyliron complexes of tachysterol (68) was obtained in good yield.⁴⁹ To date this is the best route to (68) from ergosterol. The reaction presumably proceeds via electrocyclic ring opening and trapping of the acyclic 1, 3-diene moiety by tetracarbonyliron.



α and β Tachysterol



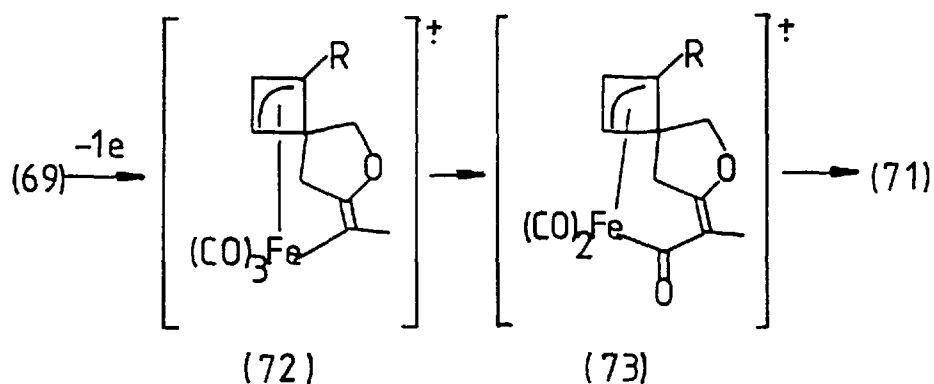
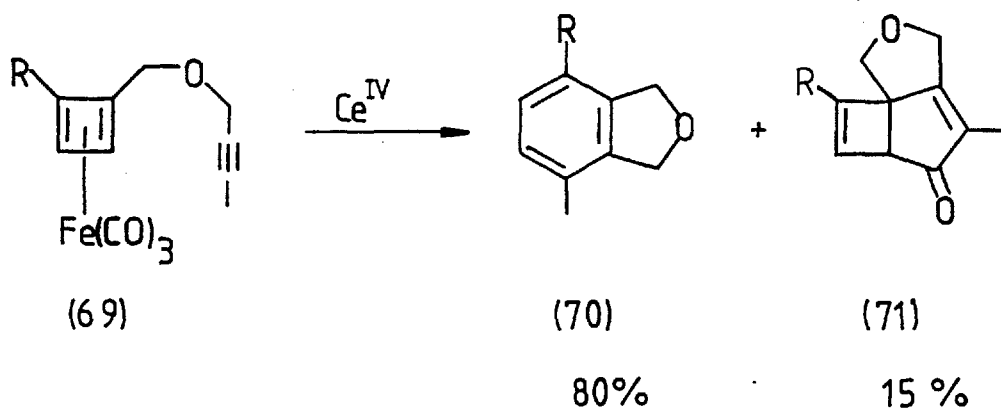
Precalciferol₂

3. IRON CARBONYL PROMOTED REACTIONS OF CO-ORDINATED LIGANDS

(a) Use of the Tricarbonyliron moiety as a Protecting Group

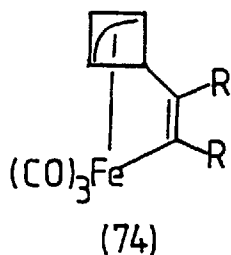
The tricarbonyliron moiety has found extensive use in the stabilisation of reactive intermediates, and in the protection of 1,3-diene units, thus allowing synthetically difficult transformations to be accomplished easily. The stabilisation of highly reactive cyclobutadiene species by iron carbonyls; and the subsequent ease with which they can be liberated from their tricarbonyliron complex is a classic example of the utility of iron carbonyls in synthesis.

The evidence for formation of free cyclobutadiene

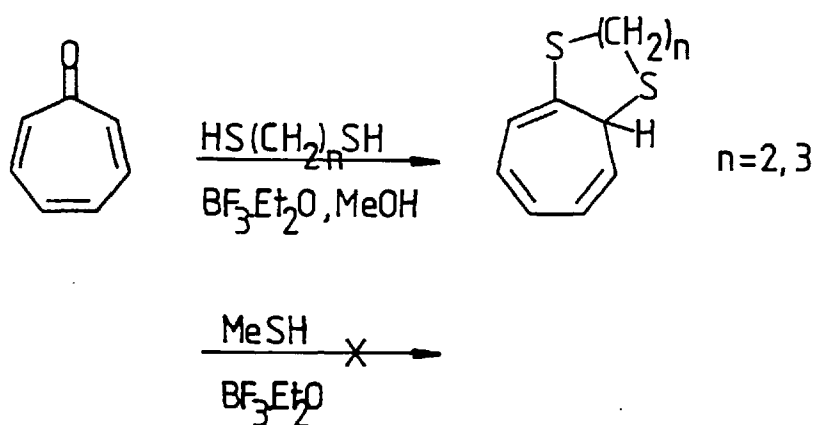


from its tricarbonyliron complex is substantial,^{50, 51} but in certain cases, reaction can only be explained in terms of an intermediate iron-cyclobutadiene substrate adduct,^{51, 52} with the carbonyliron moiety playing an important part in the direction of reaction.

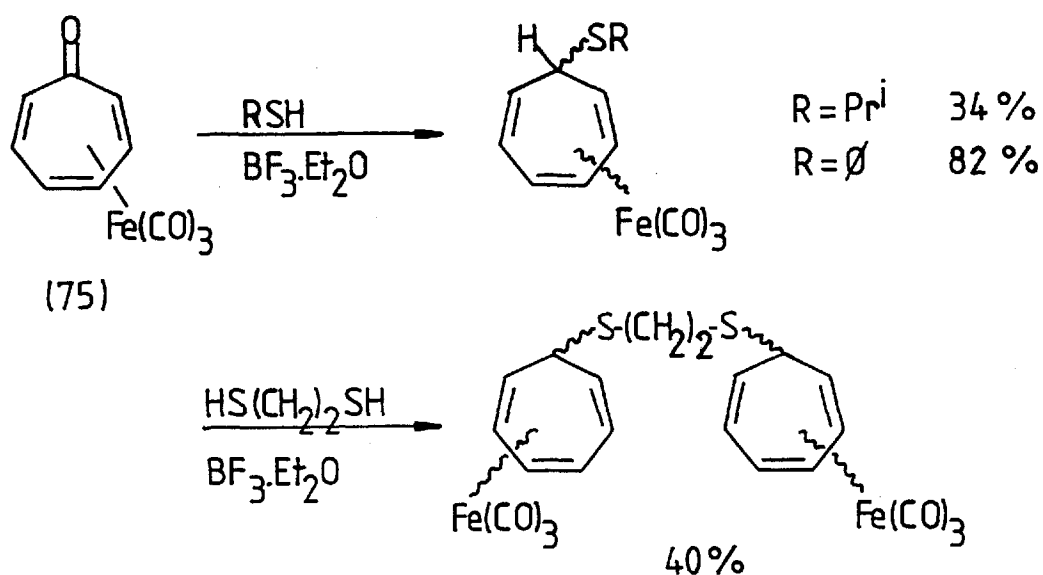
The cyclobutadiene tricarbonyliron complex (69) upon oxidation affords the product from intramolecular trapping of "free" cyclobutadiene (70), and as a minor product the tricyclic system (71), possibly via the intermediate complexes (72) and (73). Therefore in certain cases reaction of a co-ordinated cyclobutadiene species can become competitive with decomplexation to afford "free" cyclobutadiene. The photochemical reaction of η^4 tricarbonyliron cyclobutadiene with acetylenes to afford substituted benzene derivatives,⁵² cannot be considered to proceed via a "free" cyclobutanoid intermediate, and it has been suggested that a σ , π -allyl intermediate similar to (74) is involved in reaction.



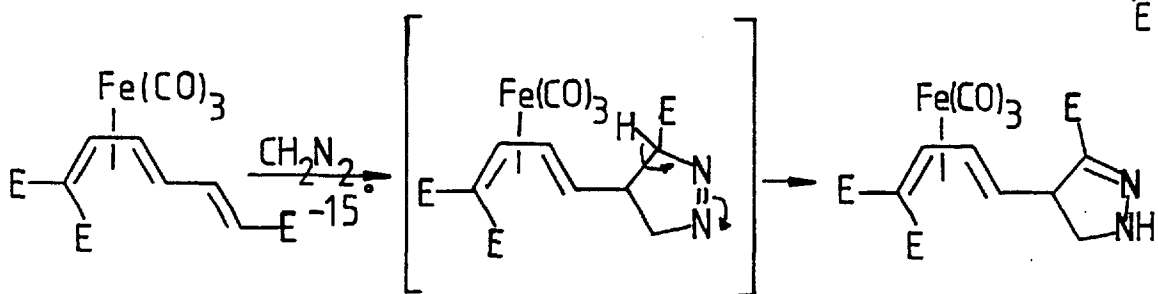
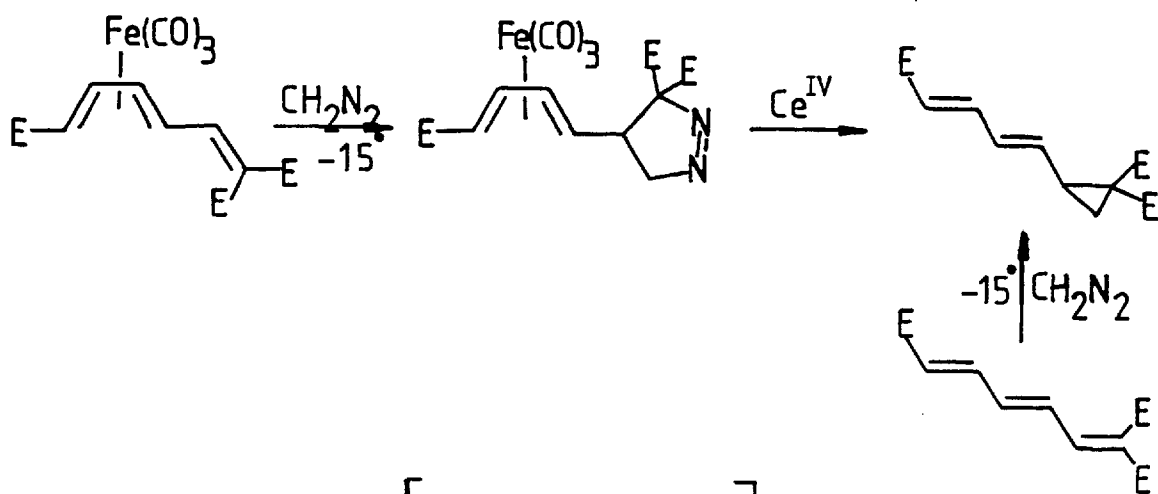
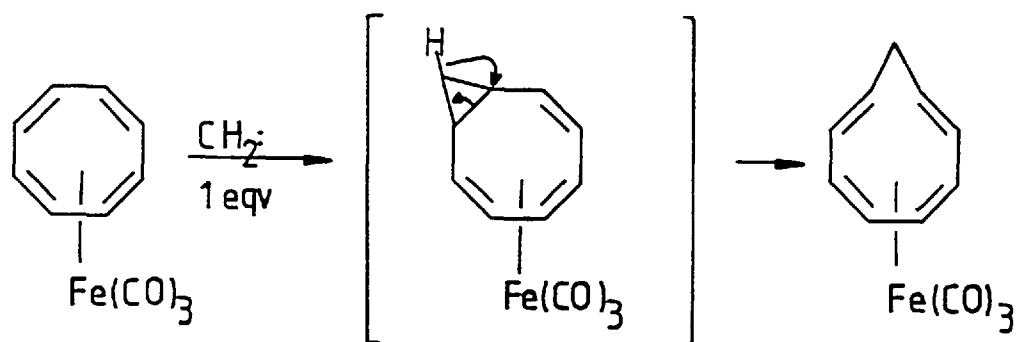
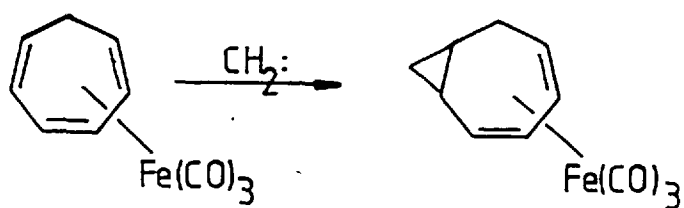
The tricarbonyliron moiety has been used in an attempt to form thioketal derivatives of tropones.⁵³ It was argued that formation of a η^4 tricarbonyliron complex would 'fix' the diene system, thus preventing re-arrangement.



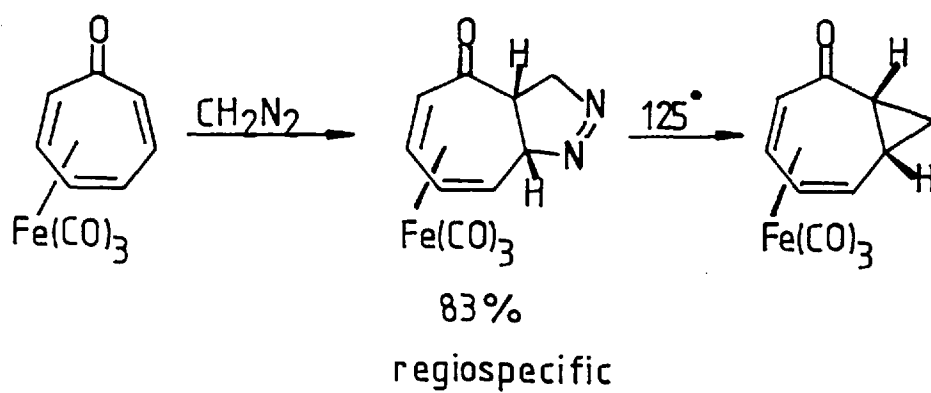
Reaction of the tropene complex (75) with thiols led to a novel reductive addition, rather than the expected thioketal.



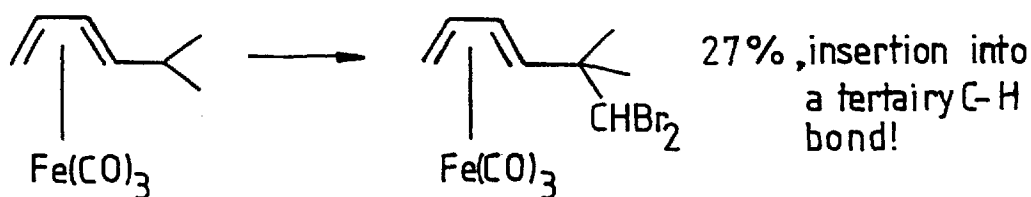
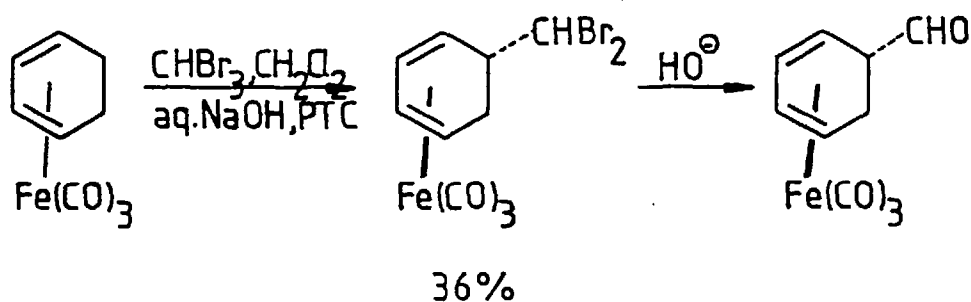
The tricarbonyliron moiety has also been used to great advantage as a protecting group of a 1, 3-diene unit in the reaction of carbenes⁵⁴ and diazomethane^{55, 56} with trienes.



$\text{E} = \text{CO}_2\text{Me}$

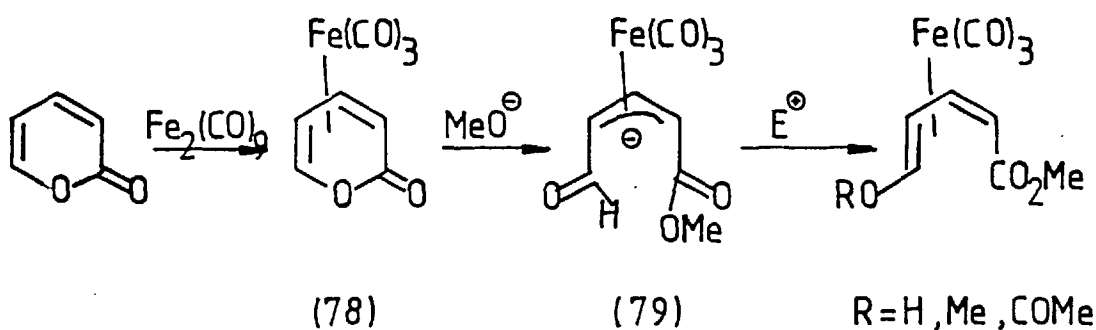
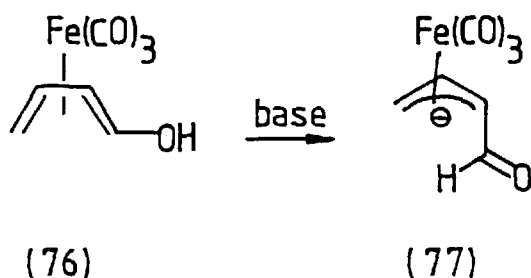


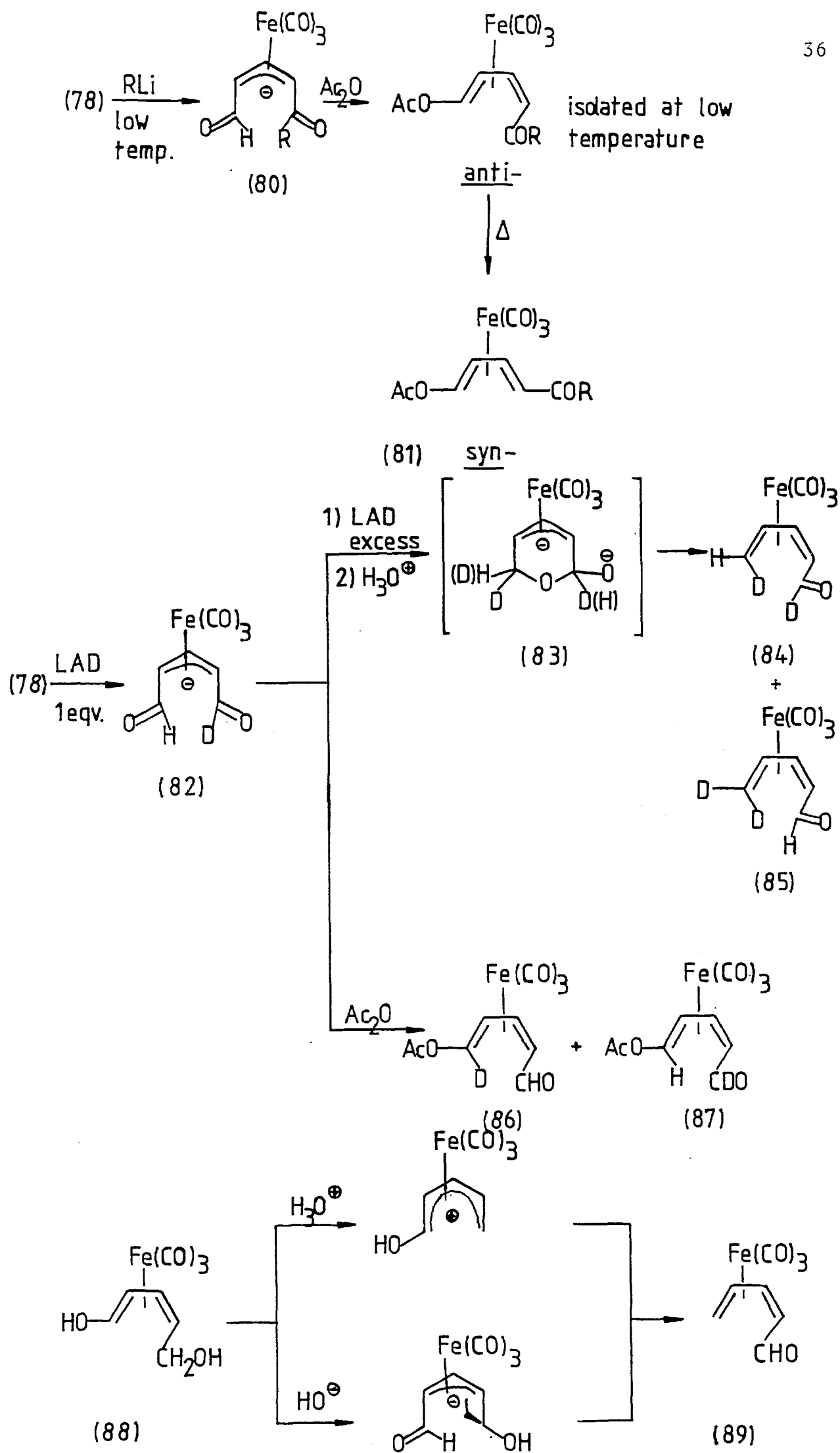
The use of the tricarbonyliron moiety as a protecting group allows the selective insertion of dihalocarbenes into the carbon-hydrogen bond of adjacent methylene and methine groups.⁵⁷



(b) Reactions of Co-ordinated Ligands with bases

Treatment of the hydroxybutadiene tricarbonyliron complex (76) with base resulted in proton abstraction and



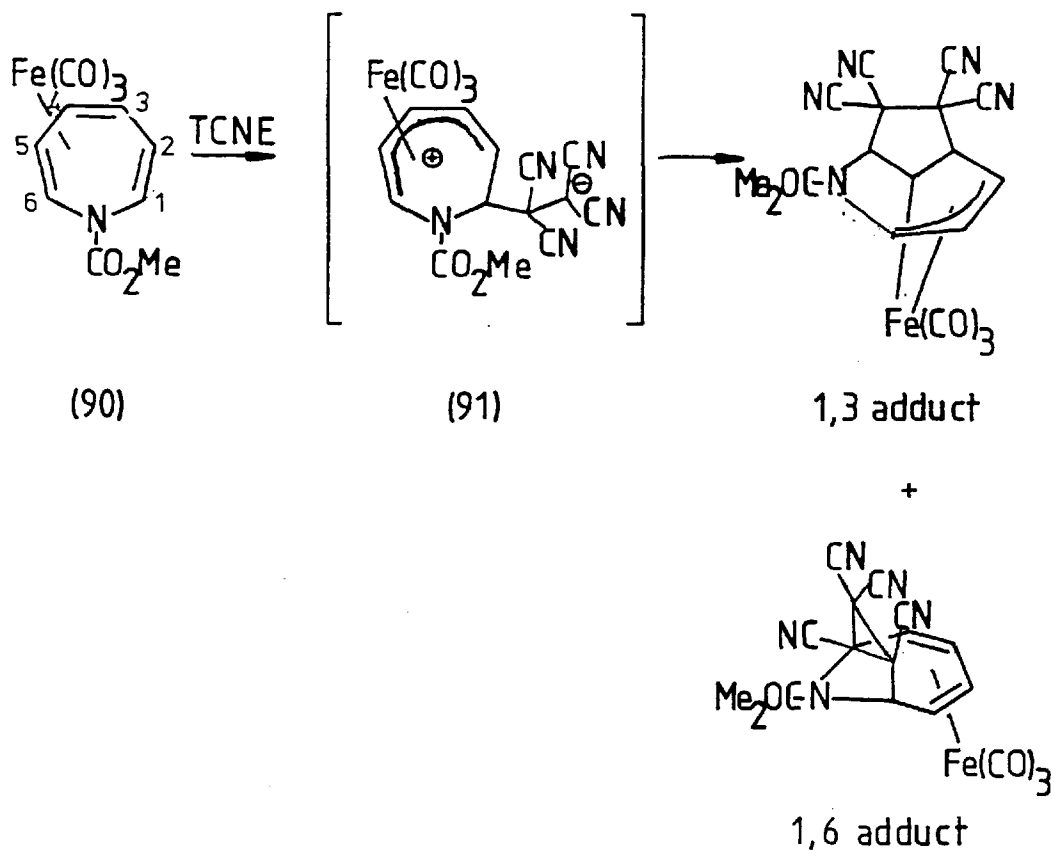


formation of an anionic complex, which is best formulated as the formyl, π -allyl anion (77),⁵⁸ the negative charge being stabilised through the tricarbonyliron moiety. In a similar manner treatment of the η^4 tricarbonyliron α -pyrone complex (78) with sodium methoxide, furnishes the carbonyliron stabilised species (70); this undergoes reaction with various electrophiles (H_3O^+ , Me_2SO_4 and AcCl) at oxygen affording substituted tricarbonyliron butadiene complexes.⁵⁹ Reactions of the complex (78) with other nucleophiles are summarised in Scheme 4. The general feature of all these reactions is nucleophilic attack at the lactone carbonyl, followed by rearrangement to a tricarbonyliron stabilised π -allyl anion intermediate, subsequent reaction with electrophiles taking place at oxygen to afford hetero substituted butadienes. These transformations provide a novel route to the synthetically important hetero substituted butadienes, which have found wide applicability in the synthesis of natural products.

(c) Reaction of Co-ordinated Ligands with Dieneophiles

The reactions of unsaturated hydrocarbons with powerful dieneophiles such as TCNE is greatly influenced by co-ordination of the substrate to a carbonyliron moiety. The cycloaddition reactions of co-ordinated ligands gives rise to different products than those obtained from the free olefin. Reaction of tricarbonyliron complexes of

substituted cycloheptatrienes and cyclooctatetraenes with TCNE normally affords products of 1, 3 and 1,6 attack.⁶⁰ The reaction is presumed to proceed via a Zwitterionic intermediate (91), followed by ring closure, to afford the



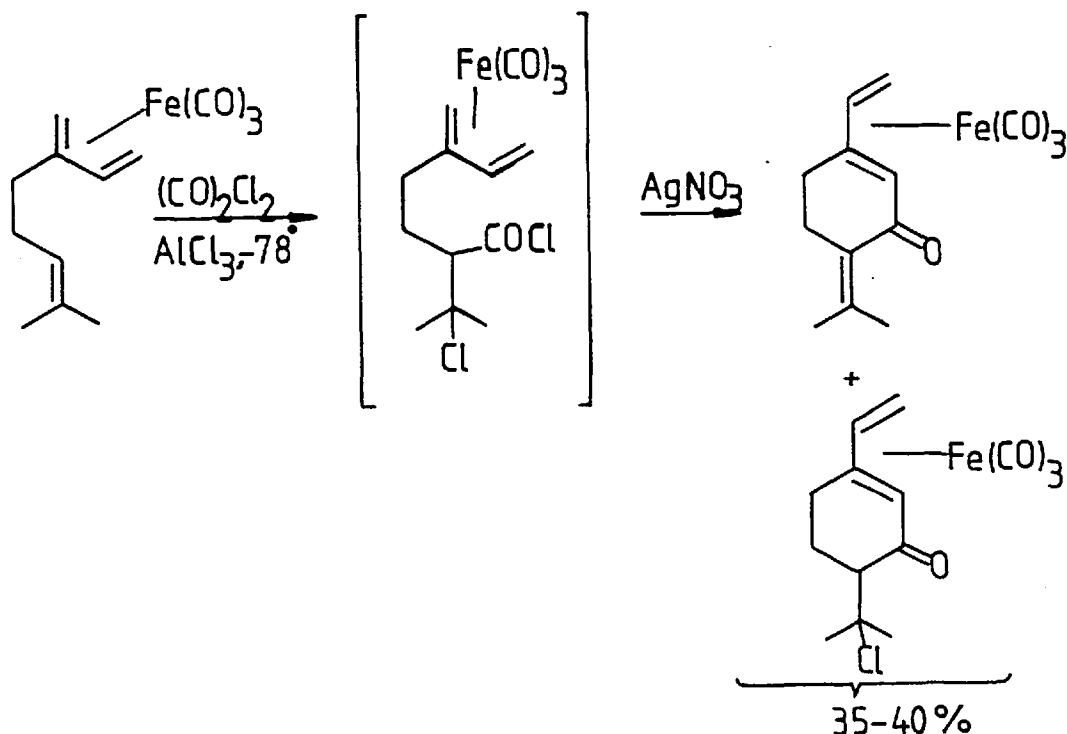
adduct. The tricarbonyliron moiety has a powerful effect upon the course of reaction via stabilisation of the intermediate dienyl cation. There is a great deal of experimental evidence in support of this mechanism. However certain anomalies such as solvent effects has led to the proposal of an alternative mechanism invoking a concerted cycloaddition.⁶⁰ Analysis of the transition states for such reactions using the Woodward-Hoffmann topological rules predicted 1, 6 and 1, 3 addition to be symmetry allowed while 1,2

1,4 and 1,5 additions would be forbidden. The arguments put forward for such process however are not sufficiently convincing, and the question of the mechanistic pathway of reaction still remains.

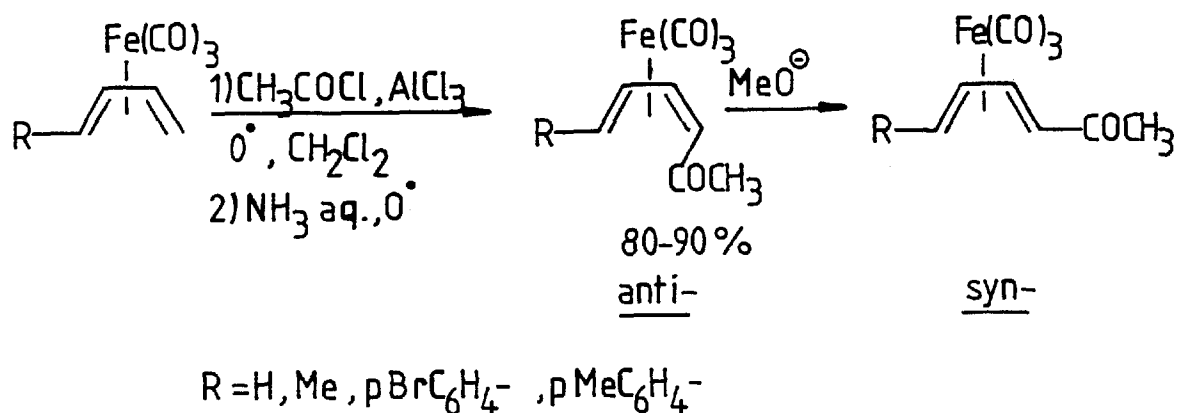
It has been reported⁶¹ that η^4 cycloheptatrienone tricarbonyliron underwent a novel 1,5 addition of TCNE, but other workers have shown reaction to proceed via the normally observed 1,3 adduct which readily undergoes rearrangement to the 1,5 adduct under the previous conditions reported for its isolation.

(d) Reactions of Co-ordinated Ligands with Lewis Acids

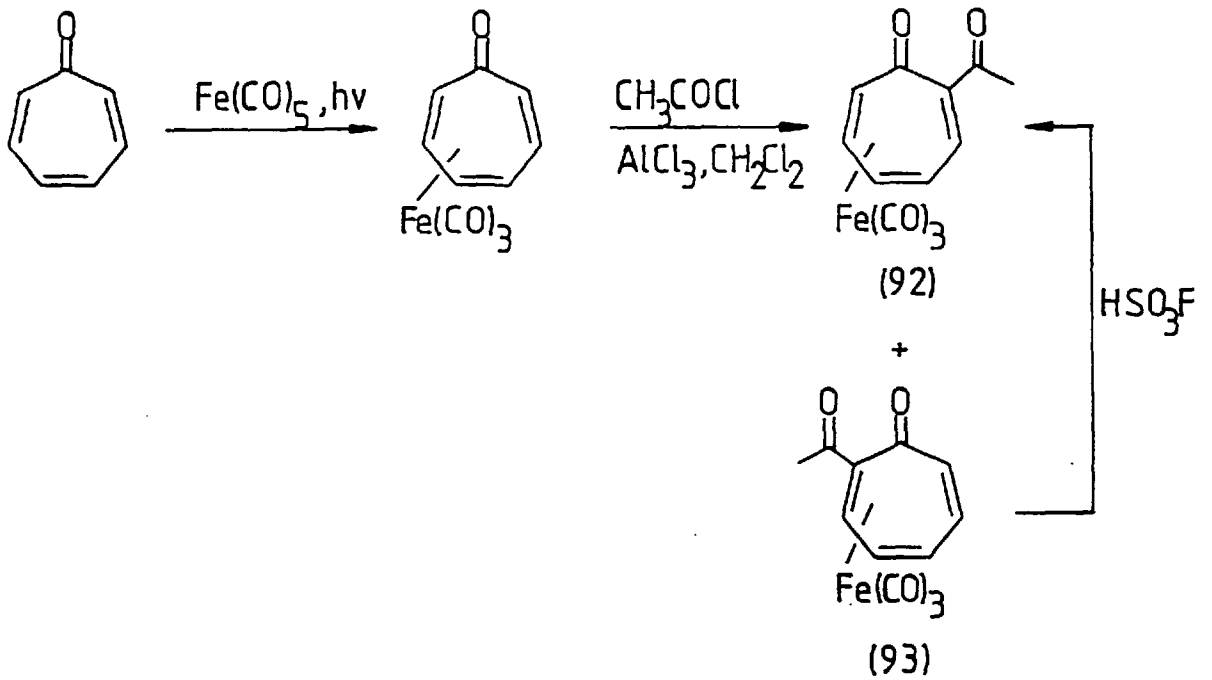
Reaction of conjugated 1,3-dienes under Friedel Crafts acylation conditions normally give rise to polymeric materials. Therefore to be able to accomplish such a transformation would be synthetically useful. The tricarbonyliron unit has been used to effect an intramolecular cyclisation



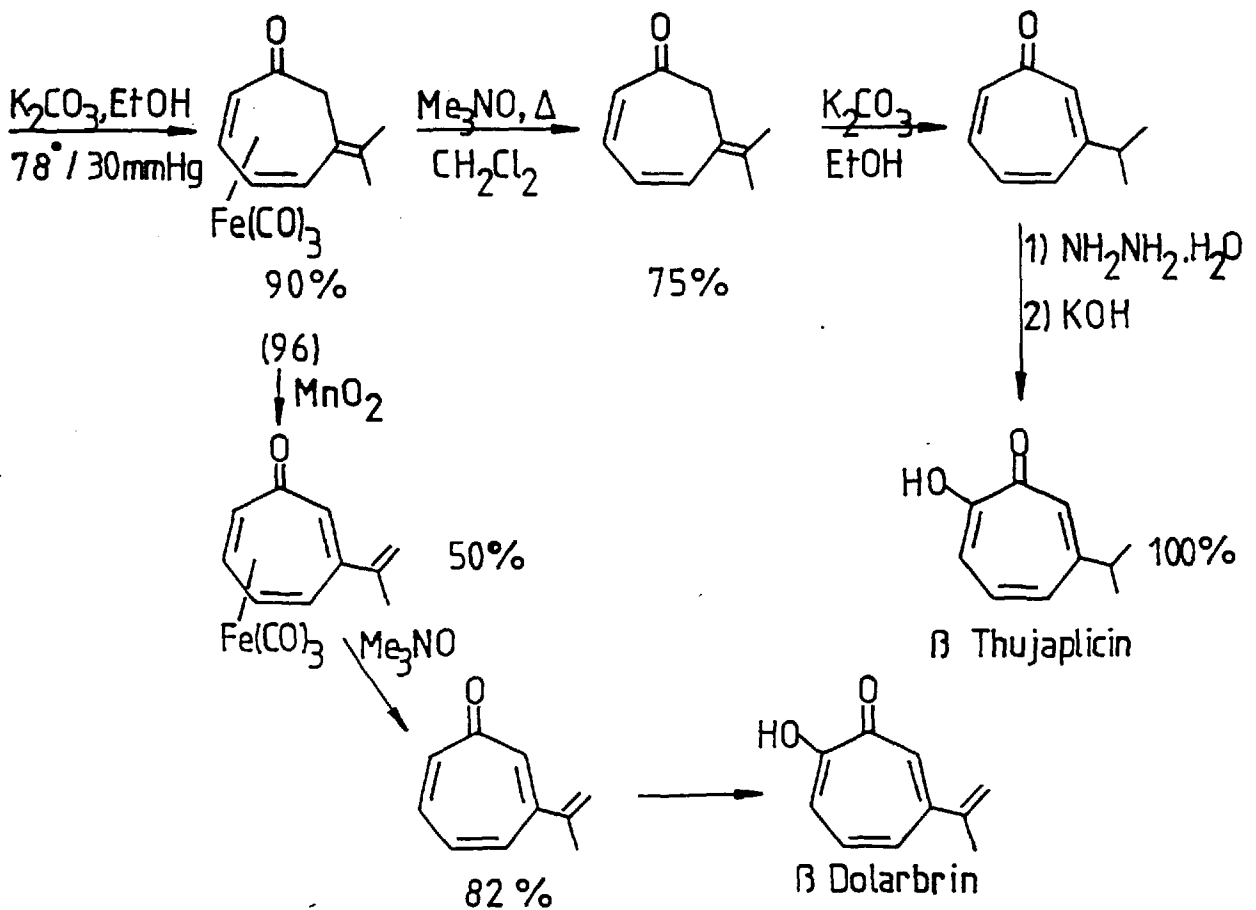
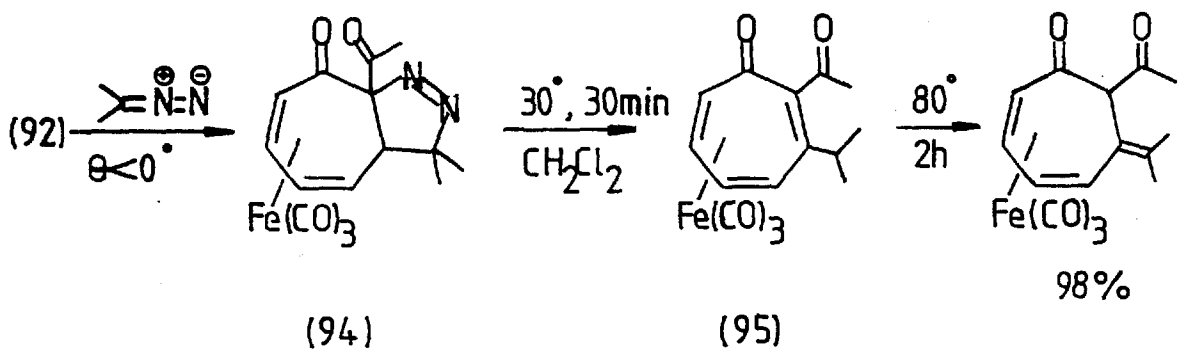
via a Friedel Crafts reaction by Birch and co-workers, but in general yields were low.⁶² Reaction of η^4 diene tricarbonyliron complexes under Friedel Crafts conditions proceeds smoothly at or near room temperatures to yield diene complexes in high yield.^{63, 64} The reaction is regio-selective, with substitution occurring at the least substituted terminus of the diene complex; reaction proceeding via a tricarbonyliron stabilised allyl cation. The introduction of the acyl group deactivates the product with respect to further reaction and work up into cold aqueous ammonia gives the anti-complex as the only product, which is easily isomerised to the syn-complex by treatment with



methoxide anion. The reaction is very susceptible to steric hindrance, and thus works best for acyclic dienes. Electron releasing substituents such as methoxy cause the reactions to proceed so fast such that useful products are rarely obtained. However this procedure still represents a synthetically useful, stereospecific route to α, β -unsaturated trans-dienones, and their derived products.



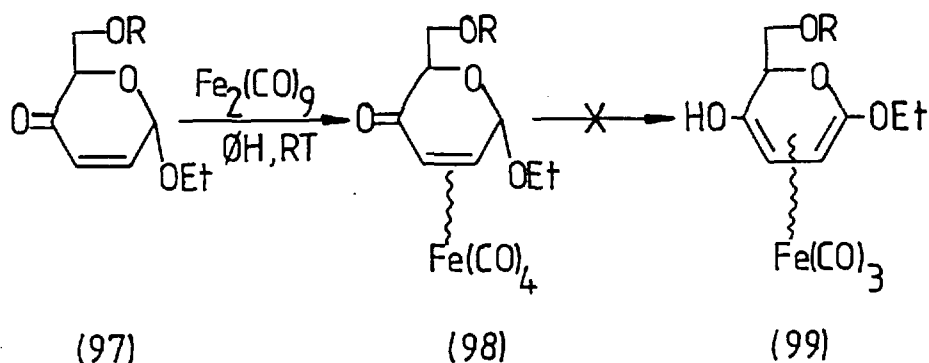
4:1, (92) : (93)



Introduction of an acyl group into an organoiron complex in a similar manner to that described above has been used to great advantage in the synthesis of β Thuja-plicin and β Dolarbrin.⁶⁵

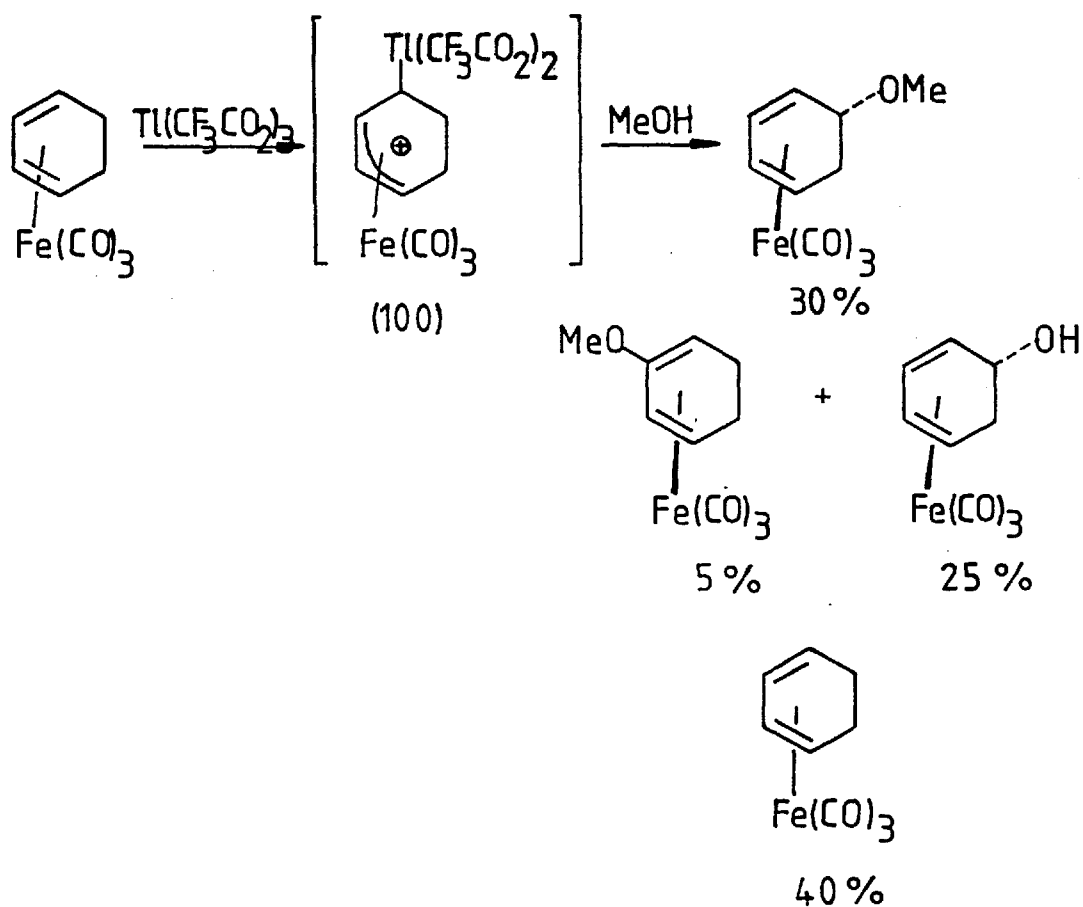
This elegant reaction sequence illustrates the utility of carbonyliron complexes in synthetic chemistry. The tricarbonyliron moiety is used to regiospecifically introduce an acyl group, which in conjunction with the iron moiety controls the direction of cycloaddition of diazo iso-propane to afford the desired intermediate (94). Further transformations are also controlled by the tricarbonyliron moiety to afford the desired products via the common intermediate (96).

The carbonyliron promoted acylation of dienes was proposed as a key step in the synthesis of carbohydrate derivatives⁶⁶ via the η^4 diene tricarbonyliron complex (99).

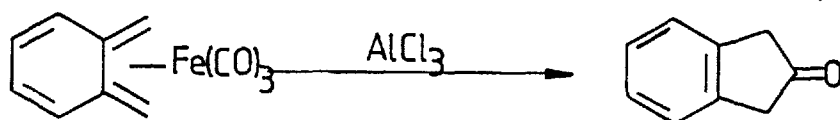
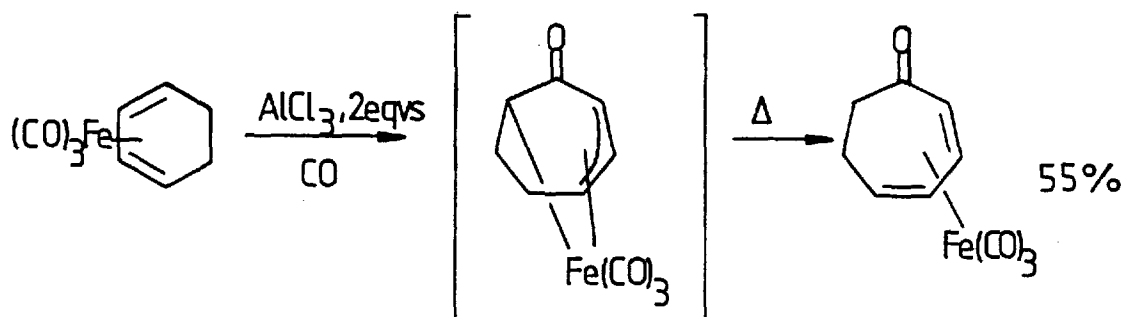


However the acylation was never attempted, since all attempts to synthesise the required diene complex yielded

only the mono olefin complex (98). It is extremely doubtful that this approach would succeed owing to the number of highly activating substituents on the desired η^4 diene complex (99). Reaction of η^4 tricarbonyliron cyclohexa-1,3-diene with the powerful electrophile thallium (III) trifluoroacetate⁶⁷ afforded an intermediate π -allyl cation (100). This reagent reacts preferentially with the organic ligand rather than oxidising the tricarbonyliron moiety. Thus it becomes a relatively easy matter to activate the diene towards nucleophilic attack. The nature of the electrophile does however severely limit the application of this approach towards the synthesis of complex molecules.



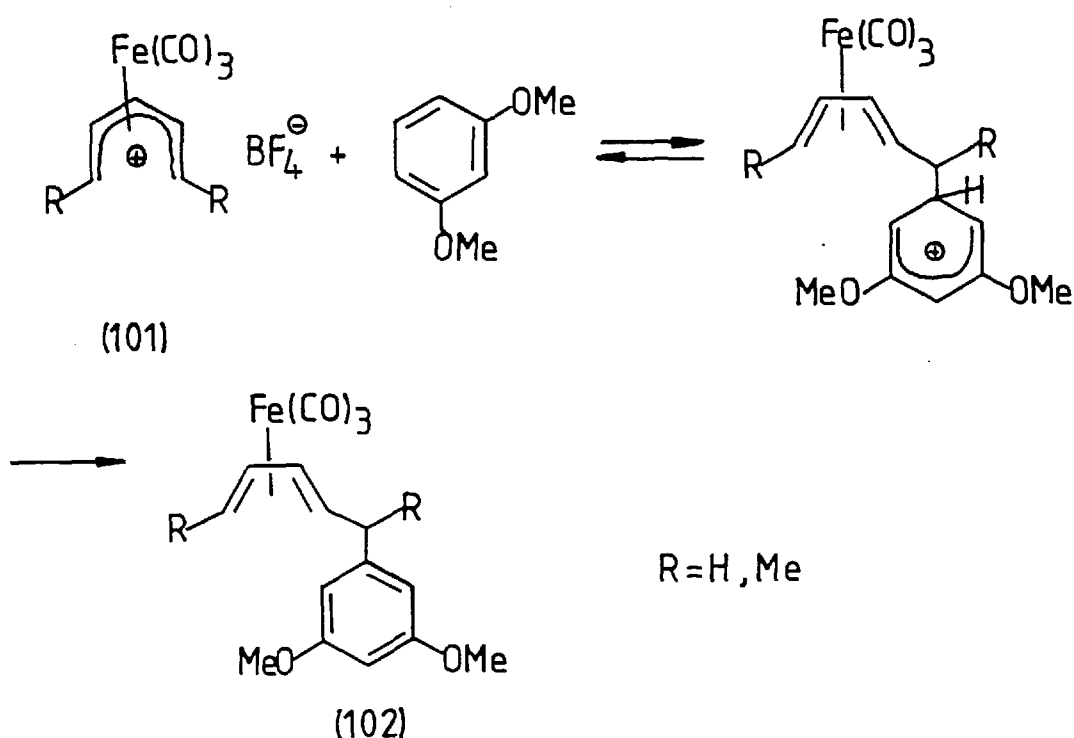
Reaction of η^4 tricarbonyliron diene complexes with Lewis Acids and carbon monoxide generally affords products of carbonyl insertion,^{68, 69, 70} and such procedures have been used to synthesise complex hydrocarbons such as bar-baralone. However reactions with more complex, highly functionalised substrates have not been investigated to any great extent, and therefore further such work is required if any practical use is to be made of this reaction.



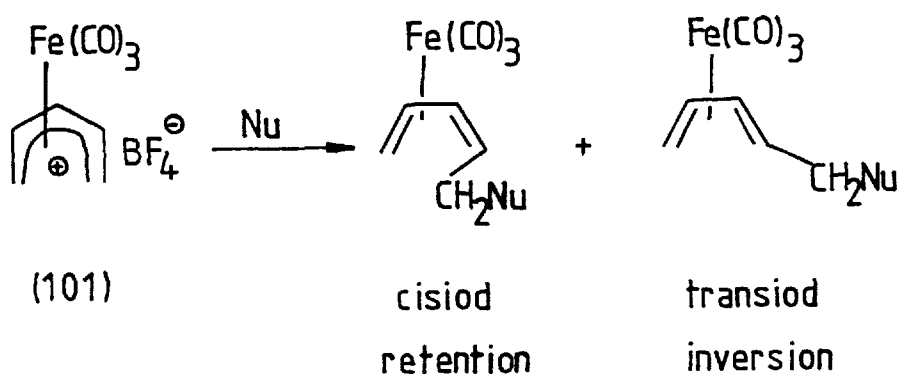
4. IRON CARBONYL STABILISED DIENYL CATIONS: SYNTHETIC APPLICATIONS

Tricarbonyliron stabilised dienyl cations represent an increasingly important class of electrophile in synthetic chemistry. They are mild and versatile alkylating agents which react with nucleophiles in many cases in a stereospecific and regiospecific manner, in high yield. They are normally prepared, and used as salts of the non-nucleophilic fluoroborate anion, either by hydride abstraction from a η^4 diene complex or by protonation of a suitable substrate.^{71, 72}

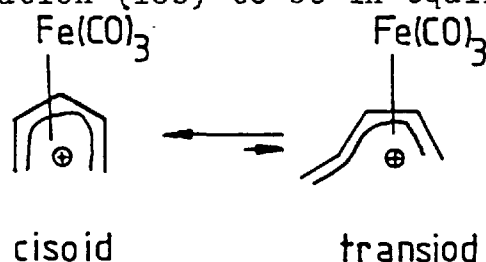
The pentadienyl cation⁷³ (101) reacts in high yield with substituted methoxy benzenes; to afford the trans, trans arylated product (102). If however the R groups are both phenyl, the reaction is reversible. The



reaction is thought to proceed via a trans cation, which would lead directly to the trans, trans product (102), rather than attack of the methoxy benzene in the cis cation (101), followed by isomerisation of the product. However it has been shown that this is the nature of the nucleophilic species which determines the geometry of the product in the case of a pentadienyl system.⁷⁴ Reaction of the dienyl cation (101) R = H, with various nucleophiles⁷⁴



and various borohydride reagents is summarised in Scheme 6. The results can be rationalised by considering the cisoid cation (103) to be in equilibrium with a small



amount of trans cation, the transoid cation being more reactive towards nucleophiles. Therefore weakly basic nucleophiles will give the products of thermodynamic control,

Nu = $\text{H}_2\text{O}, \text{ROH}, (\text{MeO})_n\text{Ar}$

total inversion - transiod product.

Nu = R_2Cd

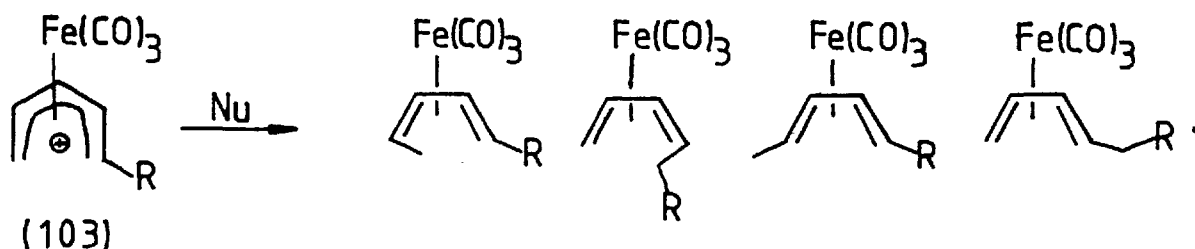
total retention - cisiod product.

Nu = Amines

(a) weakly basic-retention, cisiod product.

(b) strongly basic-inversion, transiod product.

(c) intermediate basicity - mixture of products.



Nu = NaBH_4

R = H	78	-	22	-
me	57	13	29	1
Et	85	-	11	4
Pr ⁱ	84	-	9	7

Nu = NaBH_3CN

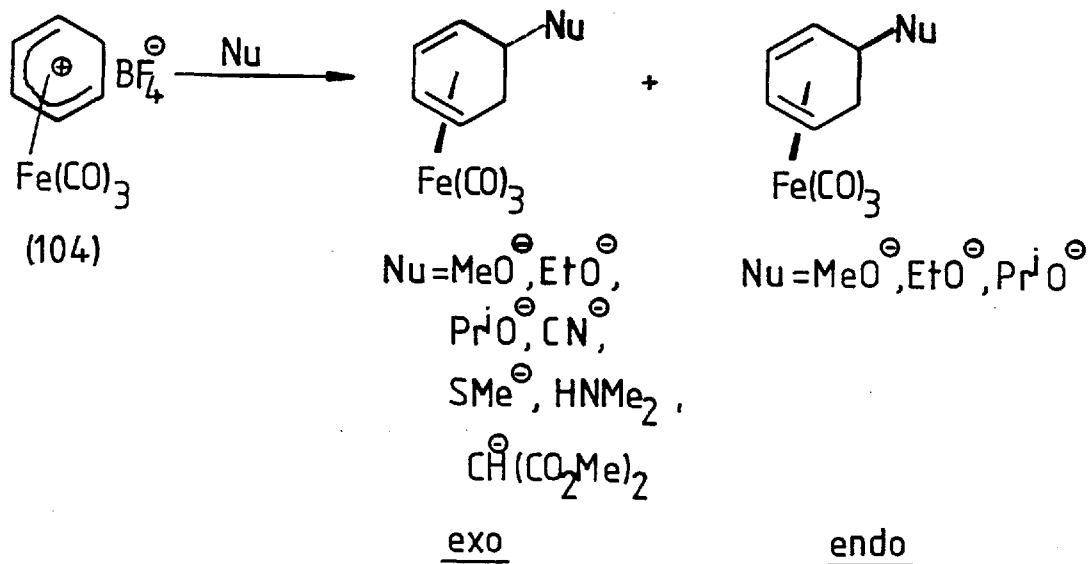
R = H	100	-	-	-
me	36	56	1	3
Et	100	-	-	-
Pr ⁱ	100	-	-	-

Nu = $\text{Li}(\text{Et})_3\text{BH}$

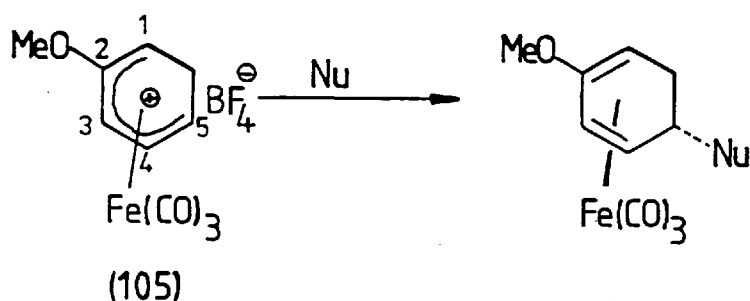
R = H	-	-	100	-
me	13	-	64	23
Et	18	-	65	17
Pr ⁱ	17	-	65	18

and strongly basic nucleophiles that of kinetic control. However it is also obvious from the results with the borohydride anion, that steric factors also play an important role in determining the course of reaction.

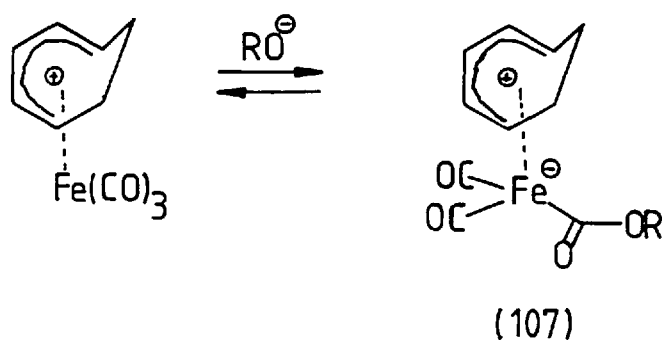
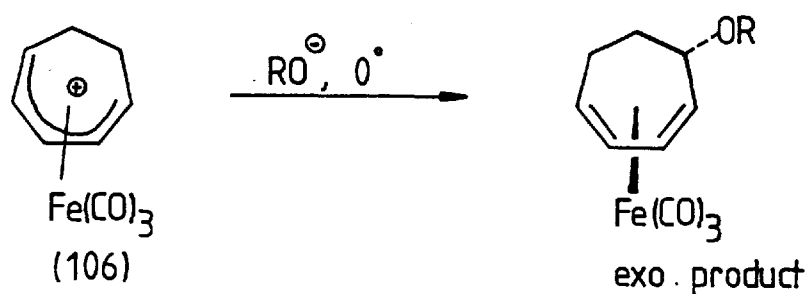
In the reaction of cyclohexadienyl cations with nucleophiles, attack by the nucleophile occurs on the opposite side of the dienyl unit to the iron moiety to give the exo product exclusively.⁷⁵ However it is possible to obtain products formally derived from endo attack, and it



has been shown that these products arise by equilibration of the initially formed exo product. The exo product can normally be obtained exclusively in these cases by performing the reaction at low temperature, upon heating an equilibrium mixture of exo and endo products is formed. It has been shown that a 2-methoxy substituent upon the cyclohexadienyl cation directs nucleophilic attack exclusively to the 5-position.⁷⁶ From the ¹³C n.m.r. of the cation (105) the Chemical Shifts of carbon atoms C₁ and C₅ indicates

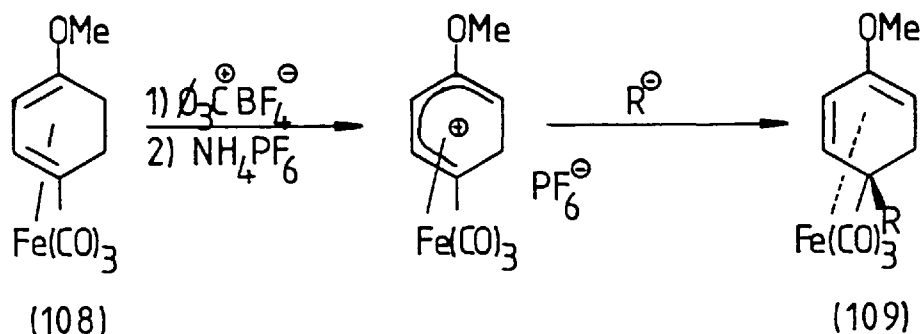


that C_1 has a greater electron density than C_5 , thus attack would be expected to occur at C_5 . That steric effects are also important in determining the regiochemistry of reaction is illustrated by the fact that a 2-methyl substituent will give rise to a mixture of products for sterically undemanding nucleophiles (the ^{13}C n.m.r. data indicates that both

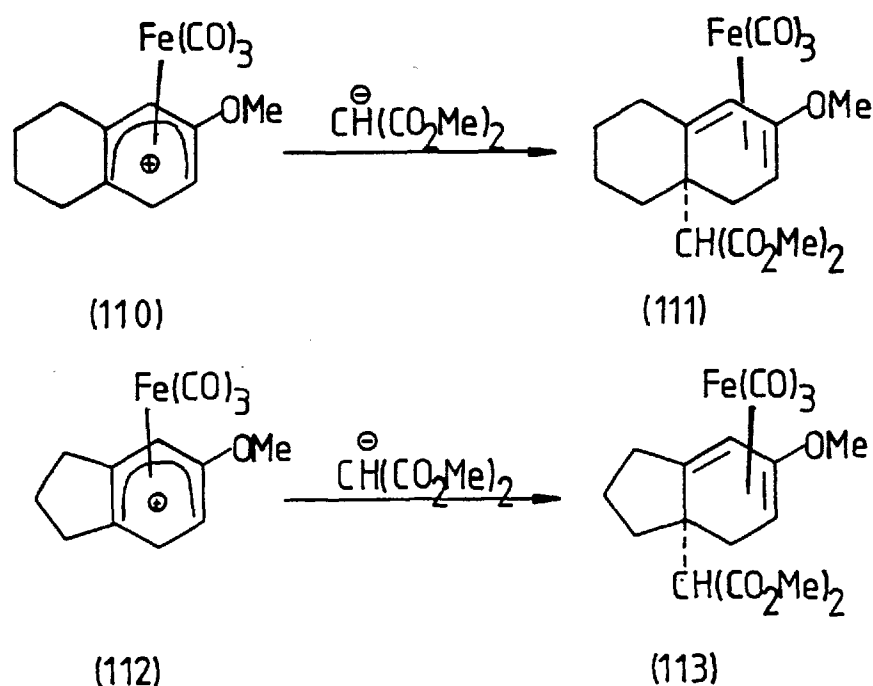


C_1 and C_5 are in a similar environment) while for more complex nucleophiles, attack occurs exclusively at C_5 . While it is generally concluded that the incoming nucleophile approaches the polyene ring on the opposite side from the metal, without involvement of the metal, it has been shown that attack by alkoxide anions upon the η^5 cycloheptadienyl tricarbonyliron cation (106) occurs initially upon co-ordinated CO to give an intermediate (107).⁷⁷ Addition of one equivalent of ethoxide anion at 0°C results in an intermediate which has an IR absorption at $\nu_{\max}$ 1650 cm^{-1} , consistent with the acycloxy species (107), and this upon warming disappears to give the isolated exo product. Therefore it would seem that this process is reversible, and upon warming the normal exo attack of the nucleophile upon the ligand is observed. It seems in this case that the energy barriers between the different modes of nucleophilic attack must be small, but whether this conclusion is valid for a wide range of nucleophiles and complexes is doubtful.

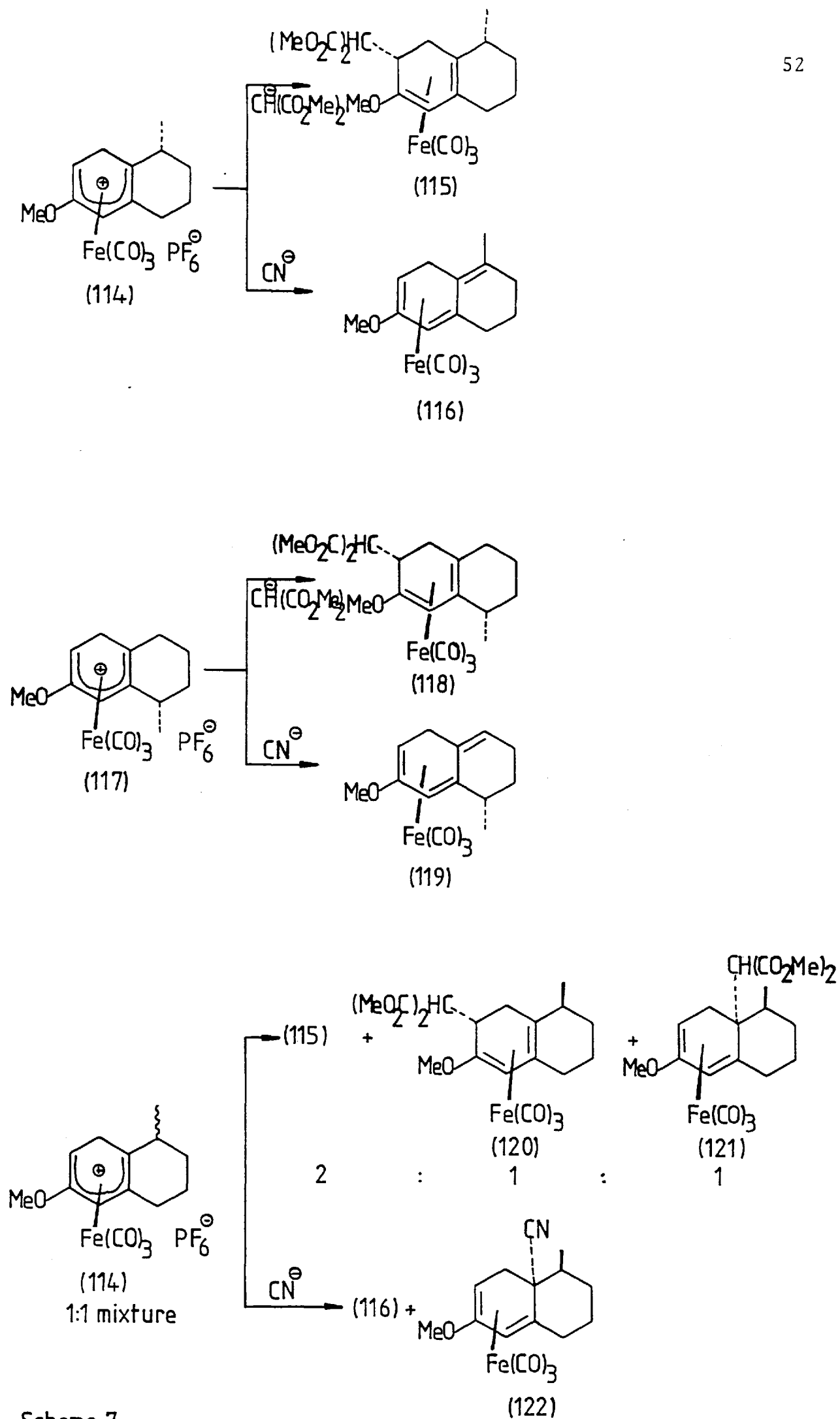
The utility of such dienyl tricarbonyliron cations



in synthesis is illustrated by the formation of quaternary centres and the introduction of angular substituents^{78, 79} by nucleophilic additions to suitably substituted cations. The electronic effect of the 4-methoxy substituents will cause C_1 to have a greater +ve charge than C_5 (^{13}C n.m.r. exhibits resonances at 91.3 ppm downfield from TMS for C_1 as opposed to 42 ppm downfield from TMS for C_5), therefore if electronic effects predominate (kinetic control) attack will occur at C_1 . Steric factors, however, would be expected to direct attack to C_5 , therefore the balance between these two competing effects will determine the course of reaction (Scheme 7).



From these results it can be seen that the directing ability of the methoxy group is insufficient to overcome steric hindrance presented by the exo methyl groups α and β to the reaction centre (C_1 - the terminus activated

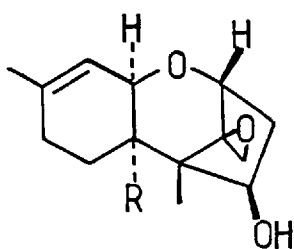


Scheme 7

towards nucleophilic attack by the methoxy substituent), as shown in compounds (115) and (117). In such cases cyanide anion causes proton abstraction to form a triene (116) (119) to occur rather than addition at C_3 . Therefore these reactions define the limits to which the application of tricarbonyliron dienyl complexes are synthetically useful.

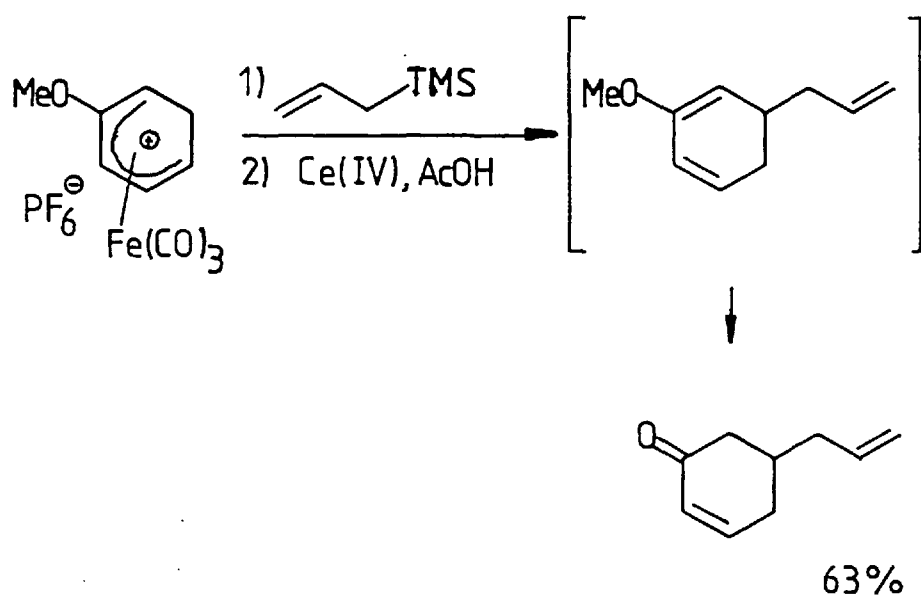
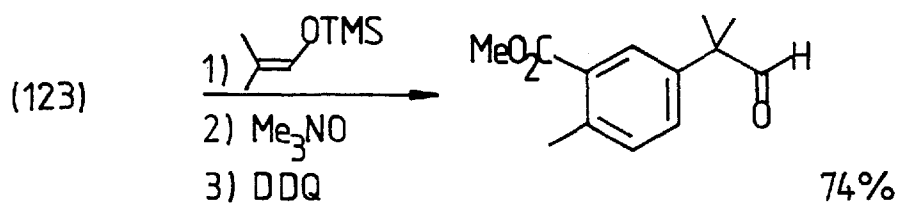
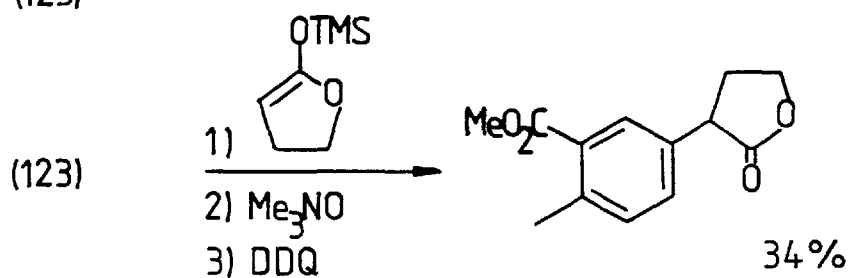
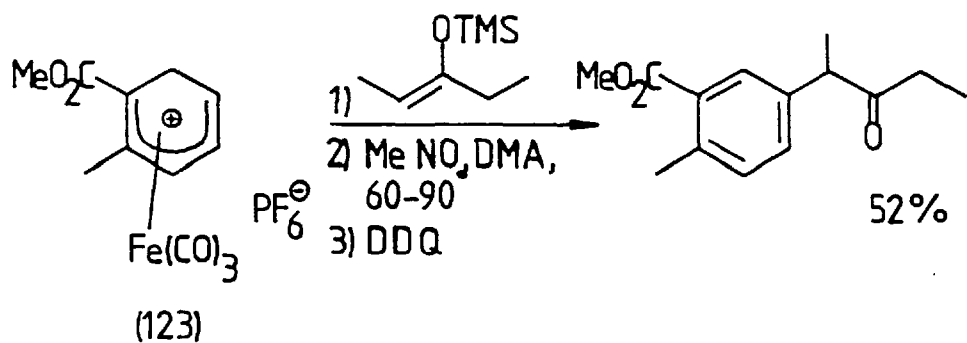
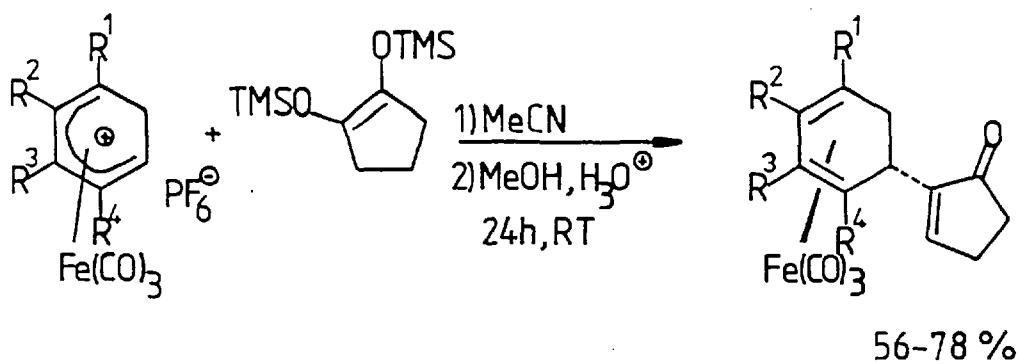
The η^5 cyclohexadienyl tricarbonyliron cation (104) reacts readily with nucleosides and nucleoside bases⁸⁰ to give mono, and in some cases bis-alkylated products. The reverse reaction can be accomplished by treatment of the adduct with trifluoroacetic acid. Other nucleophilic species such as trimethylsilyl enolethers^{81, 83} and allyl silanes^{82, 83} add readily to η^5 cyclohexadienyl tricarbonyliron cations. These reactions have been used to synthesise substituted cyclopentanones, substituted dihydrobenzenes, and benzenoid compounds. The hexafluorophosphate anion has been used as a counter ion in these procedures; and presumably acts catalytically via fluoride anion attack at the silicon based reagent.

In an approach to the synthesis of the

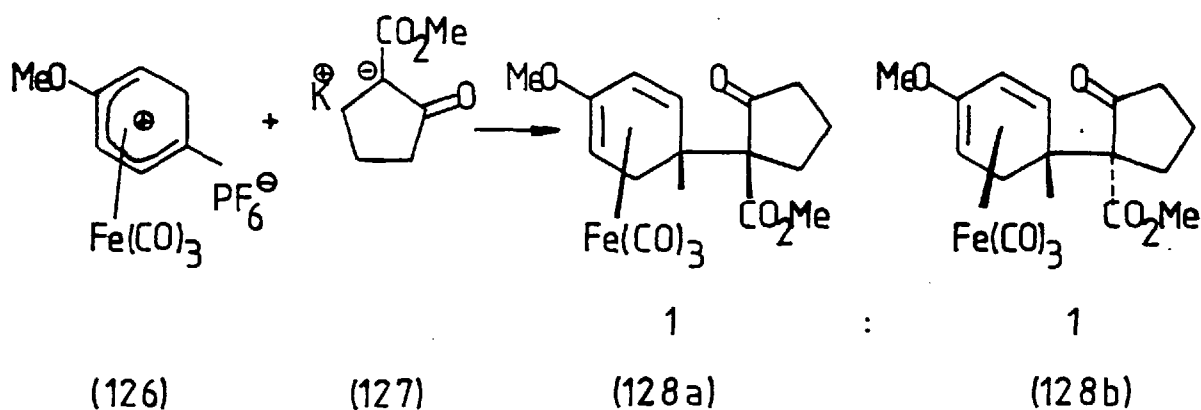


R=Me (124)

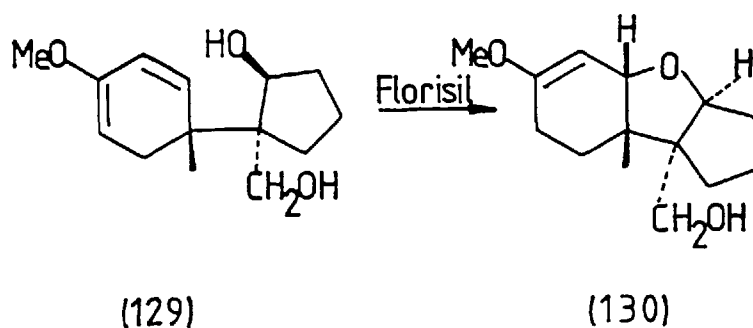
R=CH₂OH (125)



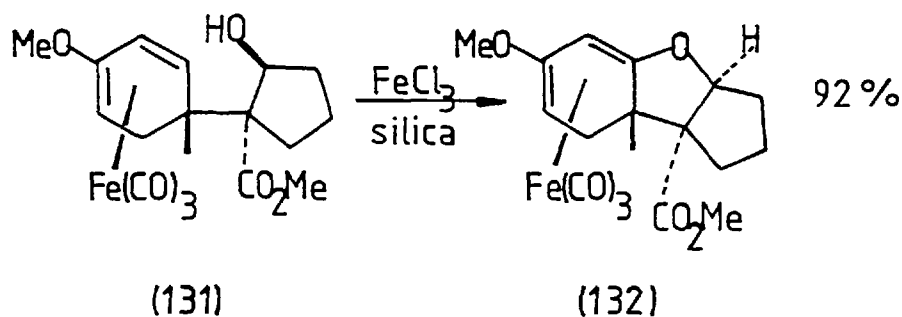
polyoxygenated sesquiterpenes^{84, 85} Trichodermin (124) and Verrucarlor (125), the dienyl cation complex (126) was quenched with the potassium enolate (127) to give a 1:1



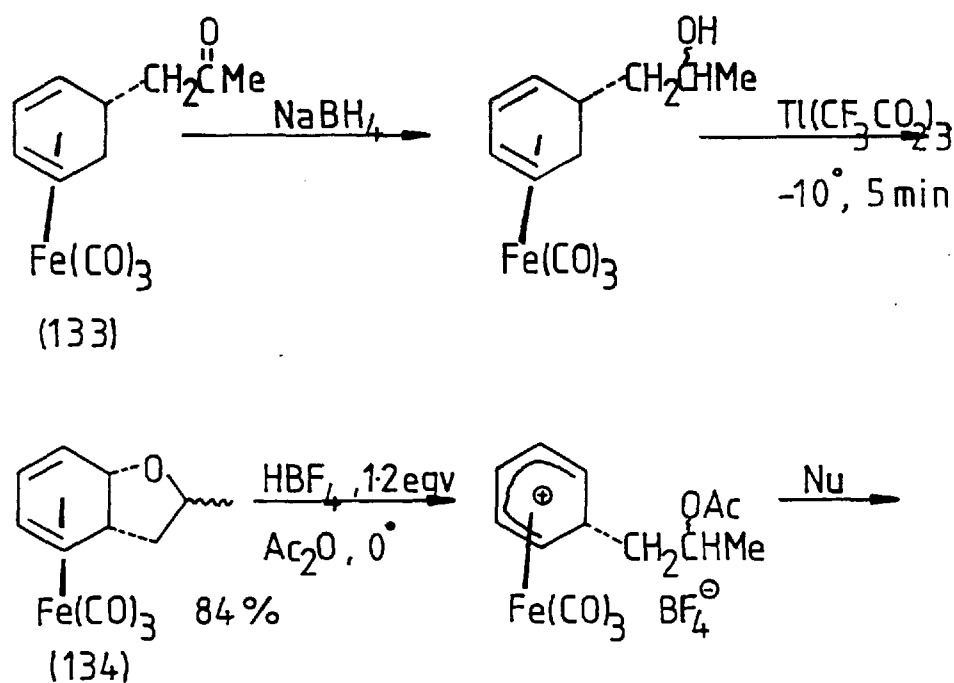
mixture of the diastereomers (128), in quantitative yield. Thus one of the quaternary centres in the final product has been introduced in one high yielding step. However decomplexation of (128b), and reduction of the keto function led to the diol (129), which readily cyclised to (130) upon chromatography on Florisil.



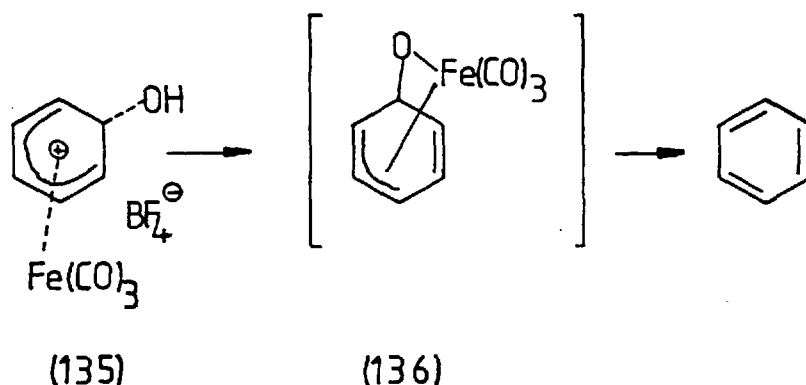
Treatment of the η^4 diene tricarbonyliron complex (131) with ferric chloride supported upon silica gel did not



dehydrate the alcohol to the alkene, but gave the cyclised product (132) in high yield. However it should be possible to overcome this problem by use of a modified enolate equivalent. Intramolecular nucleophilic additions⁸⁶ have been accomplished by treatment of the complex (133) with thallium (III) trifluoroacetate (hydride abstract by trityl fluoro-borate is not possible in this case due to steric hindrance).



The cation (135), a stable solid, when dissolved in d_6 acetone containing a trace of water undergoes

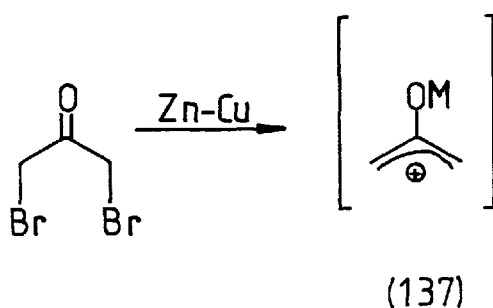


decomposition to benzene, presumably via intermediate (136).⁸⁷ No intramolecular attack was observed in this case, the endo hydroxy attacking the iron moiety rather than the dienyl system. This result indicates that a high degree of +ve charge is localised at the iron moiety, and therefore such factors must be taken into account when considering the η^5 dienyl cation as a synthetic unit.

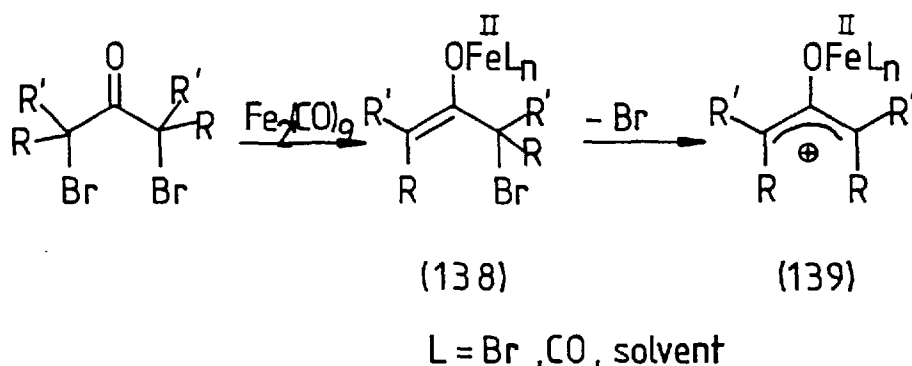
5. IRON CARBONYL MEDIATED CYCLOCOUPLING REACTIONS

Organic reactions of halo ketones have proved to be of great synthetic value. Their diverse chemical reactivity, displacement by nucleophiles, reduction, elimination of HX to afford α , β -unsaturated ketones, epoxide formation, rearrangements, alkylations and dimeric coupling has led to their widespread use in synthetic chemistry.

It is well known that α , β -dihaloketones on reaction with zinc-copper couple form a highly reactive intermediate which behaves chemically as an equivalent of an oxyallyl cation (137).



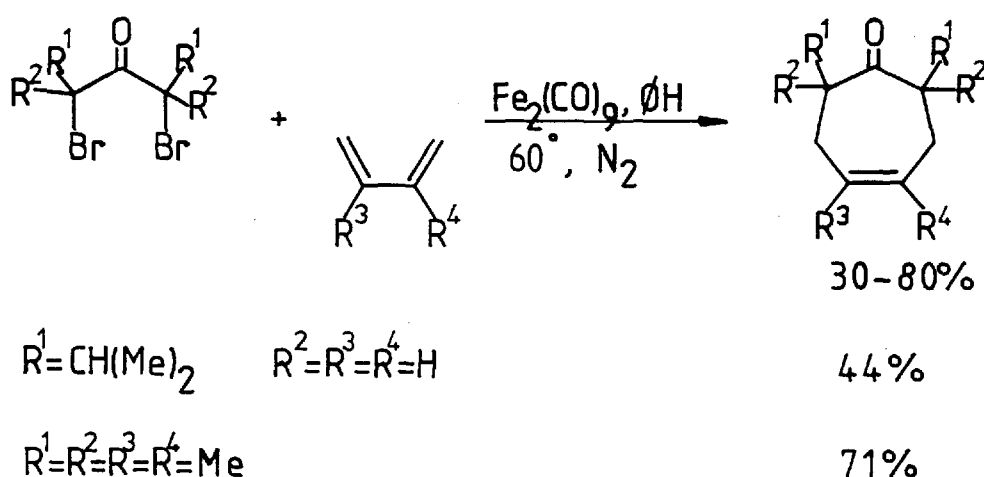
However this procedure is rather messy and not generally applicable to a wide range of substrates. The reaction of α , α' -dihaloketones with enneacarbonyl diiron⁸⁸ has been shown to produce an oxyallyl cation, and the wide ranging synthetic utility of this intermediate has been elegantly demonstrated by the work of Noyori and co-workers. From this polybromoketone/carbonyliron reagent system a wide range of synthetic procedures has been devised, and used in a number of syntheses of natural products.



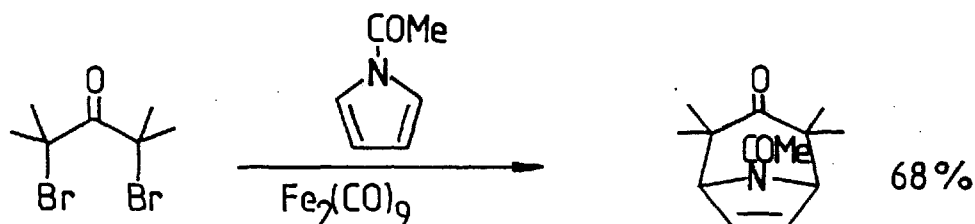
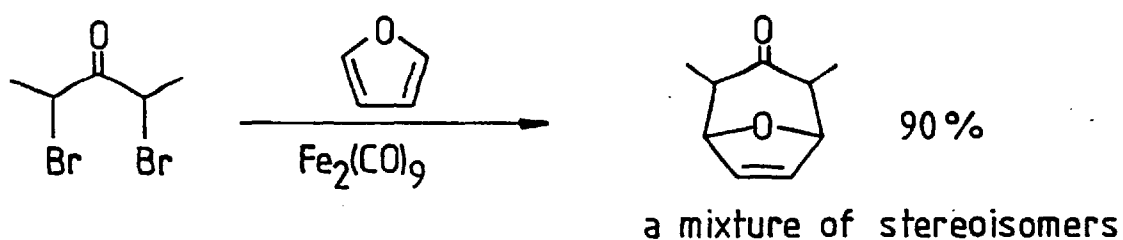
It has been shown that reaction proceeds via two electron reduction (or oxidative insertion of tetracarbonyliron into the C-Br bond) to give an intermediate ion (II) enolate (138) followed by an $\text{S}_{\text{N}}1$, type, ferrous ion assisted elimination of bromide anion to afford the reactive oxyallyl cation (139). Extensive evidence for such a pathway and an exhaustive study of its reactions has been carried out by Noyori and co-workers. The oxyallyl cation is an extremely versatile intermediate undergoing nucleophilic attack, regioselectively at the more substituted terminus (greater coefficient of the LUMO at this point), Unsubstituted dihaloketones do not give products formally derived from formation of the oxyallyl cation (139) due to their high reactivity. Therefore substituents are necessary to increase the stability of the oxyallyl cation, but have the advantage that they can by suitable choice be used to direct reaction.

Formation of the oxyallyl cation in the presence of various 1,3 dienes affords 4 - cycloheptenones^{88, 89} in

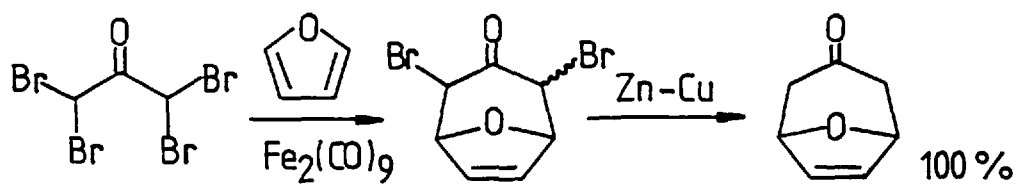
moderate yields via a 3 + 4 cyclocoupling reaction. This could be considered either as a concerted ($\pi 2_S + \pi 4_S$) cycloaddition reaction or a multi-step process. The most effective receptors are dienes of the cis - cis geometry, the regiochemistry of addition being easily rationalised in terms of frontier orbital interactions. The utility of such a procedure in the synthesis of cycloheptenone derivatives is illustrated in the following schemes.



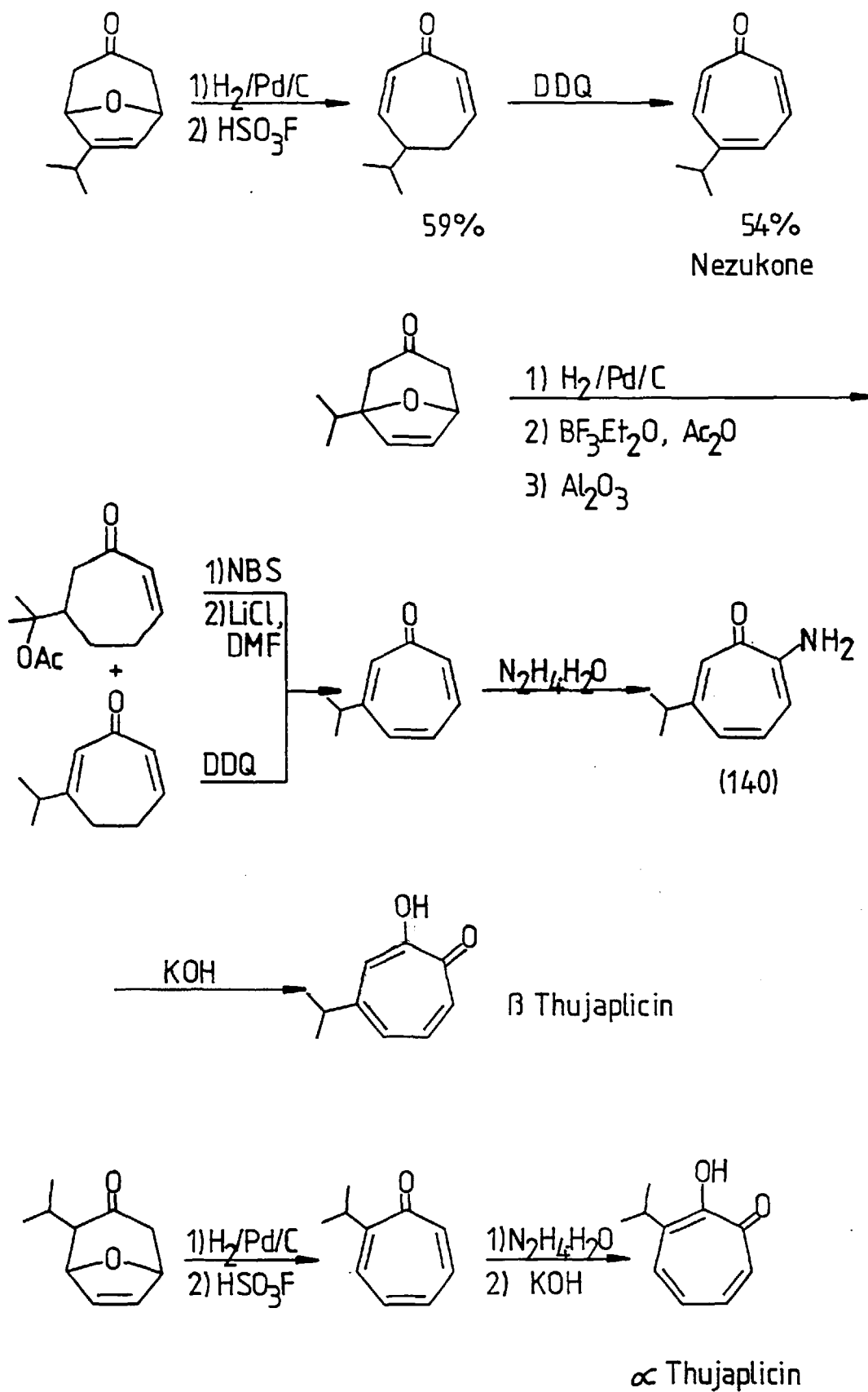
Reaction yields are improved by using a η^4 diene tricarbonyliron complex instead of enneacarbonyl diiron as the source of reducing agent. Cyclopentadiene, furan and N-acetyl pyrrole also undergo the cyclocoupling reaction in excellent yield.



It can be seen from these results that the cyclo-coupling reaction proceeds best with cyclic 1,3 dienes. The limitations to reaction arise from the type of starting materials, but suitable equivalents of methyl ketone dibromides have been used to extend the utility of this general synthesis of cycloheptene derivation. $\alpha, \alpha, \alpha', \alpha'$ - tetrabromo acetone is a suitable substrate for reaction,

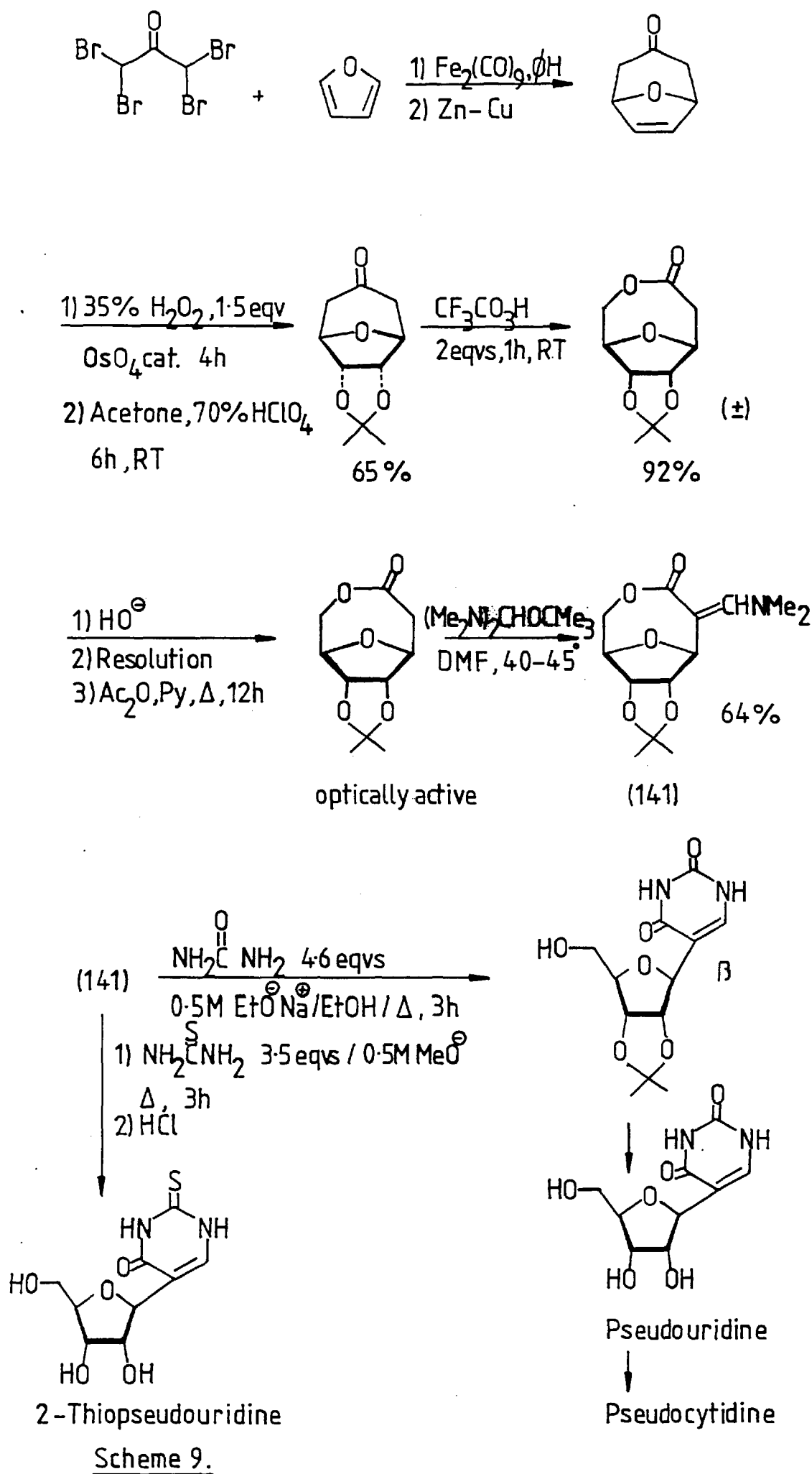


bromine being easily removed by reduction from the product of cycloaddition. This sequence has been elegantly applied to the synthesis of Nezucone and α and β Thujaplicin.⁸⁸



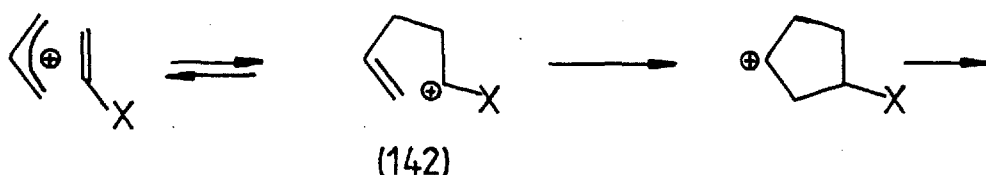
Scheme 8. Synthesis of Nezukone, αThujaplicin and β Thujaplicin

This reaction has also been elegantly applied to the stereocontrolled synthesis of C-nucleosides⁹⁰ (Scheme 9).

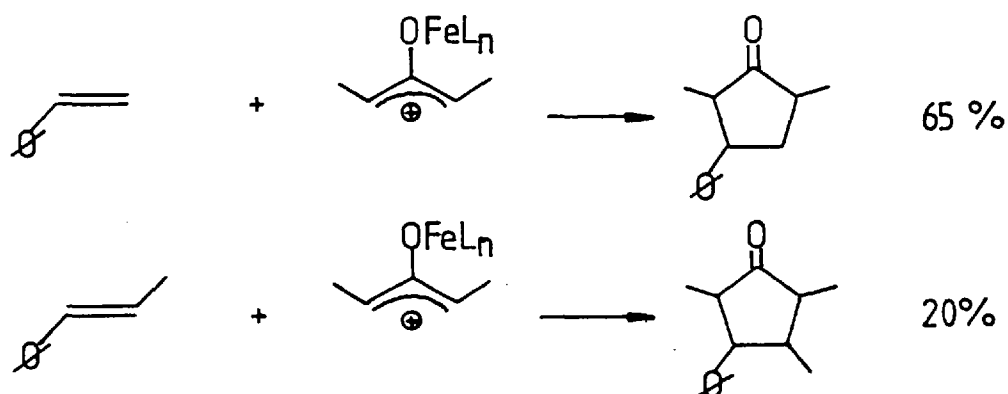


All the steps from intermediate (141) proceeded without formation of stereoisomers. This synthesis illustrates the synthetic application of the products obtained from the cyclocoupling reactions.

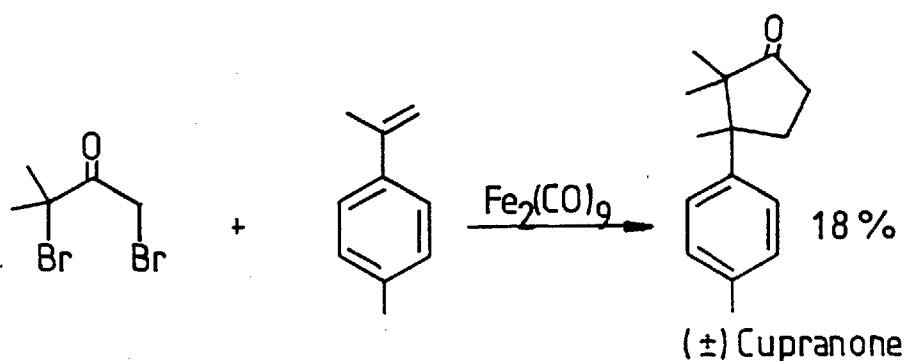
Tropane alkaloids⁸⁸ have also been synthesised via the reaction of the oxyallyl cations with N-acetyl pyrrole, and five membered carbocyclic rings⁸⁸ are available via a 3 + 2 cyclocoupling reaction between oxyallyl cations and suitably substituted olefins. A concerted 3 + 2 cycloaddition is symmetry forbidden, and therefore the reaction must proceed in a stepwise fashion. This requires that the stability of the intermediate cation (142) be of comparable



stability to the oxyallyl cation (however in certain circumstances the oxyallyl cation can undergo an ene reaction,⁹¹ to give substituted ketones), and furthermore that it undergoes irreversible reaction leading to a neutral product. This has been accomplished by the use of styrene derivatives⁸⁸ as suitable donors for the oxyallyl cations. Thus substituted cyclopentanones are obtainable by this route, the yields however are low.



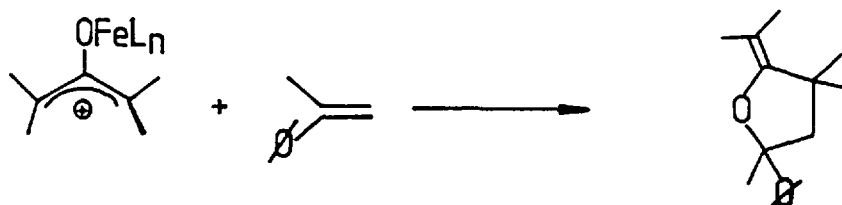
Thus a convenient one step synthesis of racemic cupranone⁹² was easily accomplished via this route.



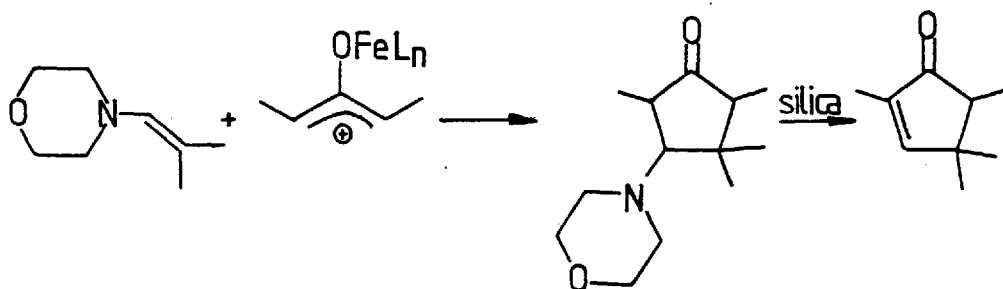
Although the yield was poor it is still a great improvement upon the previous seven step synthesis.

In principle the cation (142) could cyclise by

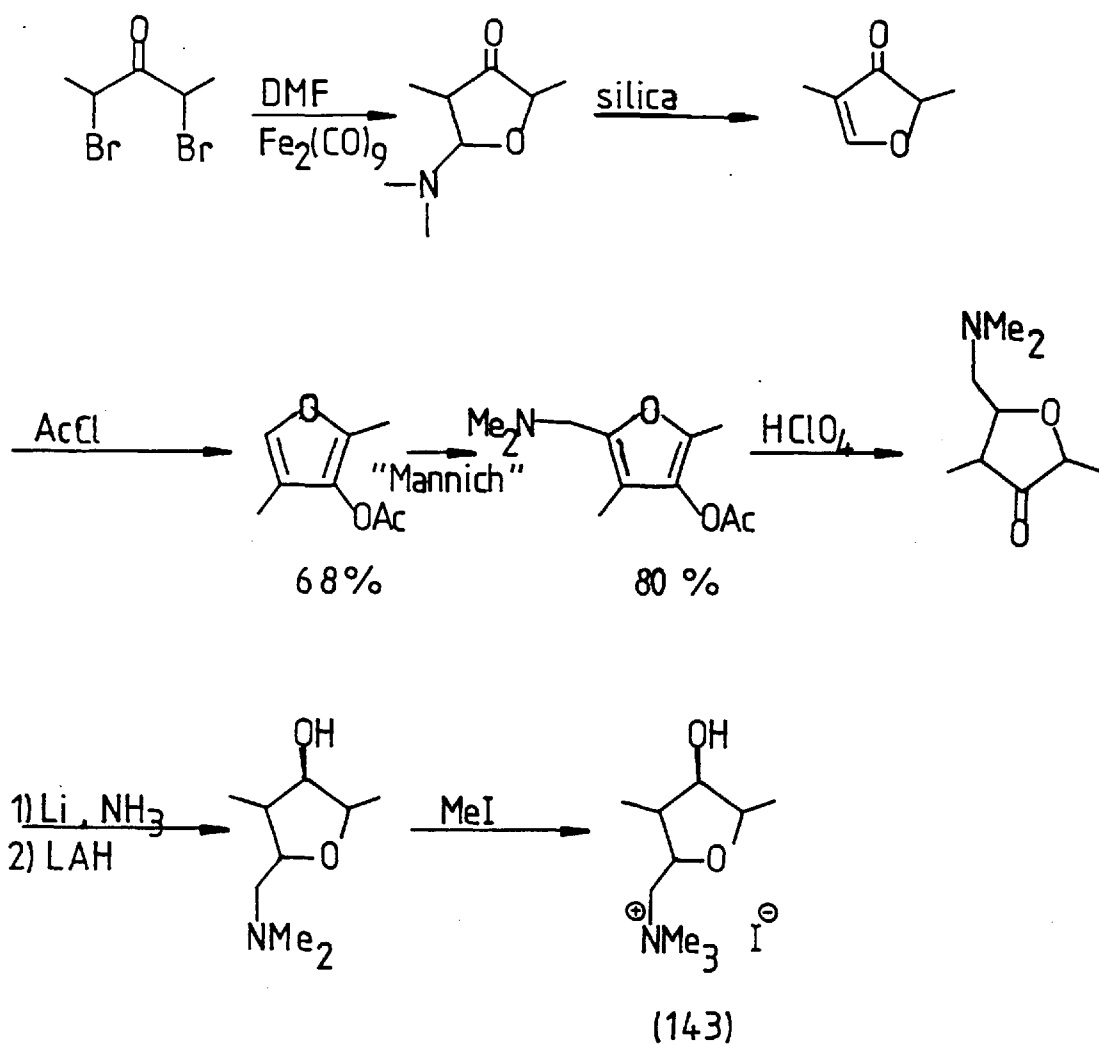
attack of the oxygen functionality on the cation centre, and this is indeed observed when tetra substituted dibromoketones are used as substrates.



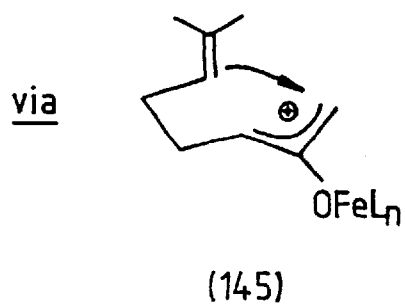
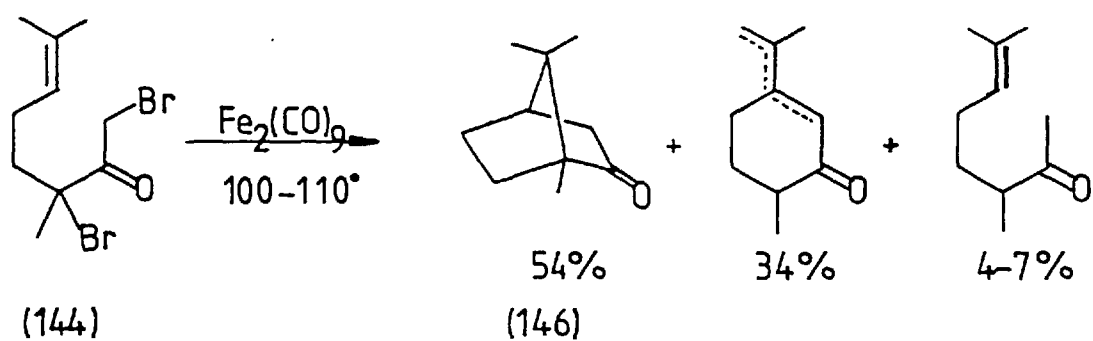
Reaction with enamines⁸⁸ can lead to cyclopentanones in high yields.



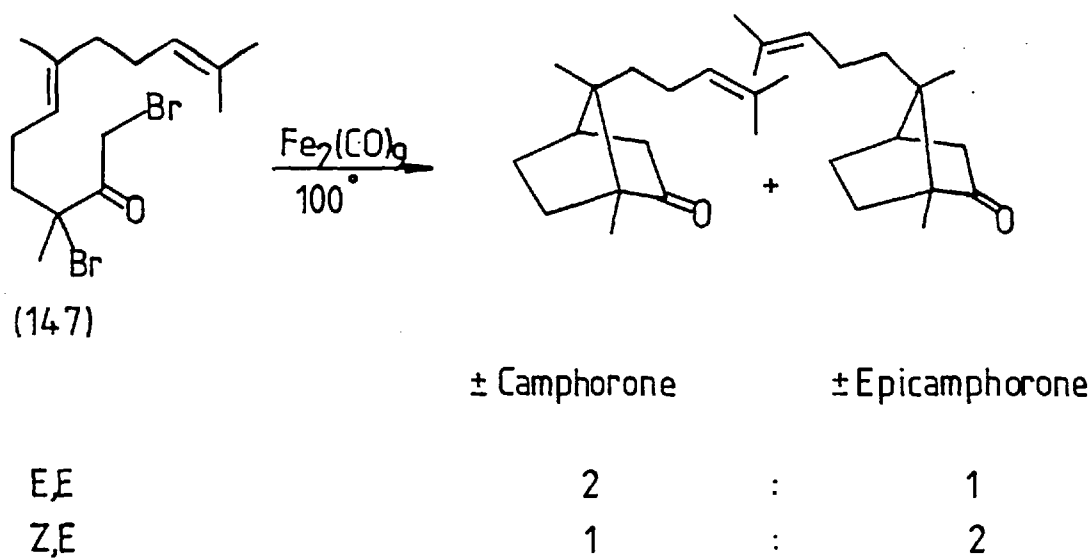
Furanones⁹³ were obtained by reaction with substituted dimethyl acetamides in moderate to good yields, this procedure leading to a convenient synthesis of the alkaloid Muscarone (143) which is difficult to obtain from natural sources.



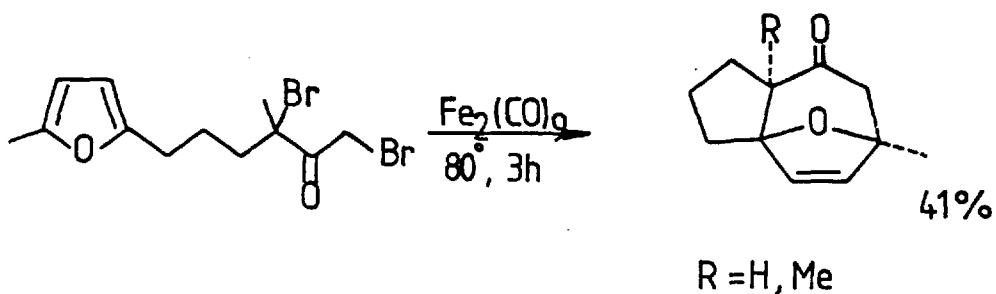
The polybromoketone - carbonyliron route has been utilised in a novel entry in the synthesis of polycyclic terpenes.⁹⁴ Treatment of the bromoketone (144) with enneacarbonyl diiron led to formation of the desired ketone (146) via intermediate (145). Thus dibromo ketone (147) afforded



($\pm$) camphorone and ($\pm$) epicamphorone in good yield.



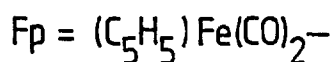
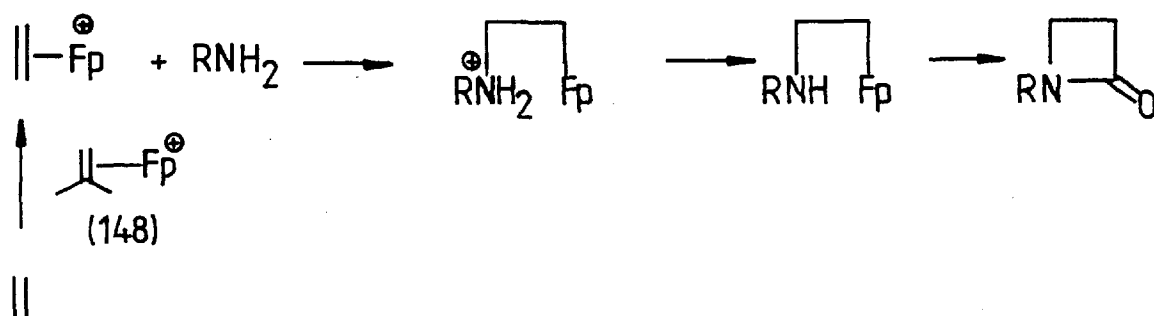
The ease to which the intramolecular (3 + 2) cyclocoupling reaction takes place is profoundly affected by the substitution pattern about the double bond. The method does however permit direct synthesis of the oxido-perhydroazulene skeleton,⁹⁴ a common structural unit of naturally occurring Ducon, Ambrosic acid and Germacrol.



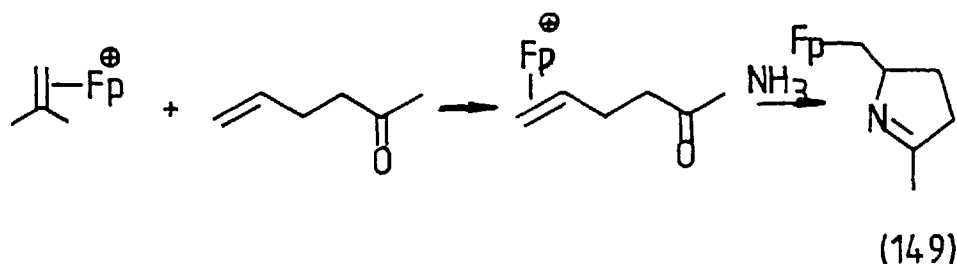
6. OTHER TRANSFORMATIONS PROMOTED BY IRON CARBONYLS

(a) Activation of Olefins by Cationic Carbonyliron Species

The synthesis of β lactams from olefins⁹⁵ has been accomplished by activation of an olefin towards nucleophilic attack by co-ordination to the η^5 cyclopentadienyl dicarbonyliron cation. Bicyclic β lactams can be synthesised

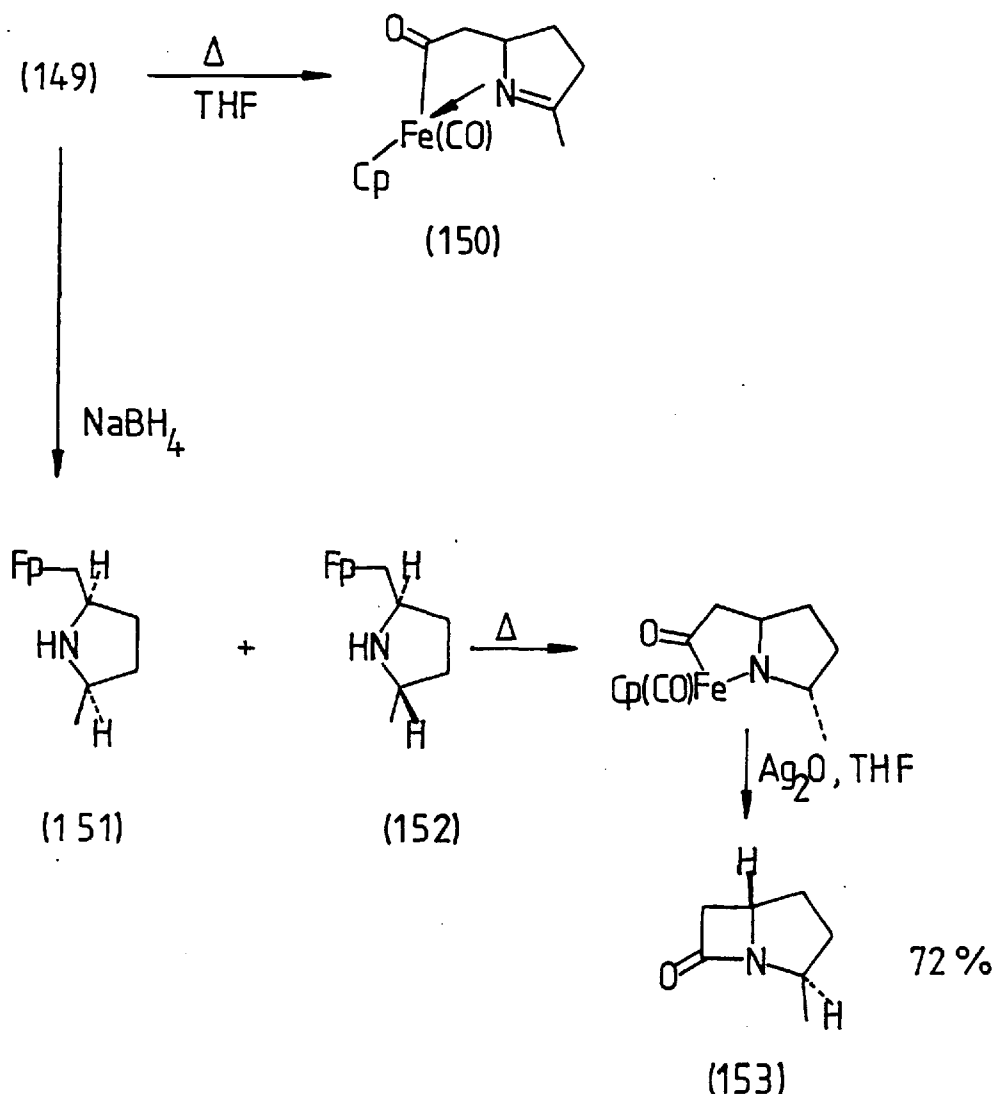


from ω -amino olefins in this manner. The olefin complexes are prepared by ligand exchange with the η^2 -propene, η^5 -cyclopentadienyl dicarbonyliron cation (148) (the oxidation state of the iron being formally +2).



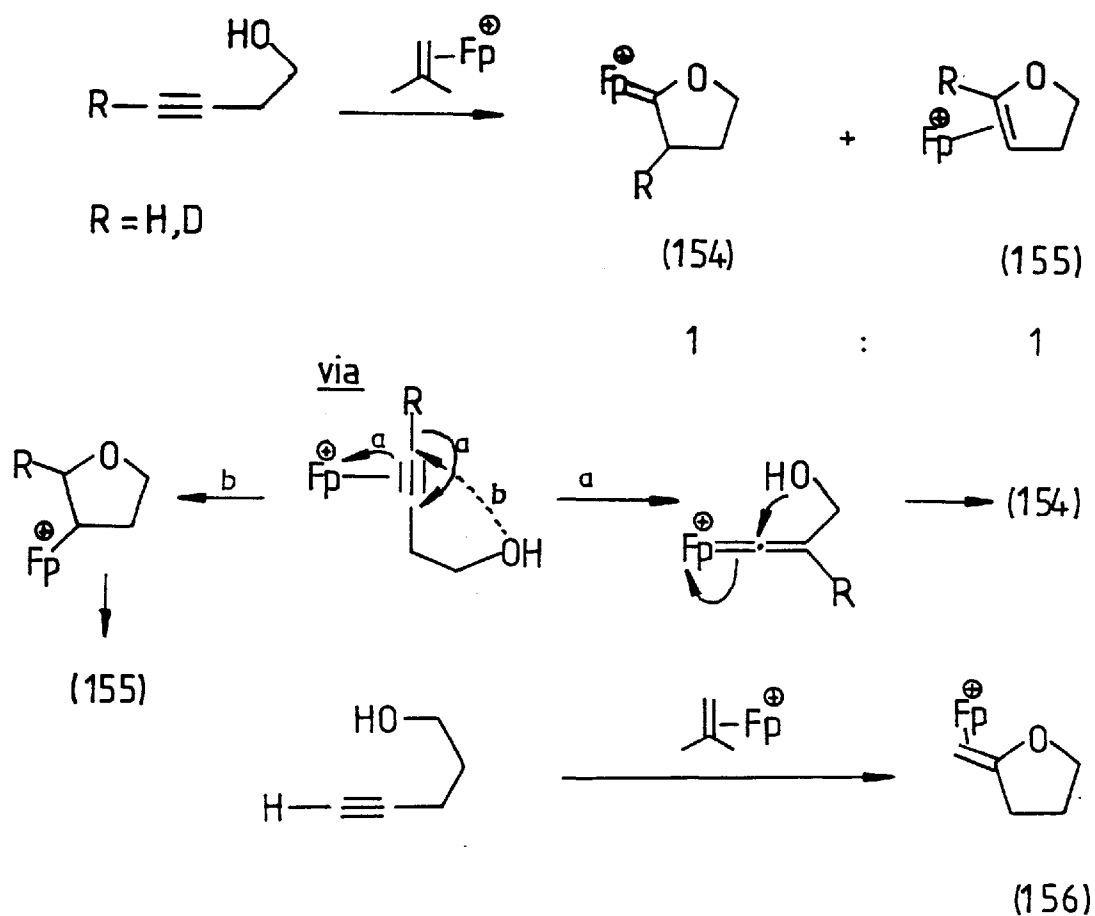
Reaction of a γ , δ -unsaturated methyl ketone with the transfer agent (148), followed by reaction with ammonia

yields the σ complex (149). This upon heating at reflux in THF undergoes CO insertion to the carbonyliron lactam (150).

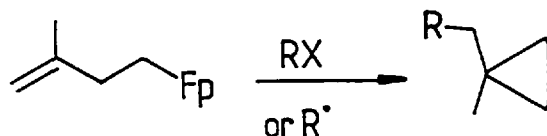


However on oxidation only a small yield of the desired β lactam was obtained. Reduction of the σ complex (149) with sodium borohydride afforded a 1:1 mixture of the cis and trans isomers (151) and (152), of which the only trans product underwent CO insertion upon heating in THF. Oxidation of this carbonyliron lactam proceeded with reductive elimination of the iron species to yield the bicyclic

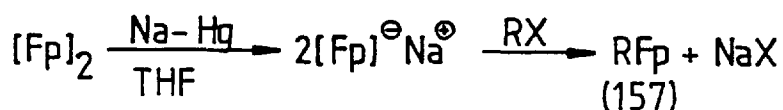
lactam (153) in good yield. The transfer reagent (148) has also been used to effect intramolecular cyclisation but - 3 yn - 1 - ol⁹⁶ to dihydrofuran (155), and carbene complex (154). Pent - 4 - yn - 1 - ol affords only one exo methylene hydrofuran (156).



Substituted cyclopropanes⁹⁷ can be obtained by the action of alkyl halides or alkyl radicals upon homo allyl σ dicarbonyliron cyclopentadienyl complexes.

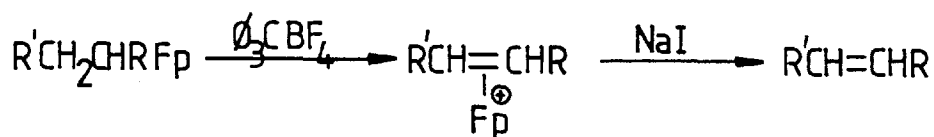


Substitution of alkyl halides with η^5 cyclopentadienyl dicarbonyliron⁹⁸ proceeds by an $\text{S}_{\text{N}}2$ pathway to give an alkyl σ complex (157), which on treatment with trityl fluoroborate



X = halide or tosylate

yields primary > secondary > tertiary

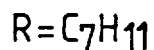
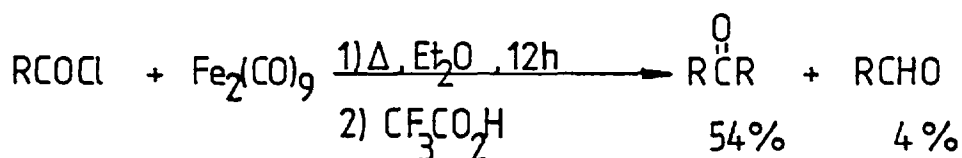


yields a cationic olefin complex via hydride abstraction. This can easily be converted into the olefin by treatment with sodium iodide in acetone. This procedure has the advantage of affording high yields of terminal olefins without any isomerisation of the double bond occurring.

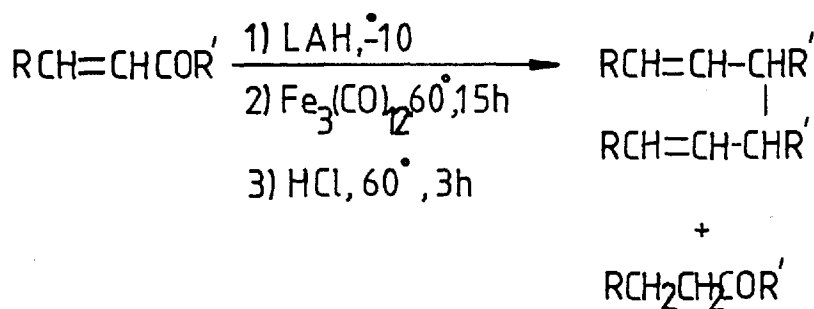
(b) Coupling reactions promoted by Carbonyliron Reagents

Acid chlorides are efficiently coupled⁹⁹ to afford

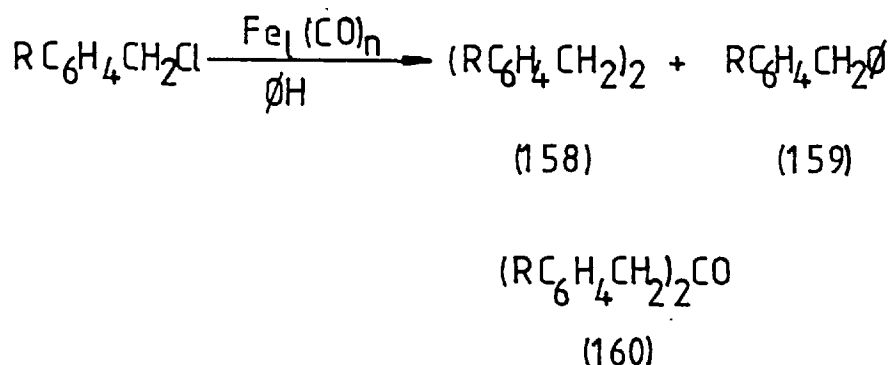
ketones by treatment with enneacarbonyl diiron at reflux. It is thought that reaction proceeds via oxidative addition to tetracarbonyliron, but this is only speculation. The reaction however is not compatible with the presence of halides and nitro groups. Reductive dimerisation of



α , β -unsaturated ketones¹⁰⁰ has been accomplished by sequential use of lithium aluminium hydride, dodecacarbonyl triiron and hydrochloric acid. The reaction has been postulated to proceed by allylic radicals, a mixture of isomers



being produced (head - head, tail - tail, head - tail) for unsymmetrically substituted α , β -unsaturated ketones. Benzylic halides will also undergo dimerisation¹⁰¹ upon treatment with carbonyliron reagents. The phenylated product (157) predominates if dodecacarbonyl triiron in



benzene is used as the reagent system, while the dimer (156) is formed selectively with dodecacarbonyl triiron and pyridine N - oxide. 1,5 - Hexadienes can be formed selectively from allylic chlorides and the $\text{Fe}_3(\text{CO})_{12}$ /Pyridine N-oxide system in moderate yield. α Bromoketones are selectively reduced by reaction with excess pentacarbonyliron in toluene at reflux,¹⁰² reaction taking place via radical intermediates, no 1,4-diketones or epoxy ketones were obtained upon aqueous work up as has previously been reported.

(c) Miscellaneous examples of Carbonyliron Reagents

An important development in carbonyliron chemistry is the development of polymer supported reagents.¹⁰³ A polymer bound (styrene-divinyl benzene polymer with phosphine residues) mononuclear carbonyliron species has been shown to be as good a catalyst for the photochemical polymerisation of olefins as pentacarbonyliron. These reagents are much easier to handle than the corresponding pentacarbonyliron, and all iron containing residues left at the end

of reaction are conveniently bonded to the resin. Therefore there is a wide synthetic application for such polymer supported species.

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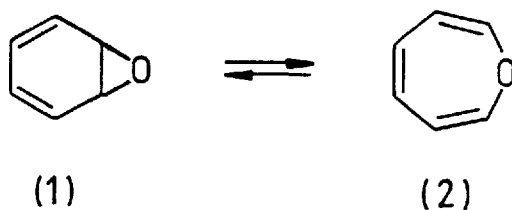
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CHAPTER 1

STUDIES DIRECTED TOWARDS THE SYNTHESIS OF EXO - 5,6-EPOXY CYCLOHEXA-1,3-DIENE TRICARBONYLIRON

Introduction

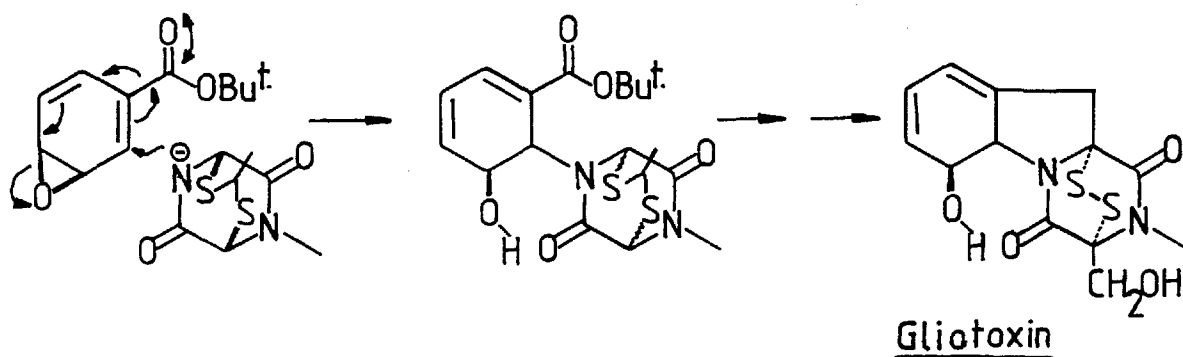
Arene oxides¹ are a subclass of aromatic hydrocarbon in which the continuous ρ - π orbital overlap is interrupted by the formation of an epoxide ring between two adjacent carbon atoms.



The parent member of the class is benzene oxide (1), which exists in tautomeric equilibrium with oxepin (2). Benzene oxide - oxepin was first prepared by Vogel and co-workers in 1964². The position of equilibrium was found to be dependent upon many factors including solvent (polar solvents favouring the more polar arene oxide tautomer) and ring substitution patterns.

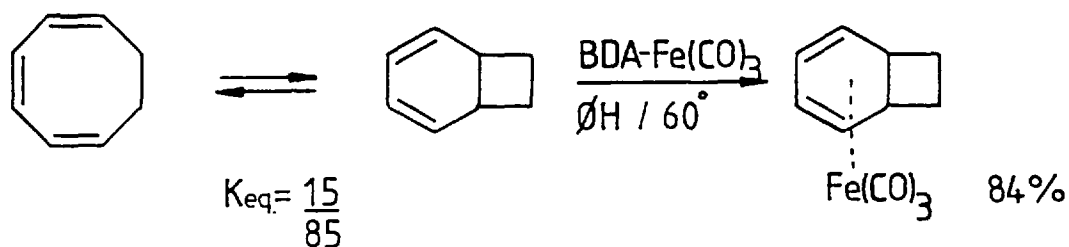
Much interest has been shown in these systems both in terms of theoretical chemistry and their biochemistry. The metabolism of aromatic hydrocarbons by biological systems

proceeds via arene oxide intermediates, which are facile in vitro alkylating agents, and therefore powerful carcinogens. Interest in these systems also arises from their use in the synthesis of natural products. In an elegant synthesis of the naturally occurring antibiotic Gliotoxin,³ Kishi and co-workers utilised a substituted benzene oxide in the construction of the two delicate ring systems of the natural product.

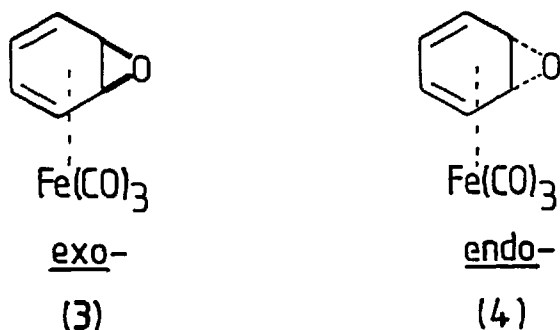


Scheme 1. Synthesis of Gliotoxin

The tricarbonyliron moiety has proven to be a versatile protecting group for labile 1,3-diene units, and as such has been utilised in the 'trapping out' of thermodynamically unstable tautomers (pages 23 - 28).



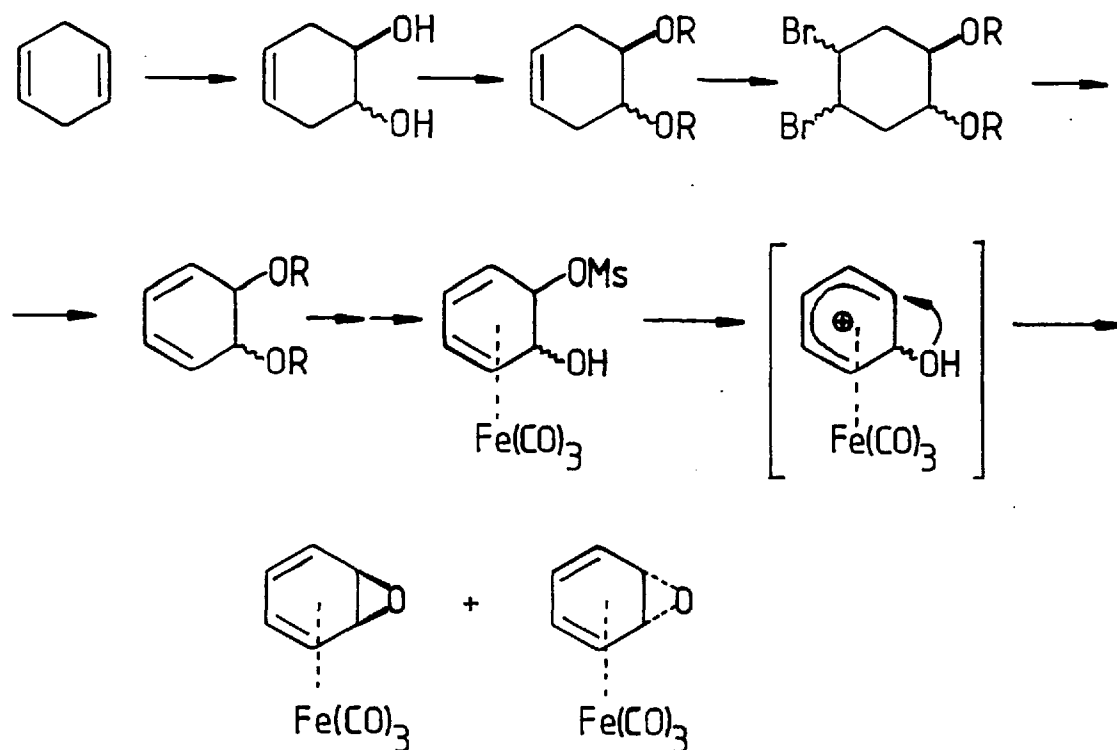
We proposed to use this methodology to accomplish the synthesis of the tricarbonyliron stabilised benzene oxide complexes (3) and (4).



Low temperature oxidation of such species would be expected to afford benzene oxide free of its tautomer oxepin, thus allowing complete characterisation of this labile species, which has never been observed in the pure state.

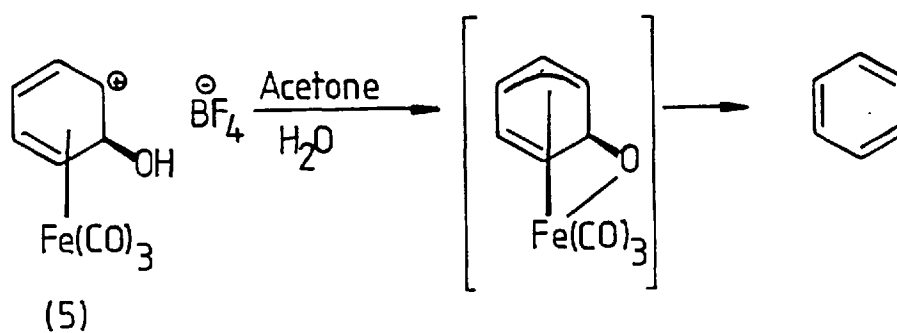
In view of the marked selectivity of reaction of the tricarbonyliron transfer reagent *p*-methoxy benzyldiene acetone tricarbonyliron towards planar 1,3-cyclohexadiene moieties vs non-planar triene tautomers (pages 23 - 28). initial efforts⁴ were directed at trapping out benzene oxide from its tautomeric equilibrium. This approach however did not produce any of the desired tricarbonyliron complexes (3) and (4). Reaction conditions required for the transfer of the tricarbonyliron moiety proving too much for the thermally labile benzene oxide (which readily undergoes isomerisation to phenol via a 1,2-hydrogen shift, the N.I.H. shift). Thus it was proposed to synthesise the desired

tricarbonyliron benzene oxide complexes (3) and (4) by the route shown below (Scheme 2).



Scheme 2. Synthesis of Tricarbonyliron Benzene Oxide

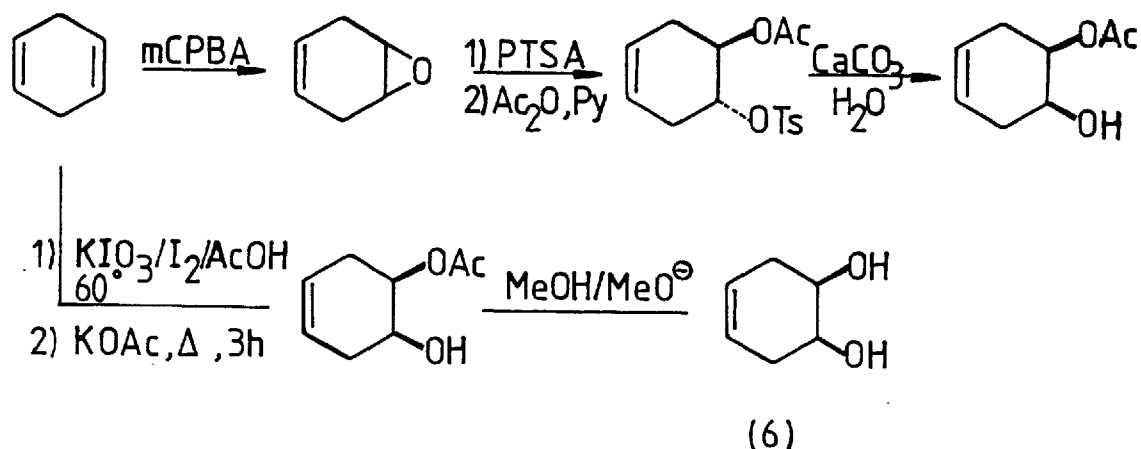
The 5-endo hydroxy cyclohexadienyl tricarbonyliron



cation (5) has previously been prepared,⁵ and was found to undergo rapid decomposition in solution, in the presence of traces of water. This suggested that attempts to synthesise the endo-epoxide (4) could produce a similar result. Thus the synthetic strategy employed in this work was directed towards the synthesis of the exo-epoxide (3) via cis-diol intermediates.

(a) Substituted Cyclohexa - 1,3-dienes via Dehydrohalogenation of Halo Compounds

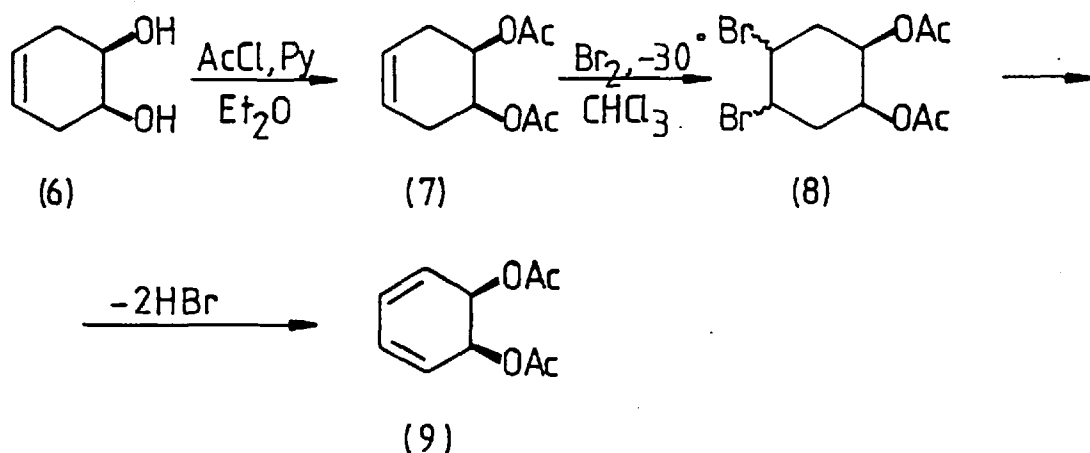
Cyclohexene 4,5-cis diol (6), the key intermediate in the synthesis of the desired exo-5,6-epoxy cyclohexa-1,3-diene tricarbonyliron complex (3) was prepared from cyclohexa-1,4-diene according to literature procedures.^{6, 7} The modified Woodward-Prevost procedure⁷, was found to be the most convenient method for the large scale preparation of the diol (6),



Scheme 3: Preparation of Cyclohexene 4,5-cis diol.

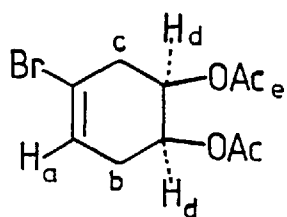
Acetylation of the diol (6) to afford the cis - diacetate (7) was accomplished by the use of acetyl chloride in the presence of pyridine at low temperature. Alternatively the diacetate (7) was prepared by reaction of

cyclohexene 4,5-cis diol monoacetate with acetic anhydride in pyridine.



Treatment of cyclohexene 4,5-cis diol diacetate (7) with bromine resulted in a quantitative yield of the dibromide (8). Therefore dehydrobromination of the dibromide (8) would be expected to furnish the cyclohexa-1,3-diene 5,6-cis diol diacetate (9). The dehydrobromination of 1,2 - dibromides can be realised with reasonable success through the use of dry lithium chloride and carbonate salts in anhydrous hexamethylphosphoric triamide solution, but this procedure often requires long reaction times and elevated temperatures. Paquette and co-workers have developed a highly efficient and less drastic procedure,⁸ again capitalising on the polar cationophilic solvent hexamethyl phosphoric triamide and the buffering capability of lithium carbonate in combination with the hard protiophilic base lithium fluoride (in the presence of powdered soft glass to facilitate carbon dioxide evolution). However attempted

dehydrobromination of the dibromide (8) under these conditions led to variable results. The reactions were carried out under a dry inert atmosphere and the extent of reaction monitored by UV spectroscopy (λ_{max} . 257 μm). The results of small scale experiments indicated that diene was being formed slowly throughout the reaction, but upon work up, yields as estimated by UV spectroscopic analysis were in the order of 10-20%. Increasing the reaction temperature from 90° to 100°C, decreased the yields of diene. When the reaction was performed on a large scale a single product was isolated in good yields (41%), by short path distillation of the crude reaction product. This was identified from its n.m.r. and mass spectra as the vinyl bromide (10). The mass spectrum possessed the characteristic isotopic substitution pattern due to a monobrominated compound, (peaks at $[M]^+$ and $[M + 2]^+$ in a 1:1 intensity ratio). ^1H n.m.r. spectroscopy shows characteristic



(10)

<u>n.m.r data</u>	<u>δ</u>
H_a	5.77 - 6.0 m
H_b, H_c	2.17 - 2.83 m
H_d	5.0 - 5.22 m
H_e	2.0 s
 m/e.	 278 $[M+2]^+$ 276 $[M]^+$ 218 $[M+2-\text{HOAc}]^+$ 216 $[M-\text{HOAc}]^+$

resonances at δ 2.0 (6H,s) and 5.77 - 6.0 (1H,m) due to the acetyl methyl groups and the single vinylic proton respectively.

Interestingly the dibromide (8) upon reaction with lithium chloride, and lithium carbonate in anhydrous hexamethyl phosphoric triamide produced encouraging results. The small scale experiments (fig. 1) indicated

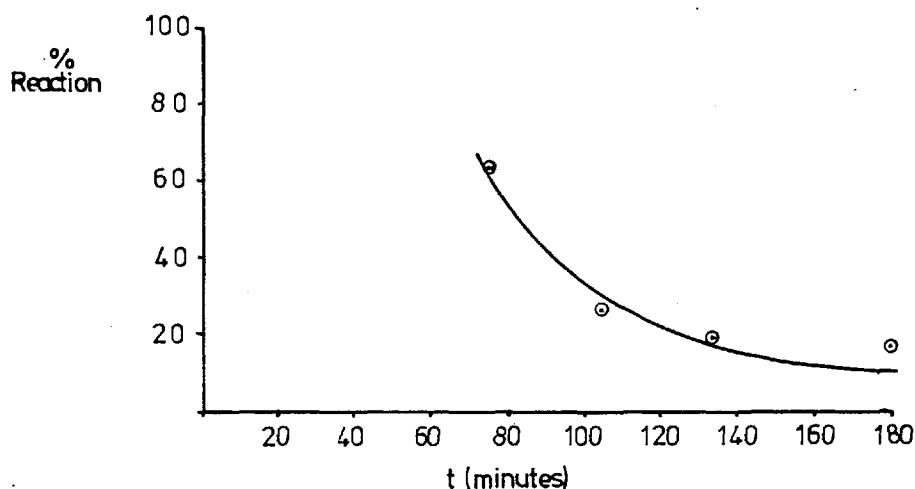
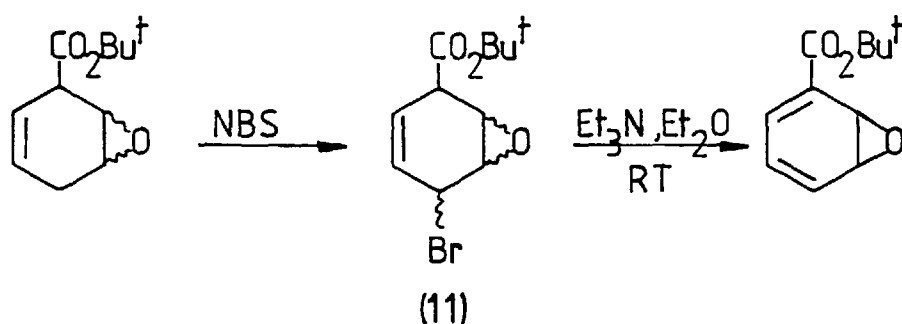


Figure 1.

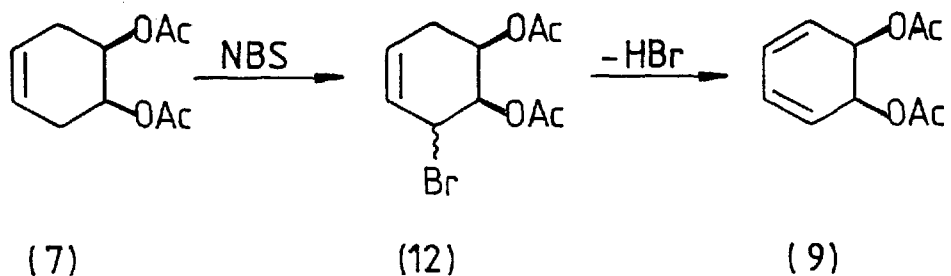
that the desired diene was being formed at a fast rate and in high yield which was in marked contrast to the result obtained using lithium fluoride as base. However, large scale reactions carried out under the same set of conditions resulted only in the isolation of aromatic materials and varying amounts of starting material.

Berchtold has accomplished the synthesis of 3-carbo-tert-butoxy benzene oxide⁹ via the facile base

induced elimination of the allylic bromide (11). Therefore it was proposed to examine the dehydrobromination of

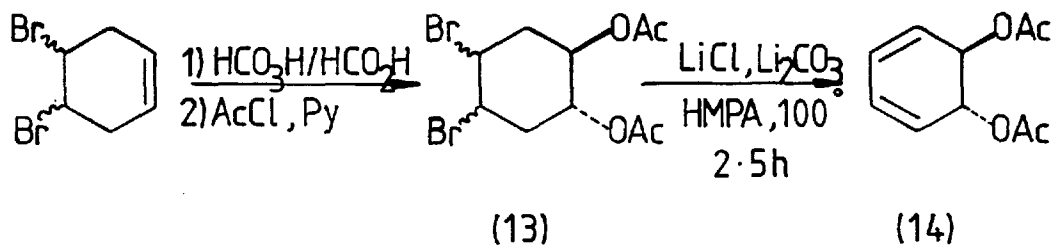


the allylic acetate (12), prepared by the action of N - bromosuccimide (NBS) on the diacetate (7).



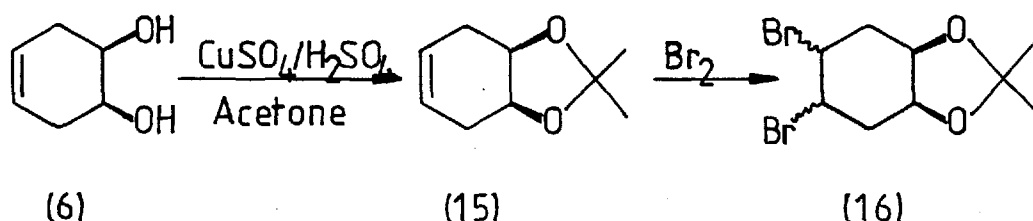
Treatment of the allylic bromide (12) with triethylamine in diethyl ether at reflux for 24h led only to the recovery of allylic bromide (12), and none of the desired diene (9). Such a result was not surprising since the high reactivity of the allylic bromide (11) towards elimination resulted from activation by the ester functionality. Reaction of the 3-bromo cyclohexane 4,5-cis diol diacetate (12) with lithium fluoride under standard conditions gave similar results to those observed for 1,2-dibromocyclohexane 4,5-cis diol diacetate (8). However

^1H n.m.r. spectroscopy of the crude reaction product exhibited resonances at $\delta 6.38 - 7.63$, indicative of aromatic material, which formed a substantial proportion of the crude product (as determined by integration of the ^1H n.m.r. spectrum). The results of these dehydrobromination reactions indicate that the lithium chloride based reagent system is superior to the lithium fluoride procedure in the case of dibromide (8). The large scale reactions utilising the lithium chloride procedure, however, have not led to the isolation of the desired cis-diacetoxo diene (9). These results contrast the previously reported synthesis of cyclohexa-1,3-diene 5,6-trans diol diacetate (14) via the same procedure.¹⁰



The success of these dehydrobromination procedures is obviously highly dependent upon the nature of the substrate. The difference in reactivity between the cis- and trans-dibromides (8) and (13) under identical reaction conditions is marked, and indicates that changes in the conformation of the cyclohexane ring can have a profound effect upon the course of reaction. It is conceivable that the conformation of the cyclohexane ring in the case of

the cis-diacetoxy dibromide (9) is such, that elimination of acetic acid becomes a competitive pathway to dehydrobromination; the high proportion of aromatic materials in the crude reaction product tends to support this idea. It was proposed that replacement of the acetyl functions by an isopropylidene moiety would reduce the possibility of a competitive elimination pathway, and would also be expected to have some effect upon the conformation of the molecule.



Reaction of cyclohexane 4,5-cis diol (7) with anhydrous acetone in the presence of anhydrous copper sulphate¹¹ afforded the volatile isopropylidene derivative (15) in quantitative yield. Bromination proceeded smoothly in the presence of sodium carbonate as buffer to give the dibromide (16) in excellent yield.

The results obtained by reaction of the dibromide (16) with various bases are summarised in Table 1. Sodium methoxide did produce some diene (as estimated by UV spectroscopic analysis (λ_{max} 274nm) but subsequent work up afforded only starting material; the yield of recovered starting material being consistent with the estimated extent

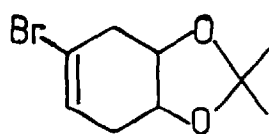
BASE	CONDITIONS	RESULT
DBU	Reflux in 60-80 Petroleum	Recovery of Dibromide ≈ 5% Reaction ^a +
TMG 1,1 3,3-Tetramethyl Guanadine	Reflux in 60-80 Petroleum	Recovery of Dibromide ≈ 5% Reaction ^a +
Sodium Isopropoxide	110°C, Triglyne ¹²	Complete reaction of Dibromide No characterisable products
Sodium Methoxide	Et ₂ O, Reflux	≈ 20% Reaction ^a 77% Recovery of Dibromide
Potassium t Butoxide	0°C, Et ₂ O	Slow build up of Diene < 10% ^a Poor material recovery - No Dibromide present in crude reaction product
Potassium t Butoxide	-15° → 0°C ¹³ Et ₂ O	Isolation of Vinyl Bromide and Dibromide in 2:1 molar ratio, quantitative yield of Vinyl Bromide based upon unreacted starting material

Notes: a. estimated by UV spectroscopic analysis of the crude reaction mixture.

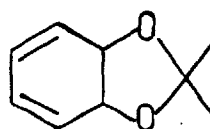
TABLE 1: REACTION OF 1,2-DIBROMO CYCLOHEXAN 4,5-CIS DIOL
ISOPROPYLIDENE WITH VARIOUS BASES

of reaction. Thus material must have been lost upon aqueous work up, and therefore it is most likely that aromatisation to phenol had occurred. Treatment of the dibromide (16) with

potassium t-butoxide in ether at 0°C produced a similar result, the poor mass balance being due to loss of material on aqueous work up. However cooling reaction down to -15°C resulted in the isolation of the vinyl bromide (17) in 66% yield (quantitative yield based upon unreacted starting material).



(17)



(18)

Treatment of the dibromide (16) with lithium fluoride or lithium chloride in hexamethyl phosphoric triamide on a small scale gave excellent results (Fig. 2).

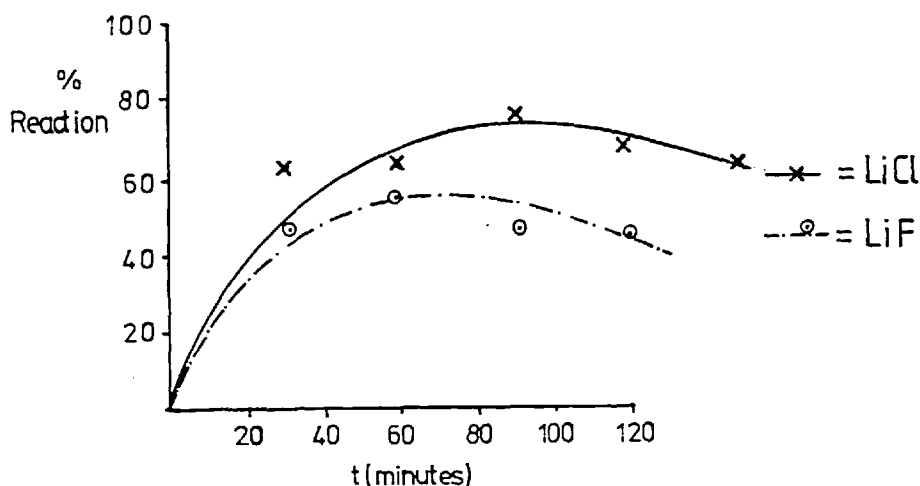
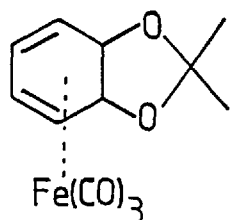


Figure 2.

Again the superiority of the lithium chloride based reagent system was apparent, but not so marked as was previously encountered for the diacetoxo dibromide (8).

Large scale experiments revealed that yields were widely variable, and that a large proportion of the diene was being lost on work up. This loss of diene was attributed to its high volatility (cf: cyclohexene 4,5-cis diol isopropylidene (15) is volatile, and requires isolation by distillation at atmospheric pressure), but even when crude reaction solutions were subjected to distillation at atmospheric pressure, pure diene was never isolated in a reasonable yield. That the diene (18) was formed under the reaction conditions was illustrated by combining a degassed solution of a crude reaction product with pentacarbonyliron, and irradiating the mixture with a UV light source. Plc of the resulting solution led to isolation of a tricarbonyliron diene complex in 50% yield (based upon estimated diene



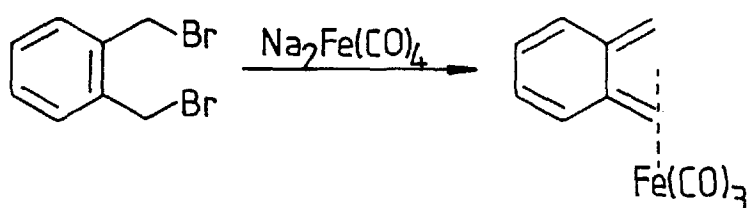
(19)

m/e.	292 [M] ⁺
	264 [M-CO] ⁺
	236 [M-2CO] ⁺
	208 [M-3CO] ⁺

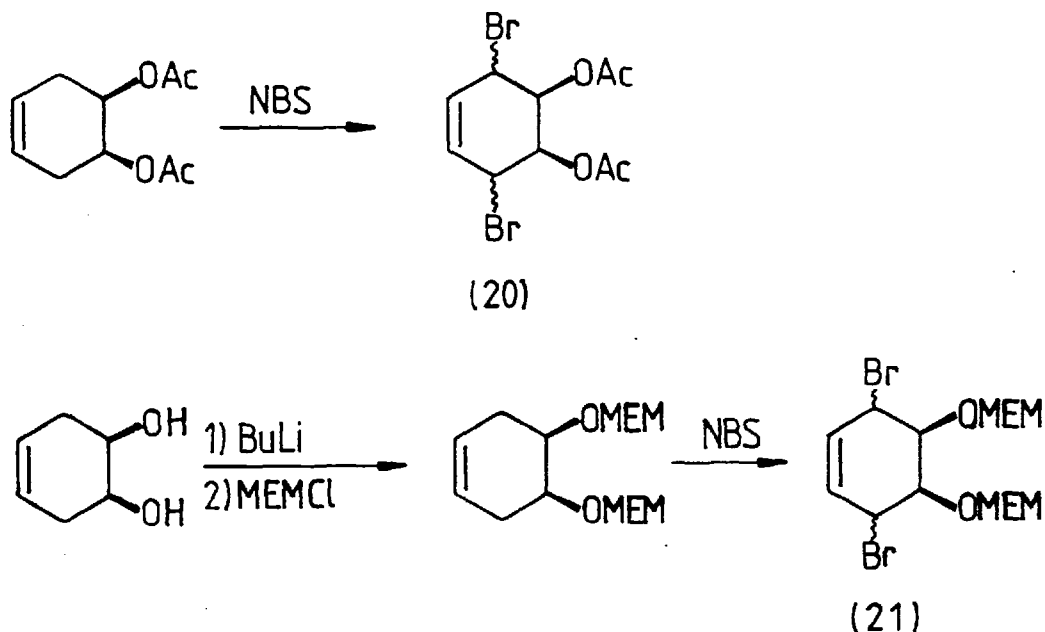
content of crude product of dehydrobromination). The mass spectrum of this compound was a perfect example of the fragmentation pattern due to a tricarbonyliron diene complex; exhibiting the sequential loss of carbon monoxide from the molecular ion. Unfortunately there was insufficient material to be able to obtain an ^1H n.m.r. spectrum.

In view of the variability of yields and difficulties in isolation, the above dehydrobromination procedures were not considered to be viable routes to the required diene (18).

Several workers have investigated the reaction of σ -dibromo xylene with iron carbonyls,¹⁴ and it was found that treatment of σ -dibromo xylene with disodium tetracarbonylferrate afforded the σ -quino dimethane tricarbonyliron complex directly, in moderate yield. The overall process



can be considered as a reductive elimination of an allylic dibromide, accompanied by trapping of the reactive diene moiety. Therefore treatment of the allylic dibromides (20) and (22), with disodium tetracarbonyl ferrate might be expected to afford the corresponding tricarbonyliron diene complex directly.

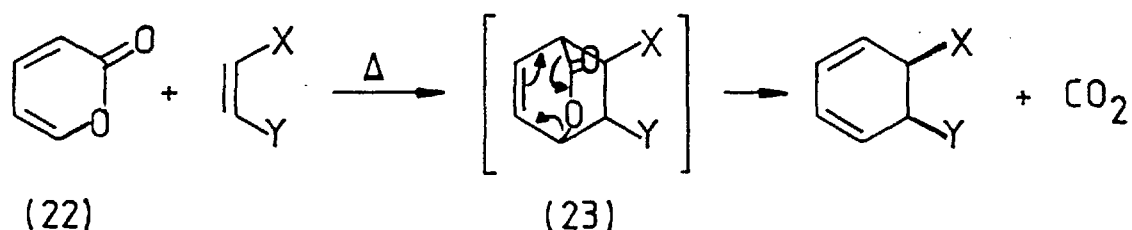


Treatment of cyclohexene 4,5-cis-diol isopropylidene (15) with N-bromosuccinimide (NBS) produced only uncharacterisable material; presumably traces of acid formed in the radical reaction caused decomposition of the acid sensitive (15). The reactions of dibromide (20) with disodium tetracarbonyl ferrate under a variety of conditions (ambient temperature to -15°C in THF) produced no isolable diene tricarbonyliron complex. The ^1H n.m.r. spectrum of the crude reaction product exhibited resonances at $\delta 6.67 - 7.33$, indicative of aromatic material. The results for the dibromide (21) were even worse, no characterisable material at all was obtained by reaction of the dibromide with disodium tetracarbonylferrate at low temperature in THF. These conditions appear far too drastic for the sensitive

allylic dibromides, and therefore it was considered that a milder reducing agent might accomplish the desired transformation. However, the dibromide (2)) upon reaction with zinc and a catalytic quantity of acid in refluxing THF afforded mainly aromatic materials, presumably the acetoxy functions were incompatible with the reaction conditions.

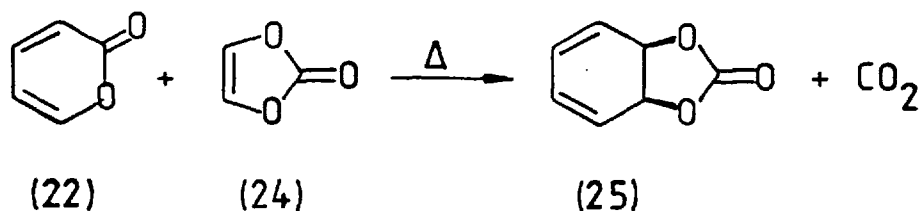
(b) The Diels-Alder reaction between Pyran-2-one and Vinylene Carbonate

Dehydrobromination and reductive elimination procedures applied to suitably substituted cyclohexane derivatives have been shown to be poor methods for the construction of derivatised cyclohexa-1,3-dienes. As an alternative to such procedures the modified Diels Alder reaction for the formation of substituted cyclohexa-1,3-dienes was investigated. Pyran-2-one (22) and its derivatives undergo the



Diels Alder reaction with suitable dienophiles to afford initially the $[4 + 2]$ cycloadduct (23), which under the

reaction conditions rapidly loses carbon dioxide to yield a substituted cyclohexa-1,3-diene.¹⁵ Thus we proposed that reaction of Pyran-2-one with the dienophile vinylene



carbonate,¹⁶ would be expected to furnish the diene (25) via loss of carbon dioxide from the initial Diels-Alder adduct. The reaction between pyran-2-one and vinylene carbonate was carried out under a variety of conditions, the results being summarised in Table 2. It can be seen from these results that the transformation is critically dependent upon reaction time and temperature. Reaction seems only to take place in evacuated sealed tubes, the analogous reactions at atmospheric pressure lead to recovery of starting materials. Reaction at 140°C in a sealed tube, for 4 h, led to partial recovery of pyran-2-one and isolation of a small quantity of UV active material. The ¹H n.m.r. spectrum of this compound exhibited resonances at δ 6.73 - 7.04 (m) and 7.09 - 7.32 (m), inconsistent with the diene (25) or phenol. It is obvious from these results that the reaction does not stop at the desired diene (25), further transformation occurring very fast under the reaction conditions to yield phenolic products.

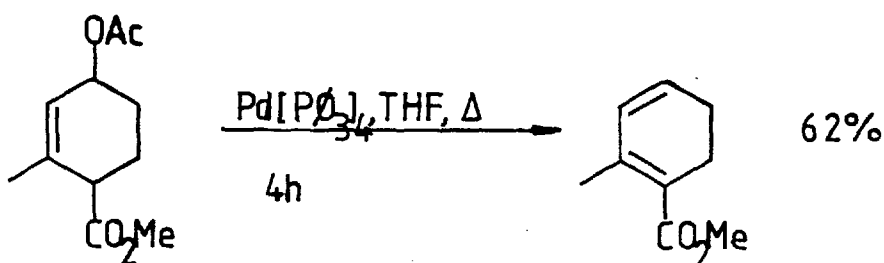
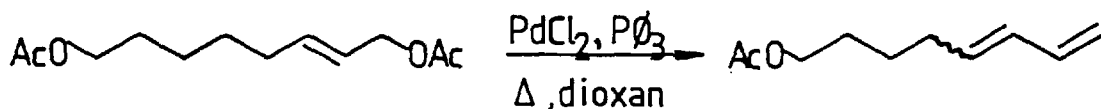
TEMPERATURE (°C)	TIME (h)	REACTION CONDITIONS	PRODUCTS
160	24	Vacuum sealed tube	Phenol (100%)
80	12	"	No reaction
100	12	"	"
120	12	"	"
140	12	"	Phenol (100%)
127	12	1 atm Argon	No reaction
140	6.5	1 atm Argon/triglyme	"
150	3	Triglyme/1 atm Ar	"
140	4	Vacuum sealed tube	+ve reaction
140	5	"	Phenol (32%)
140	4	"	+ve reaction

TABLE 2: DIELS-ALDER REACTION BETWEEN PYRAN-2-ONE AND VINYLENE CARBONATE

(c) Palladium Catalysed Elimination of Allylic Acetates

During the course of this work it has been reported that allylic acetates can be converted to 1,3-dienes via their π -allyl palladium complexes.^{17, 18} The reaction has been shown to be catalytic with respect to the palladium species, and represents a very mild procedure for the preparation of 1,3-dienes. Therefore we proposed to investigate the applicability of these procedures towards the

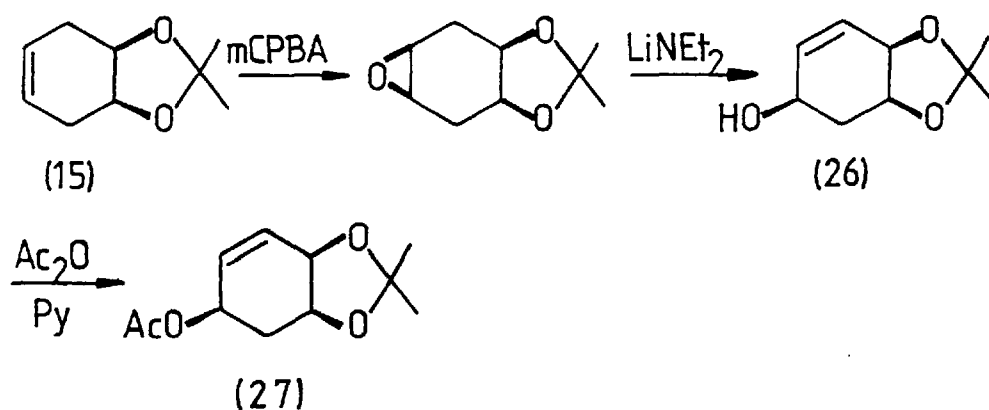
preparation of the diene (18). The allylic alcohol (26)



Examples of allylic acetate transformation

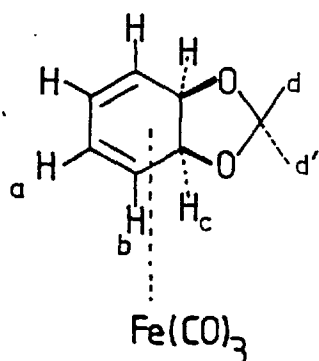
was prepared from the cyclohexene 4,5-cis diol isopropylidene (15) by base induced rearrangement of the syn-epoxide. Acetylation was accomplished by reaction of the alcohol with acetic anhydride and pyridine in the presence of a catalytic quantity of N-N-dimethyl-4-amino-pyridine (DMAP).

Attempted reaction of the allylic acetate (27) with a catalytic quantity of palladium (II) chloride in the presence of triphenylphosphine,¹⁷ resulted in total disappearance of starting material, but no diene was



isolated. The tetrakis triphenylphosphine palladium (0) complex has been reported¹⁸ to function as a superior catalyst for this transformation; and upon reaction with the allylic acetate (27), in a sealed bomb, the desired diene was at last obtained ! Removal of the palladium species afforded a solution of crude diene, which was immediately combined with enneacarbonyl diiron and a catalytic quantity of *p*-methoxy benzylidene acetone in degassed diethyl ether. Thermolysis, and plc of the crude reaction mixture afforded the desired tricarbonyliron diene complex (19) in 14.5% overall yield from the allylic acetate. This represents a significant improvement over all other procedures and illustrates the utility of the palladium catalysed elimination of allylic acetates in the synthesis of

highly labile dienes. The ^1H n.m.r. spectrum was characteristic of a tricarbonyliron diene complex; the outer 1,4



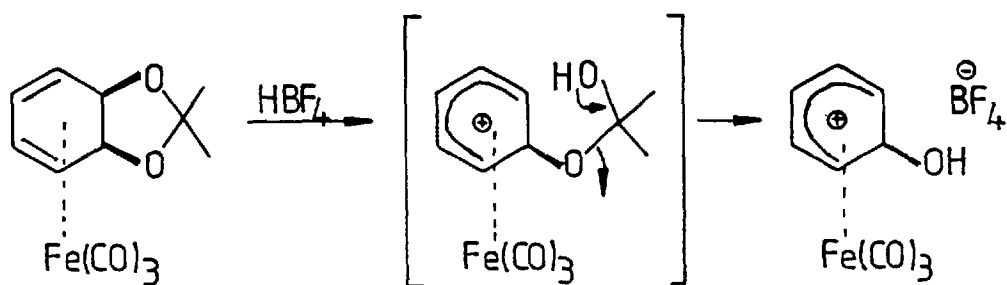
(19)

n.m.r. data δ

H_a	5.55 dd J 7.8, 2.6 Hz
H_b	2.88 ddd J 7.6, 2.6, 2.5 Hz
H_c	4.54 t J 2.5 Hz
H_d	1.33 s
$\text{H}_{d'}$	1.16 s

protons of the diene system (H_b) resonating approximately 2.5 ppm to higher field than the inner 2,3-protons (H_a). That protons on complexed ligands almost invariably resonate at higher field than in the free ligand is probably due to the diamagnetic anisotropy of iron rather than to any major net flow of electron density onto the ligand. The amount proton ^{resonances} shift upon complexation, however, is characteristic of the metal-ligand bonding system and is well documented.¹⁹

In principle treatment of the tricarbonyliron



(19)

(28)

diene complex (19) with fluoroboric acid should furnish the 5-exo hydroxy tricarbonyliron η^5 dienyl fluoroborate salt (28), in accordance with literature precedents.²⁰ We proposed that the complex (28) upon treatment with a suitable base, should undergo ring closure to form the desired exo-epoxide (3). Preliminary experiments have been carried out along these lines, but use of technical grade fluoroboric acid ($\approx 40\%$) under a variety of conditions, produced only decomposition of starting material. Traces of water present in the acid could be responsible for this unfortunate result.

Work is currently in progress relating to reactions of the tricarbonyliron complex (19) with pure fluoroboric acid under carefully controlled conditions, and it is hoped that these experiments will result in the synthesis of exo - 5,6-epoxy cyclohexa-1,3-diene tricarbonyliron (3).

CHAPTER 2

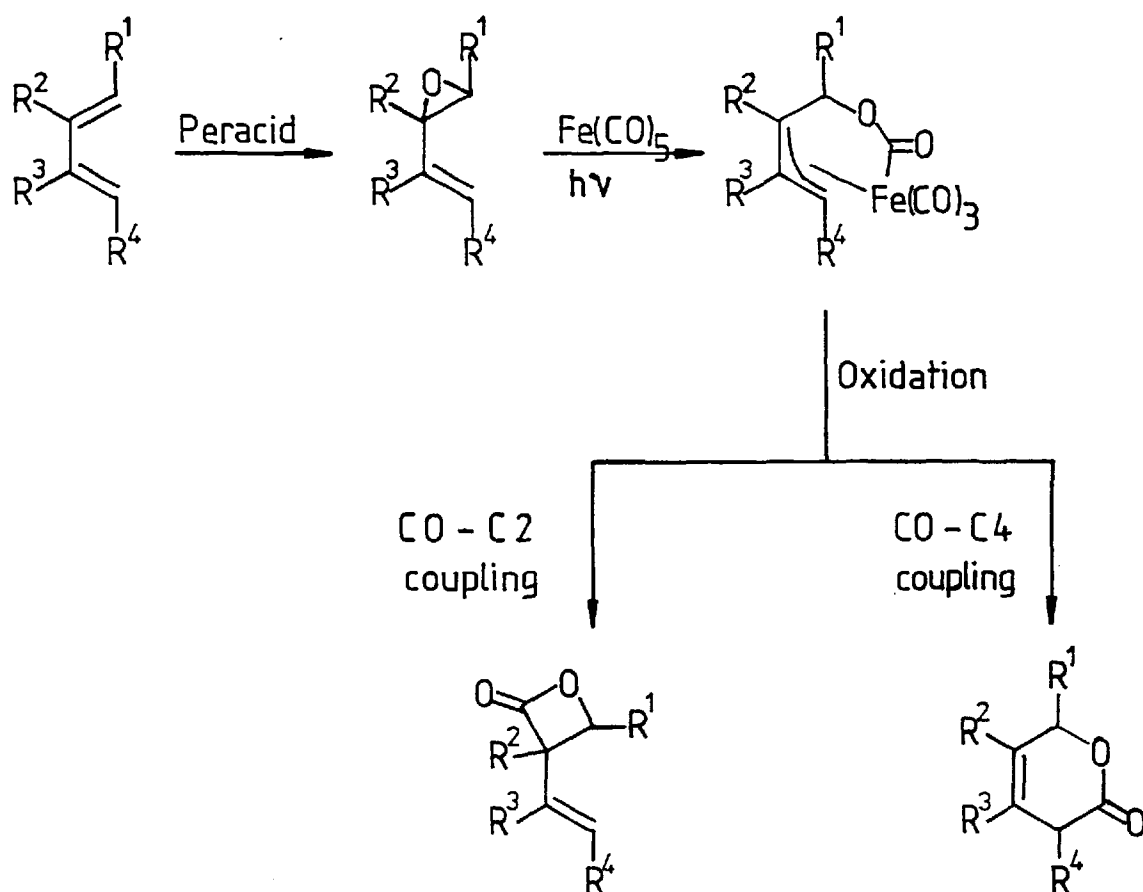
FORMATION OF LACTONES FROM TRICARBONYLIRON

LACTONE COMPLEXES

Introduction

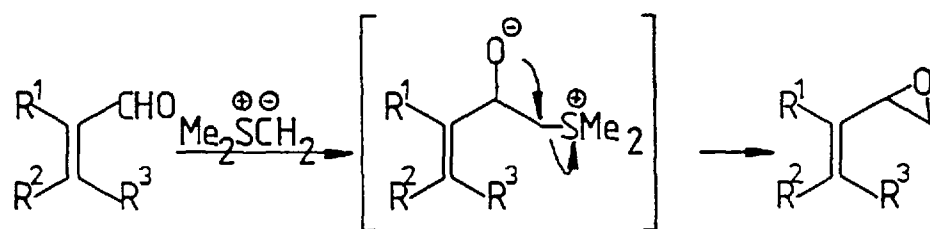
The preparation of σ , π -allyl tricarbonyliron lactone complexes from dienes via their mono regiospecific epoxides is known,^{21, 22} and a preliminary investigation into their chemistry has been carried out in these laboratories. This work has shown that upon oxidation, tricarbonyliron lactone complexes readily extrude the tricarbonyliron moiety to afford β and δ lactones.^{23, 24} In principle the overall transformation could be viewed as a synthetic equivalent for the addition of carbon dioxide to a diene. This is difficult to achieve by conventional methods, as they often require high temperatures and pressures and are not necessarily regiospecific.²⁵

The work presented in this section deals with efforts directed towards increasing the scope of this reaction in the synthesis of β and δ lactones. It is relatively easy to convert a 1,3-diene into its regiospecific mono epoxide by treatment with one equivalent of an organic peracid (reaction occurring at the more electron rich double bond). However a useful reversal of this normal



SCHEME 1

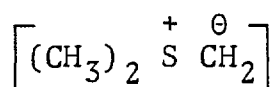
regioselectivity of epoxidation of a 1,3-diene can be obtained by reaction of dimethyl sulphonium methyl ylid upon



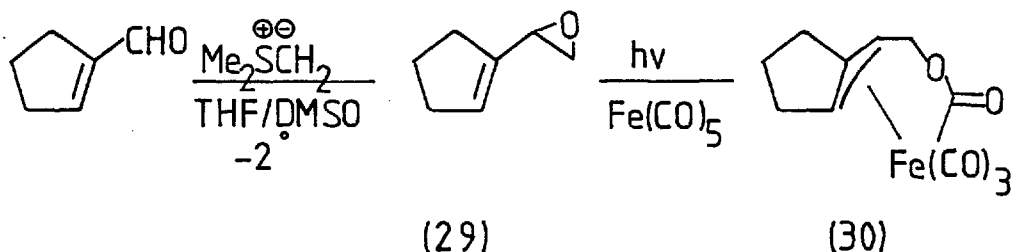
α,β -unsaturated aldehydes,²⁶ to afford terminal vinyl epoxides. The reaction of this type of vinyl epoxide with pentacarbonyliron, and subsequent oxidation of the tricarbonyliron lactone complex has not previously been investigated.

(a) Preparation of Tricarbonyliron Lactone Complexes

Formyl cyclopentene²⁷ upon treatment with dimethyl ylid

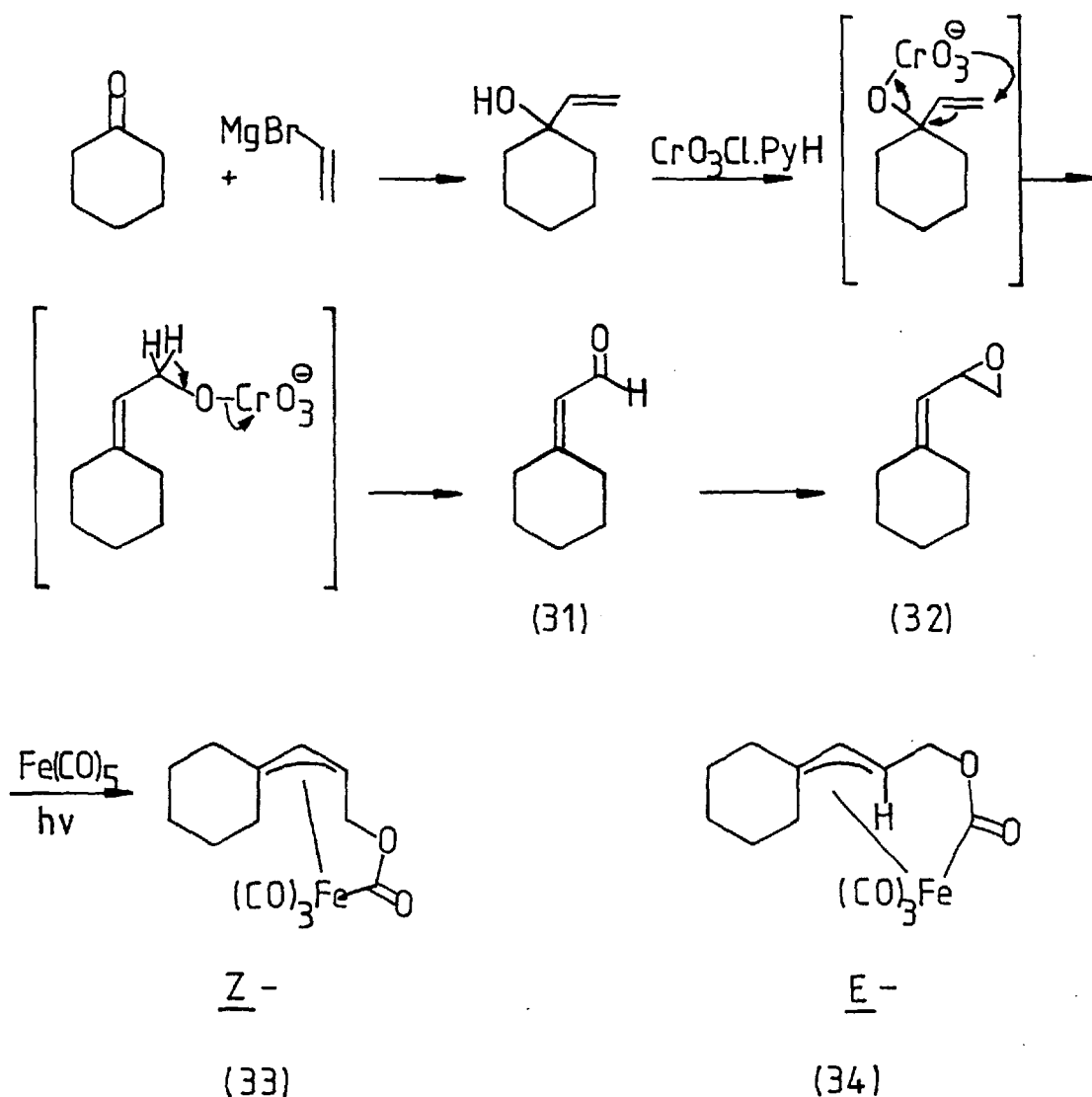


in THF/DMSO at -2°C afforded, after careful distillation of the crude reaction product, the vinyl epoxide (29).



The epoxide proved to be both acid and base sensitive, but could be stored for months without appreciable decomposition at -30°C . The epoxide was readily characterised by examination of its ^1H n.m.r. spectrum which exhibited resonances at δ 3.53 (t, J 3.5 Hz) due to the methine proton, and δ 2.83 (m) corresponding to the methylene protons on the epoxide ring.

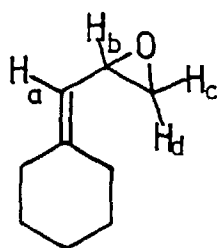
Treatment of cyclohexanone with vinylmagnesium bromide, and oxidative rearrangement²⁸ of the thus derived carbinol afforded the enal (31) in high yield. Upon



Scheme 2: Synthesis of Tricarbonyl (1,1',2'-n-1-propylidene cyclohexane-1-yl)-3'-oxycarbonyl iron

reaction with dimethylsulphonium methyl ylid in THF/DMSO at -2°C , the enal (31) gave the vinyl epoxide (32) in 83% yield. Again the epoxide was readily characterised by

examination of its ^1H n.m.r. spectrum, the methine proton^{resonance} appearing as a ddd at δ 3.32.



(31)

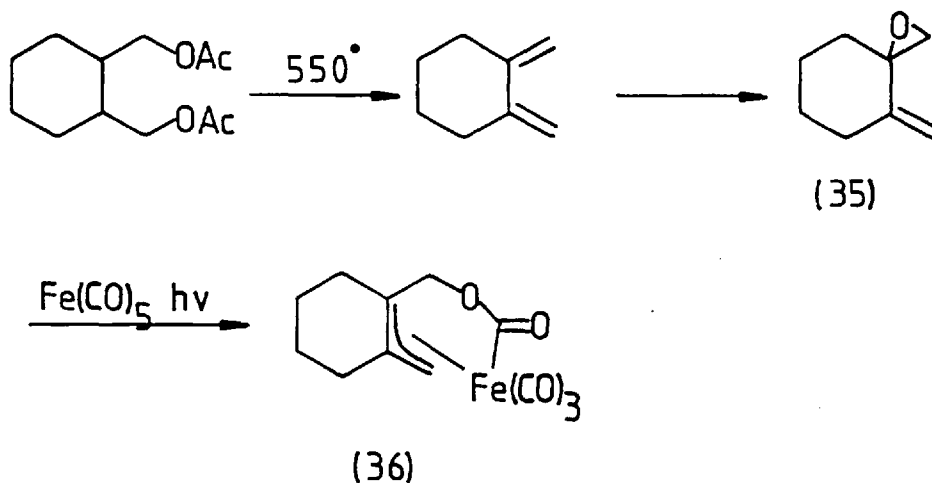
<u>nmr data</u>	<u>δ</u>
H_a	4.77 d J 8 Hz
H_b	3.32 ddd J 8, 4, 3 Hz
H_c	2.42 dd J 5, 4 Hz
H_d	2.77 dd J 5, 3 Hz

Irradiation of the vinyl epoxide (29) in the presence of pentacarbonyliron furnished the single tricarbonyliron lactone complex (30) in 72% yield. However irradiation of the vinyl epoxide (31) under the same conditions produced an oil, the IR spectrum of which possessed an absorption at ν_{max} 1670 cm^{-1} , characteristic of a tricarbonyliron lactone complex. Repeated attempts at crystallisation finally produced the tricarbonyliron lactone complex (33) in 49% yield. The geometry of this complex was assigned on the basis of its ^1H n.m.r. spectrum from a comparison with other complexes reported in the literature²⁹ (a detailed analysis of the ^1H n.m.r. spectrum will be given in a later section). The crude product from the photolysis reaction was extremely labile, and decomposed rapidly in solution. It was possible to obtain crystalline material from one recrystallisation of the crude reaction

product, but this decomposed rapidly at room temperature; repeated crystallisation producing the tricarbonyliron complex (33), which appeared to be of greater stability. The nature of the material obtained from one recrystallisation was investigated by high field n.m.r. spectroscopy (250MHz). It was shown to be a mixture of two isomeric tricarbonyliron lactone complexes (33) and (34), differing only in the geometry at the terminus of the π -allyl system. The isomeric complexes (33) and (34) were present in the ratio 4:1 respectively. The assignment of geometry was based upon similar arguments to that of the complex (33) and will be discussed in detail in a later section. It has not been possible to isolate the complex (34), and therefore it seems that this compound is inherently unstable, in contrast to its isomeric complex (33). All further reactions were carried out on the pure complex (33).

Pyrolysis of cyclohexane bis methylene diol diacetate at 550°C afforded bis methylene cyclohexane in 43% yield.³⁰ Epoxidation was effected by peracetic acid in the presence of sodium carbonate as buffer, and irradiation of the epoxide (35) in the presence of pentacarbonyliron afforded the tricarbonyliron lactone complex (36) in moderate yield. (See p. 31)

That the tricarbonyliron complexes could be prepared from the vinyl epoxides by the thermolytic decomposition of enneacarbonyl diiron has been demonstrated, but the yields were generally lower and the reactions much more



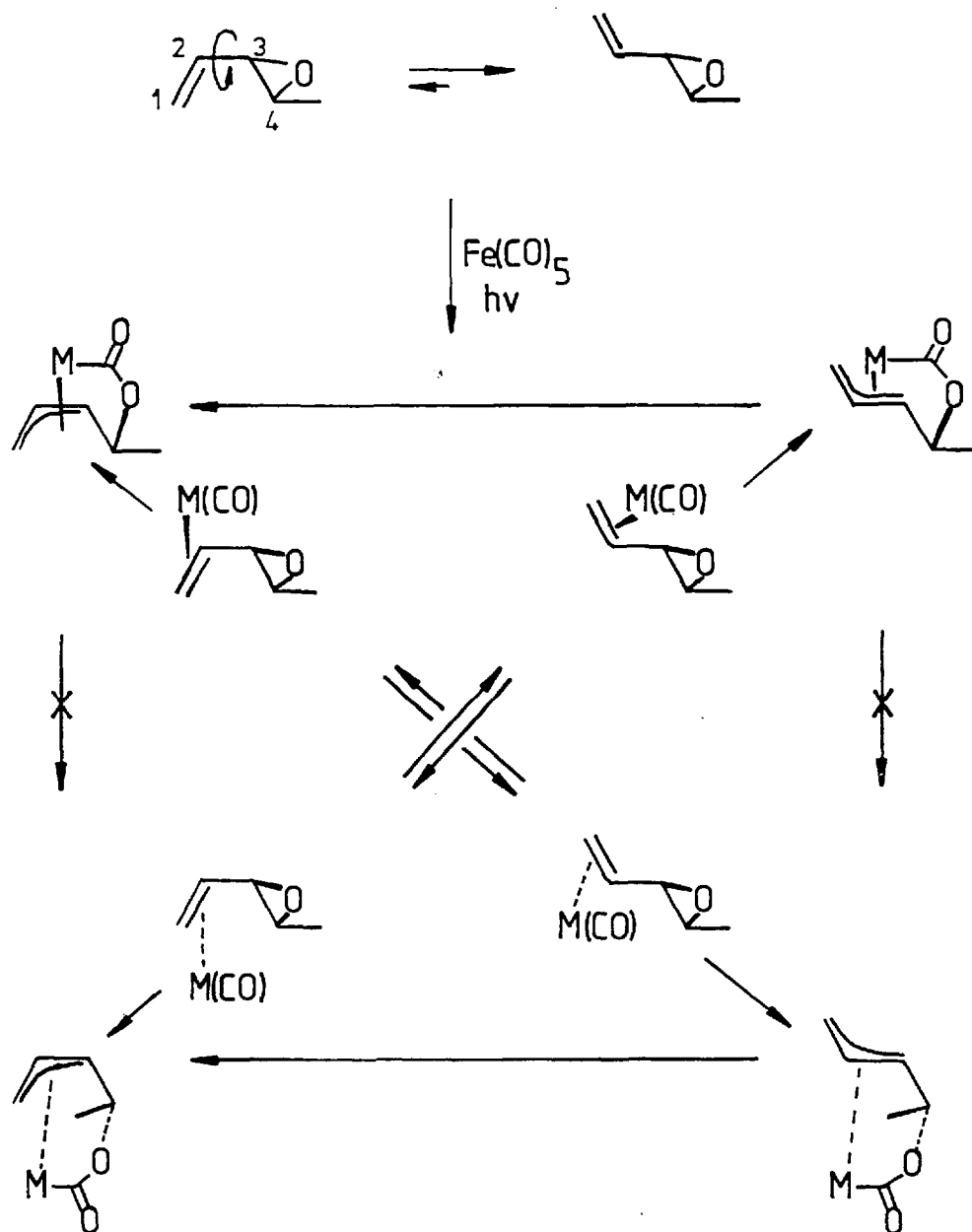
difficult to work up. The photolytic route was found to be superior in most respects.

In order that optimum yields of the tricarbonyliron lactone complexes were obtained it was found that irradiation with a restricted band width of UV radiation was desirable. This was accomplished either by use of an internal well photolytic reactor, in which the coolant for the UV source was replaced by an aqueous solution of sodium bromide (spectral transmission 310nm $\rightarrow$)³¹ or by use of an external UV source in conjunction with Chance OX1 glass filter elements (spectral transmission 280nm $\rightarrow$ 400nm). The use of the internal well photolytic reactor was found to be most convenient in practice; reaction times were in the order of 10 $\rightarrow$ 15 minutes. To avoid decomposition of the tricarbonyliron lactone complex once formed, it was necessary to cool the reaction solution such that the temperature did not rise above 30°C. Reaction was conveniently

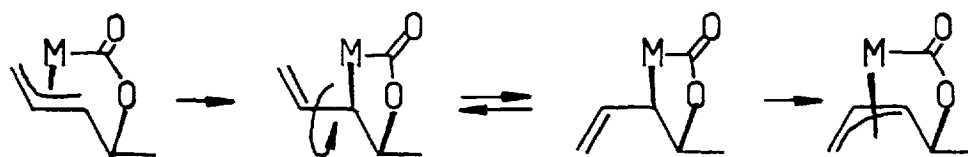
monitored by IR spectroscopy, and upon completion removal of solvent and excess pentacarbonyliron was best accomplished by freeze drying. Recrystallisation of the residues from diethyl ether/petroleum ether afforded the tricarbonyliron lactone complexes as thermally labile yellow-white crystalline solids, which were ^{stable} indefinitely at -30°C .

(b) Mechanism of Formation of Tricarbonyliron Lactone Complexes

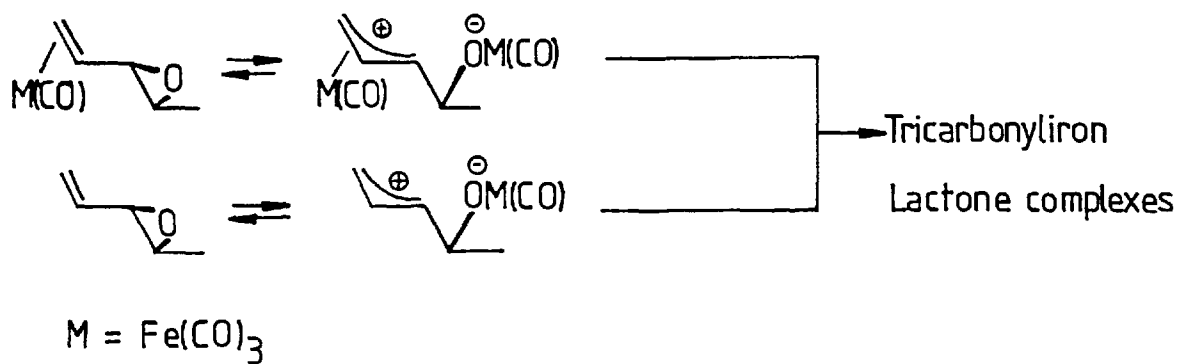
The mechanism of formation of tricarbonyliron lactone complexes from vinyl epoxides has been investigated by Aumann and co-workers.²⁹ The study, although limited to vinyl epoxides derived from methyl substituted buta-1,3-dienes, illustrates clearly the reaction sequence. Photolysis generates coordinatively unsaturated tetracarbonyliron, which in turn reacts with the vinyl epoxide (in the absence of pentacarbonyliron the epoxide remains unchanged). The tetracarbonyliron moiety behaves as a Lewis acid causing cleavage of the C3-oxygen bond, subsequent rotation about the C3-C4 bond can give rise to two isomeric complexes, with the tricarbonyliron moiety above, or below, the plane of the molecule. Whether ring opening of the epoxide occurs by reaction with an olefin-tetracarbonyliron complex, or the free vinyl epoxide is unknown, both possibilities being equally likely. The main points relating to the reaction sequence are summarised in the scheme. The



Scheme 3. The reaction of Tetracarbonyliron with vinyl epoxides

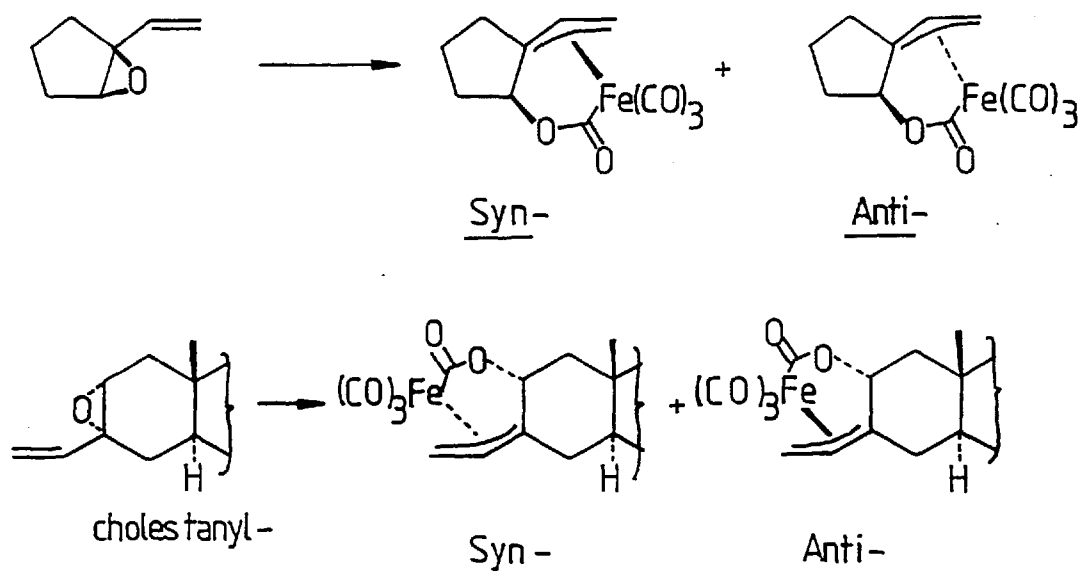


Scheme 4. $E-Z$ Isomerisation



E-isomer once formed undergoes thermal rearrangement to the thermodynamically more stable Z-isomer (however in the case of 1,4 tri and tetra substituted butadiene moieties a high proportion of the E-isomer is isolated from reaction) via a pathway involving a σ bonded intermediate (scheme). Therefore the C-3 carbon of the allyl unit would be expected to show a high degree of sp^3 character, and this is indeed supported by the X-ray crystallographic data of such complexes, and those of similar complexes reported by our laboratories.³²

We have reported isolation of a different type of isomer to those discussed by Aumann, involving the relationship of the bridging oxygen atom to the tricarbonyliron moiety.³² These isomers can easily be rationalised

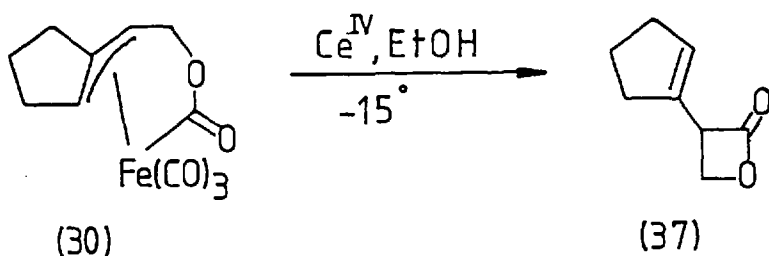


within the same reaction scheme; here rotation about the oxygen-carbonyl bond would be expected to give rise to the observed syn- and anti-isomers.

(c) Oxidation of Tricarbonyliron Lactone Complexes

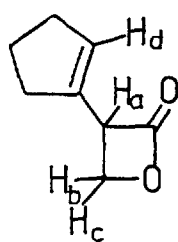
The oxidation of the tricarbonyliron lactone complexes was accomplished by the use of ceric ammonium nitrate in a suitable solvent. Other oxidants were investigated (iron(III) chloride, copper (I) chloride and manganese dioxide) but proved to be less satisfactory. The choice of solvent, in the case of ceric ammonium nitrate oxidations was found to be crucial. Polar solvents such as methanol, ethanol and acetonitrile were found to give the best results.

Addition of the tricarbonyliron lactone complex (30) to a stirred ethanolic solution of ceric ammonium nitrate at $-10^{\circ} \rightarrow -15^{\circ}\text{C}$ resulted in smooth oxidation of the



complex, as indicated by tlc. Removal of the solvent at 0°C , followed by extraction with ether afforded crude

β lactone (37) as the only product (as shown by IR spectroscopy, $\nu_{\max}$ 1825 cm^{-1}). The β lactone (37) could be obtained in quantitative yield by careful column chromatography on silica gel at 0°C . This is indeed a remarkable result, as previous examples²⁴ have generally afforded a mixture of both β and δ lactones. However, on closer inspection of previous results it becomes apparent that there seems to be a marked preference for the formation of the smaller ring β lactone vs the larger ring δ lactone. Generally lowering the temperature of the oxidation increases the yield of β lactone with respect to δ lactone. ^1H n.m.r. spectroscopy shows characteristic resonances at δ 5.55 due to the vinyl proton and δ 4.6 - 4.14 (3H, ABC spin system) due to methine and methylene protons H_a , H_b and H_c . At 60MHz it was impossible to assign the individual protons



(37)

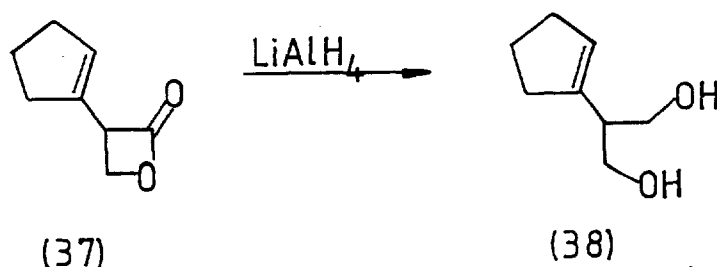
<u>n.m.r. data</u>	<u>δ</u>
$\left. \begin{array}{l} \text{H}_a \\ \text{H}_b \\ \text{H}_c \end{array} \right\}$	4.6 - 4.14
H_d	5.55

due to the complexity of the signal. The 100 MHz n.m.r. spectrum however was much clearer, and it was possible by calculation to derive the chemical shifts and spin - spin coupling constants of the protons H_a , H_b and H_c . These

values were then used to calculate and refine a theoretical n.m.r. spectrum, whose degree of fit with the recorded spectrum was within the limits of measurement.

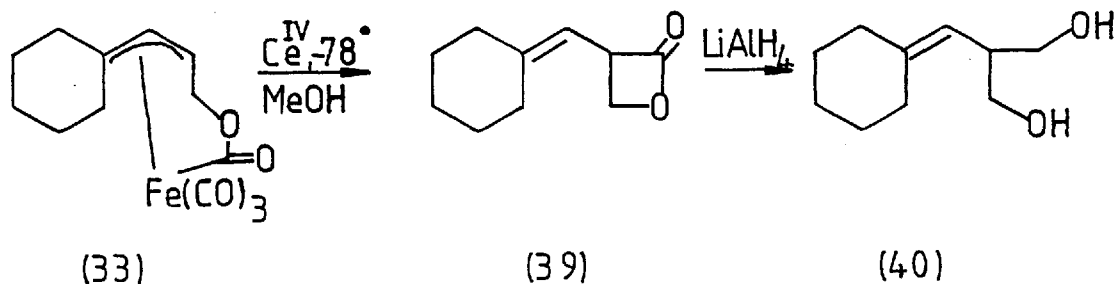
<u>Proton</u>	<u>δ</u>	<u>Coupling Constant</u>
H _A	4.21	JAB 3.7 Hz, JAC 3.8 Hz
H _B	4.42	JBC -10.7 Hz,
H _C	4.52	

The β lactone however proved to be highly labile, and a satisfactory micro-analysis could not be obtained, although recently an accurate mass has been obtained. As final confirmation of structure the β lactone was reduced to the diol (38) with lithium aluminium hydride for which an analysis was easily obtained.

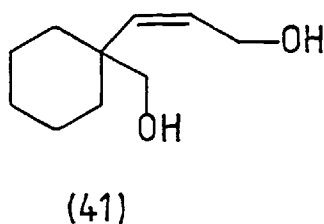


Oxidation of the tricarbonyliron lactone complex (33) under a variety of conditions proved to be difficult. Low temperature oxidation with ceric ammonium nitrate in ethanol or methanol, led to formation of β lactone (39) (as detected by IR spectroscopy of the crude reaction product), but

attempted isolation resulted in decomposition. The best procedure was found to be oxidation with ceric ammonium nitrate at -78°C in methanol, the reaction being allowed to warm to 0°C , whereupon removal of solvent at 0°C and fast column chromatography also at 0°C furnished a solution of the β lactone. Upon removal of the solvent, the solution turned black, indicating extensive decomposition had occurred. Therefore as it was not possible to isolate the β lactone (39), the crude material from the oxidation was immediately reduced with lithium aluminium hydride, and the diol (40) isolated by repeated plc in 43.2% overall yield.



The diol gave a satisfactory microanalysis result, and was



further characterised by examination of its ^1H n.m.r.

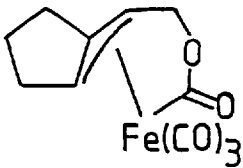
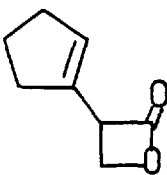
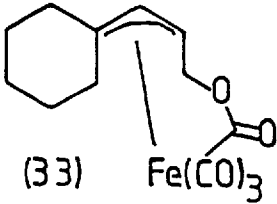
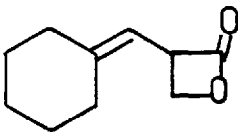
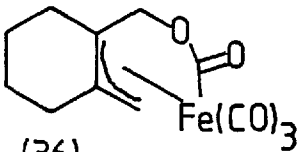
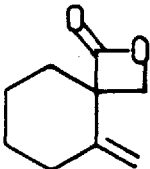
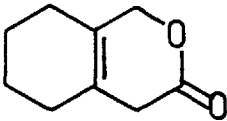
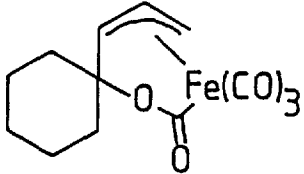
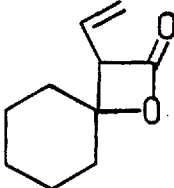
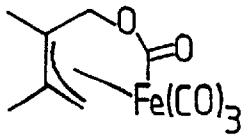
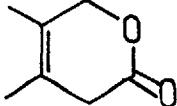
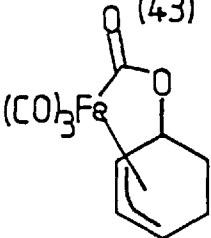
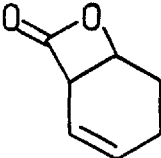
spectrum. The appearance of only one vinyl proton^{resonance} at δ 4.9 confirmed the structure of the diol as that due to reduction of the β lactone (40) and not the diol (41), expected from reduction of a δ lactone.

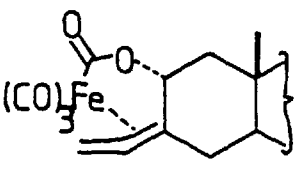
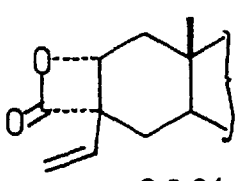
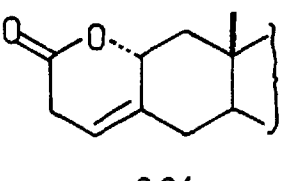
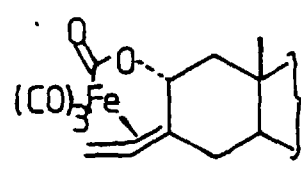
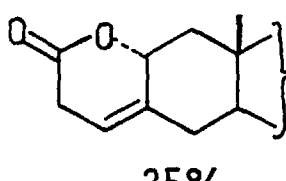
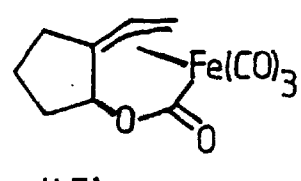
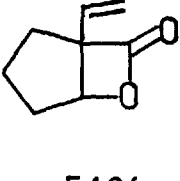
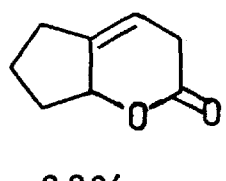
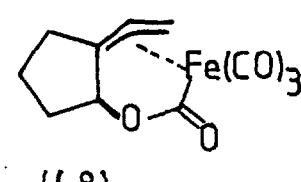
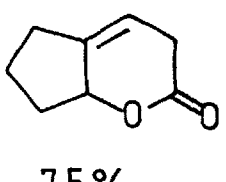
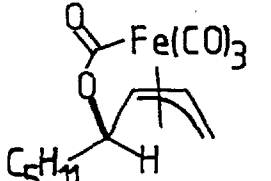
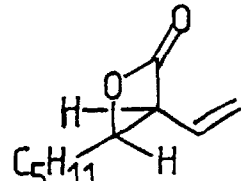
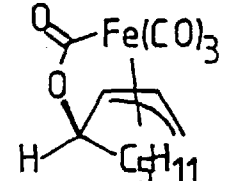
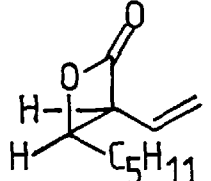
(d) Mechanism of Oxidation of Tricarbonyliron Lactone Complexes

The results of the oxidations of various tricarbonyliron lactone complexes completed in our laboratories are summarised in table 1.

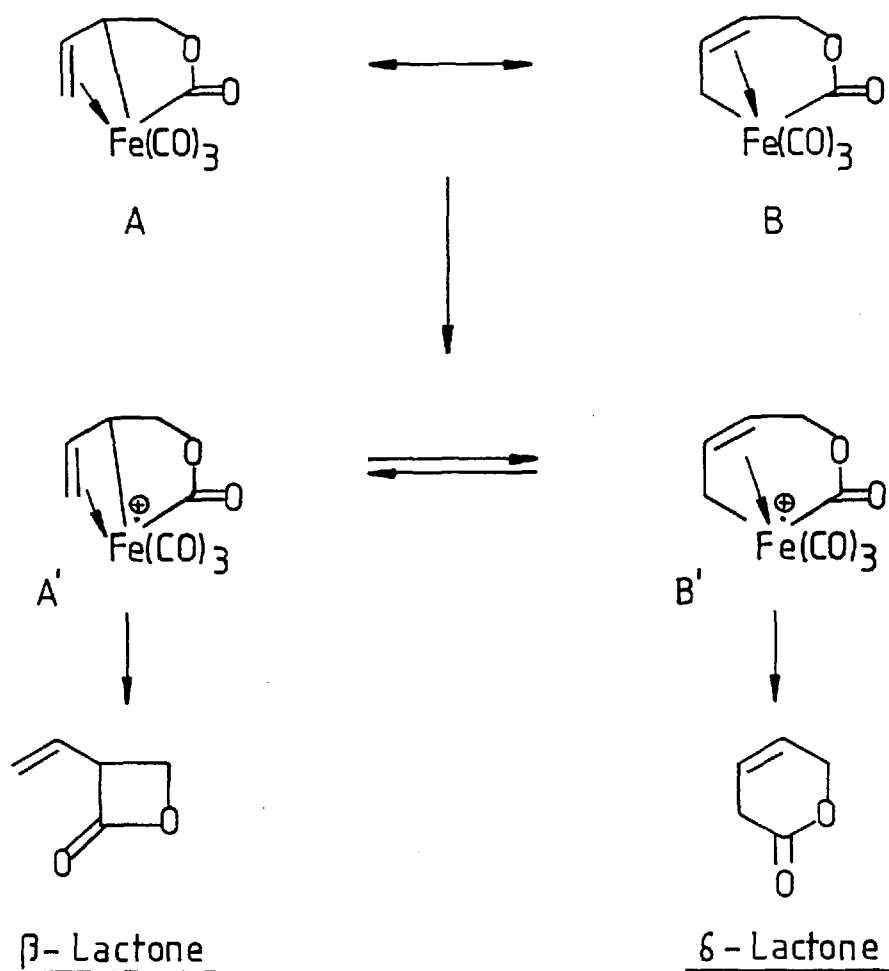
It is apparent from these results that there is a marked preference for the formation of the smaller ring β lactone vs the larger ring δ lactone. That the isomeric complex pairs (45) and (46); (47) and (48); (49) and (50): behave differently towards oxidation indicates that the stereochemical integrity of the original tricarbonyliron lactone complex is reflected in the formation of the oxidation products. Corresponding β lactones from oxidation of complexes (46) and (48) would be trans-fused and therefore precluded by ring strain.

Therefore the mechanism for production of the lactones from the tricarbonyliron lactone complexes must take into account the preferential formation of β vs δ lactones and the observed retention of the initial

Tricarbonyliron Lactone	β Lactone	δ Lactone
 (30)	 100%	-
 (33)	 -	-
 (36)	 14%	 40%
 (42)	 52%	-
 (43)	 41%	 16%
 (44)	 94%	-

Tricarbonyliron Lactone	β Lactone	δ Lactone
 (45)	 28%	 9%
 (46)	—	 25%
 (47)	 51%	 29%
 (48)	—	 75%
 (49)	 68%	—
 (50)	 64%	—

stereochemical features.

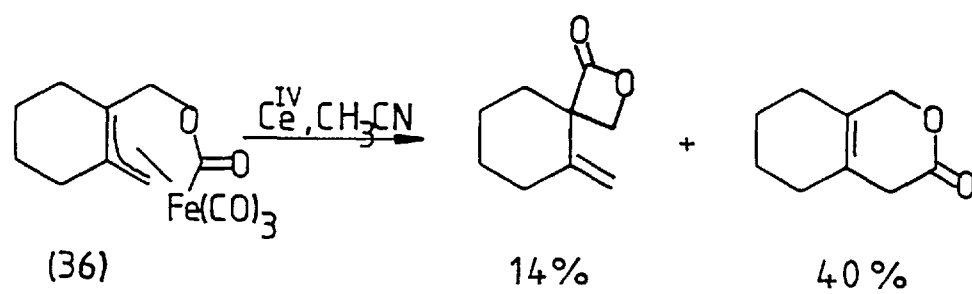


Scheme 5:

A σ, π allyl complex may be regarded as two contributing $2\sigma, \pi$ complexes such as (A) and (B).

That these structures really do contribute to the overall bonding scheme in these complexes is illustrated by the X-ray crystallographic structure determinations³² of the tricarbonyliron lactone complexes (47) and (48). The C3 terminal of the allyl unit is some 0.24°A out of

plane relative to the neighbouring carbon atoms and indicates that this carbon does possess a high degree of sp^3 character. This is further reinforced by X-ray crystallographic data obtained for the complex (49); the C-3 hydrogen atom being $0.5\text{\AA}$ out of plane with respect to the neighbouring carbon atoms. Oxidation of the tricarbonyliron lactone complex by single electron oxidation could lead to an equilibrating mixture of intermediate radical cations (A^1) and (B^1), which upon concerted fragmentation would give the β and δ lactones. More rapid decomposition of (A^1) would lead to the preferentially formed β lactones. If oxidative decomposition were to take place via possible allylic cation intermediates products of solvent trapping and/or structural isomeration would have been expected, and as yet none have been observed. That initial oxidation involves loss of an electron from, and predominant localisation of positive charge on the metal atom is supported by the ionisation potentials and mass spectral fragmentation patterns of organoiron complexes.¹⁹ Other considerations such as steric interactions would also be expected to affect the balance between the formation of β vs δ lactones. This is illustrated by the oxidation of the tricarbonyliron lactone complex (36), where the major product of oxidation is the δ lactone. Examination of the molecular models indicates that formation of the spiro β lactone could be expected to be hampered by steric interactions between the iron moiety and the two axial hydrogens



of the cyclohexane ring.

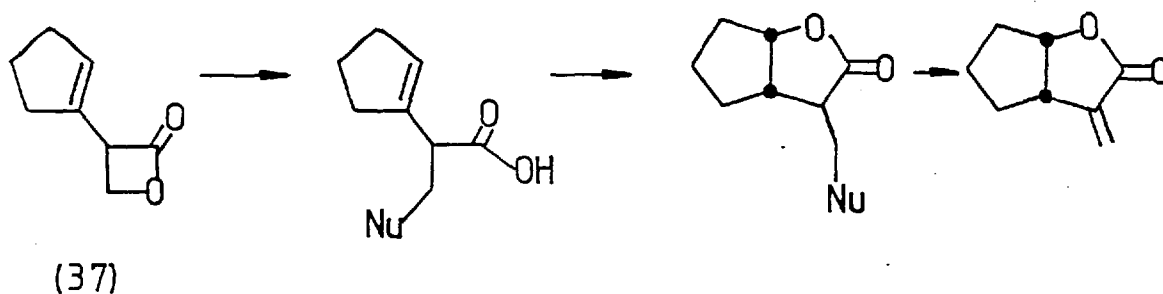
CHAPTER 3

THE CHEMISTRY OF α -VINYL β -LACTONES

Introduction

Oxidation of tricarbonyliron lactone complexes has led to the isolation of a novel class of compound, the α -vinyl β -lactone. As little is known about these compounds it was proposed to investigate their reactivity and chemistry in more detail.

Of particular interest to us was the possibility that a suitably substituted α -vinyl β -lactone could be transformed into an α -methylene γ -lactone. This class of compound is known to possess significant biological activity.³³ One could envisage such a process proceeding via alkyl-oxygen



fission of the β -lactone, lactonisation and subsequent elimination to afford the α -methylene γ -lactone. This section

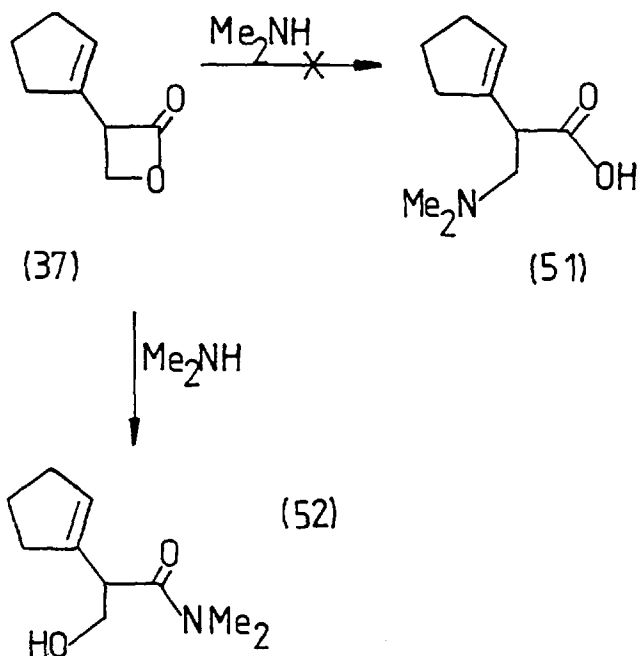
deals with the work related to this proposal.

Other work relating to similar transformations of α -vinyl β -lactones will also be presented in this section.

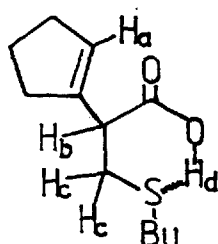
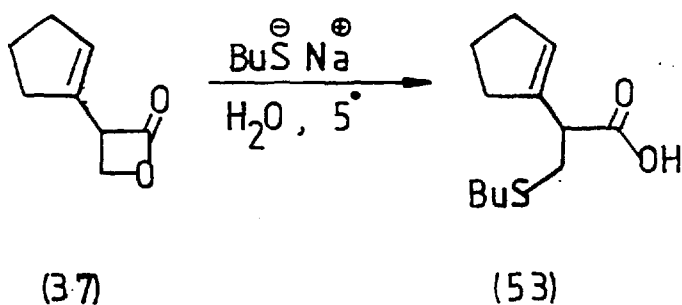
(a) Reaction with Nucleophiles

β -Lactones have been reported to react with thiols and secondary amines with alkyl-oxygen fission of the lactone.³⁴ β -Propiolactone on treatment with dimethylamine gas has been reported to afford the corresponding β -amino acid. However treatment of the β -lactone (37) with dimethylamine under a variety of conditions failed to produce any of the desired β amino acid (51). The only product isolated from these reactions was the amide (52), readily identified from its IR and ^1H n.m.r. spectra. Therefore reaction of the β -lactone (37) with dimethylamine is not proceeding with alkyl-oxygen fission, possibly dimethylamine is too powerful a base to accomplish this transformation.

n-Butylthiolate is another nucleophile that has



been reported to cleave simple β -lactones with exclusive alkyl-oxygen fission,³⁵ and reaction of the β -lactone (37) with this nucleophile at 5°C in aqueous solution afforded the desired adduct (53) in high yield. The adduct was characterised by examination of its IR and ^1H n.m.r. spectra. The ^1H n.m.r. spectrum fitted well with the



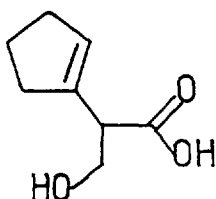
(53)

n.m.r.	data	δ
H_a		5.6 br s
H_b	}	3.57 m
H_c		
H_d		7.0 br s

$V_{\text{max.}} 1710 \text{ cm}^{-1}$

structure (53), however the resonance due to the carboxylate proton H_d occurred at δ 7.1, which is some 3-5 ppm upfield from the expected resonance due to such a proton. The tlc behaviour also appeared anomalous, the compound appearing very much less polar than expected. On the basis of these observations it was concluded that strong hydrogen bonding was occurring between sulphur and the carboxylate proton, such an interaction being favoured by formation of a six membered ring. The reaction however proved difficult to reproduce, with varying amounts of the hydrolysis product

(54) being isolated. This was thought to be due to incomplete formation of the thiolate anion, the presence of unreacted sodium hydroxide in aqueous solution giving

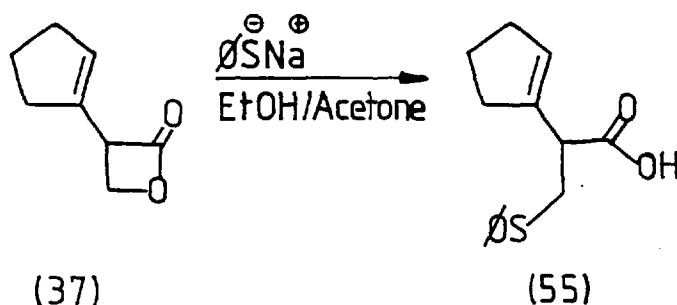


(54)

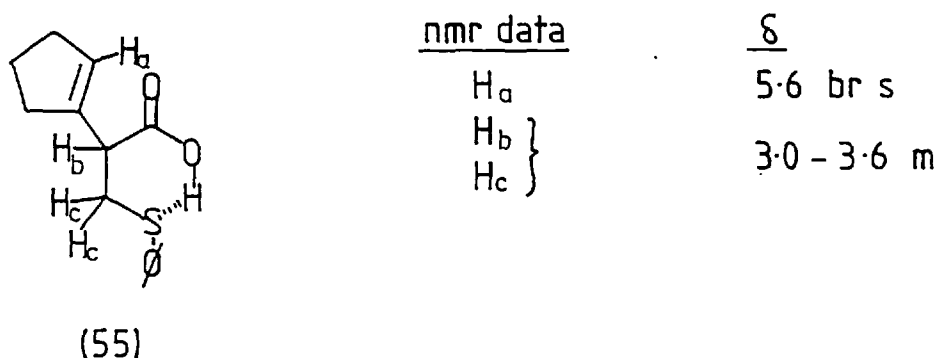
rise to the hydroxy acid (54). Therefore it was proposed to use the more easily formed sodium thiophenoxide to effect alkyl-oxygen cleavage of the β -lactone.³⁶

Reaction of the β -lactone (37) with sodium thiophenoxide (prepared by the action of sodium hydroxide on freshly distilled thiophenol) produce a mixture of products. From the IR spectrum of the crude reaction product (ν_{max} 1770-1710 cm^{-1}) it was clear that a number of products had been formed. Tlc indicated the presence of substantial amount of diphenyl disulphide. It seems that upon reaction of thiophenol with sodium hydroxide solution, oxidation of thiophenol is occurring. Therefore such a solution of sodium thiophenoxide would contain excess sodium hydroxide, subsequent reaction resulting in base hydrolysis of the β -lactone (37). To overcome this problem sodium thiophenoxide was prepared by the action of sodium on dry freshly distilled thiophenol, in ether, the solid sodium thiophenoxide being collected by vacuum filtration.

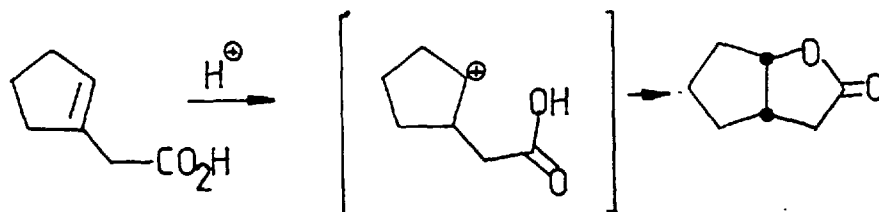
Reaction of sodium thiophenoxide prepared in this manner with the β -lactone (37) in acetone or absolute ethanol led to a mixture of products. The desired adduct (55) was obtained in moderate yield by aqueous sodium



hydrogen carbonate extraction of the crude reaction product, followed by acidification, re-extraction into ether and p.l.c. of the thus derived crude product. The ease of purification by p.l.c. was again attributed to strong hydrogen bonding between sulphur and the carboxylate proton. The ^1H n.m.r. spectrum was consistent with the assigned



which exhibited an IR absorption at $\nu_{\text{max}} 1740\text{cm}^{-1}$. The ^1H n.m.r. spectrum exhibited no resonance due to the olefinic proton of the starting material (54), but neither was it consistent with the γ -lactone (55). Reaction with trifluoroacetic acid was performed in d_6 -benzene, the reaction being followed by ^1H n.m.r. spectroscopy. After 24h at room temperature, work-up afforded a single component in good yield; the IR spectrum of which possessed an absorption at $\nu_{\text{max}} 1750\text{cm}^{-1}$. ^1H n.m.r. spectroscopy however was not consistent with the structure (56), there being no resonance due to the methine proton on the oxygen bearing carbon atom. There was a total absence of a peak at 248 a.m.u. in the mass spectrum of the crude product (corresponding to the molecular ion from the γ -lactone (56)); the only assignable peaks being due to diphenyl disulphide at 218 a.m.u. Therefore it has been shown that the acid catalysed cyclisation of the β , γ -unsaturated acids (53)



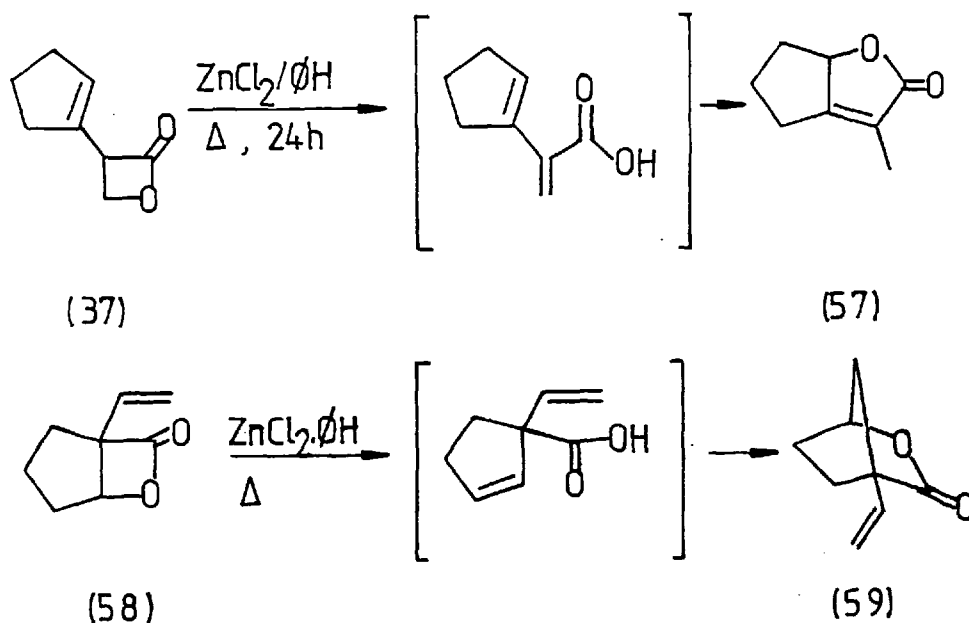
and (55) does not proceed; a result in marked contrast to the reported acid catalysed cyclisation of cyclopentene-1-yl acetic acid.³⁷

If it assumed that protonation of the carbon - carbon double bond affords an intermediate carbonium ion (subsequent intramolecular cyclisation leading to the γ -lactone) the initial protonation must occur in an anti - Markovnikov manner. This would give rise to the thermodynamically less stable secondary carbonium ion. It is more likely that the cyclisation approaches a concerted reaction pathway, by trapping of a developing carbonium ion centre. The reaction pathway however is not clear, nor the factors which influence it, and therefore attempted cyclisation of the adducts (53) and (55) by such a route was abandoned.

When the thiophenol adduct (55) was subjected to the classical iodolactonisation procedure, an intractable product was obtained. This was not surprising, since the thiophenyl grouping would not have been expected to be compatible with the presence of Iodine.

(b) Reaction with Lewis Acids

Preliminary work carried out in our laboratories³⁸ indicated that reaction of an α -vinyl β -lactone directly with a Lewis acid resulted in low yields of products derived from rearrangement. The major disadvantage of this

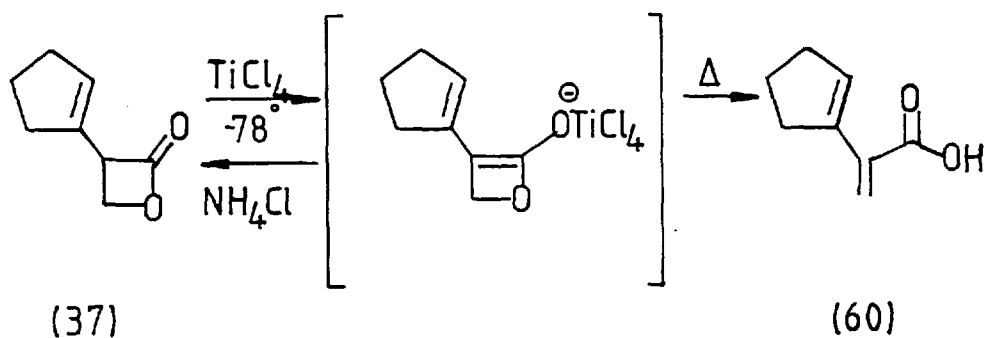


procedure is that the thermodynamic product is obtained, in the case of the γ -lactone (57), the carbon-carbon double bond being endocyclic. This contrasts the previously described route in which the exocyclic double bond isomer would have been obtained.

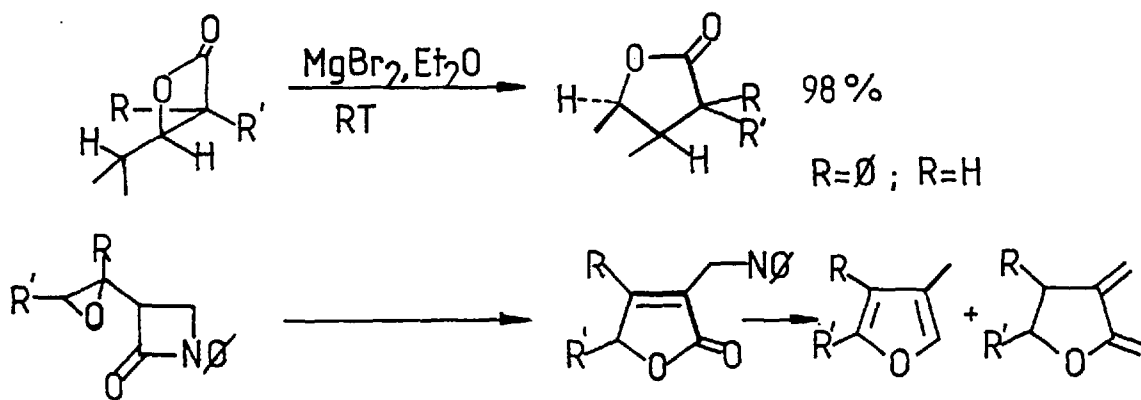
This reaction was studied in greater detail in order to obtain significant improvements in the isolated yields of products.

Treatment of the β -lactone (37) with tin tetrachloride in methylene chloride at -23°C , removal of solvent and Lewis acid at reduced pressure, and aqueous work up led to an uncharacterisable mixture of products in

extremely poor yield. The reaction was repeated using the more powerful Lewis acid titanium tetrachloride, at -78°C . Upon addition of the Lewis acid an immediate red colour developed, which persisted even on warming to -10°C . Quenching with aqueous sodium hydrogen carbonate afforded an oil, which exhibited absorptions at ν_{max} 1825, 1765, 1725 cm^{-1} in its IR spectrum. P.l.c. of this material produced no identifiable materials. Addition of the Lewis acid as a solution in methylene chloride to the β -lactone (37), followed by quenching with aqueous ammonium chloride at -78°C led to a similar result; this time with a greater proportion of β -lactone in the crude product. Under dilute conditions reaction seems to proceed via formation of an enolate, which is stable under these conditions, quenching reforming the β -lactone. Carrying out the reaction at higher temperature, followed by a low temperature quench results in the disappearance of β -lactone from the crude product. However the material recovered seems to consist of dienoic acid (60). No further reaction occurs after the formation of this product, presumably because the Lewis acid is strongly bound to the carbonyl moiety. Reactions of the β -lactone (37) with titanium tetrachloride at temperatures above ambient were not attempted, since it was considered that a lactonic product, if formed, would decompose under such vigorous conditions.

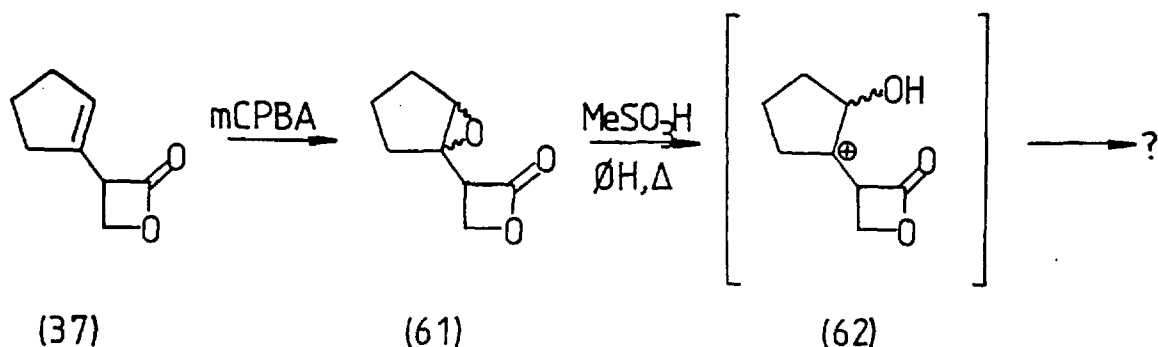


During the course of this work it was reported that β -lactones underwent rearrangement in the presence of the mild Lewis acid magnesium bromide;³⁹ and the epoxides



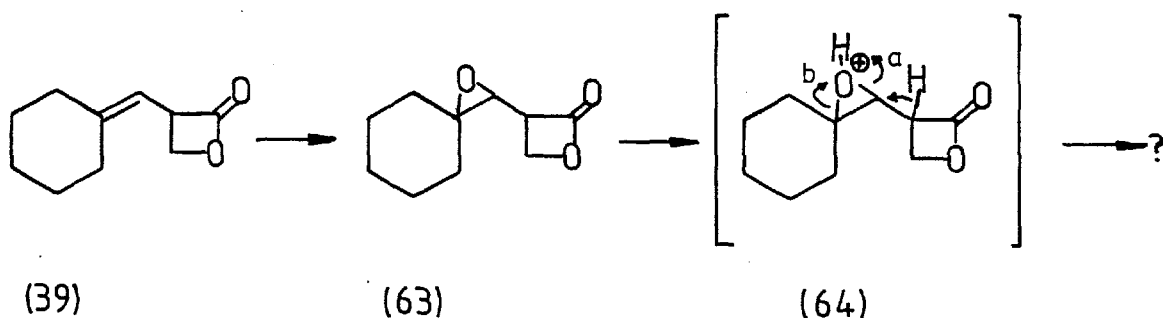
derived from α -vinyl β -lactams underwent facile acid catalysed rearrangement in the presence of methane sulphonic acid.⁴⁰ We therefore proposed to investigate similar reactions of epoxides derived from our α -vinyl β -lactones.

The β -lactone (37) upon treatment with *m*-CPBA furnished the epoxide (61) as a mixture of diastereomers in 51.5% yield. Acid catalysed rearrangement of the diastereomeric mixture of epoxides led to isolation of a single product. This material possessed characteristic absorptions in its IR spectrum at $\nu_{\max}$ 1750, 1690 (w) cm^{-1} . The ^1H n.m.r. spectrum exhibited resonances at δ 4.88 (m), 3.6 (brs), and 2.5 - 1.82 (m) and 1.53 - 1.05 (m). The resonance at δ 4.88 was most probably due to a methine proton, and the absence of a resonance in the region 5 - 6 δ implied that elimination of the elements of water to afford an olefin had not taken place. Therefore it seems that a simple rearrangement had taken place, the product still retaining a carbonyl functionality. The reaction might be



expected to proceed via the protonated intermediate (62), which could then undergo rearrangement. However from the spectral data alone it has not been possible to determine the structure of the product of reaction, and it is hoped that further work will solve this problem.

A similar sequence of reactions was carried out on the β -lactone (39); treatment with *m*-chloroperbenzoic acid affording the epoxide (63) in moderate yield, which was readily characterised from its ^1H n.m.r. and IR spectra. Reaction with methane sulphonic acid in benzene at reflux,



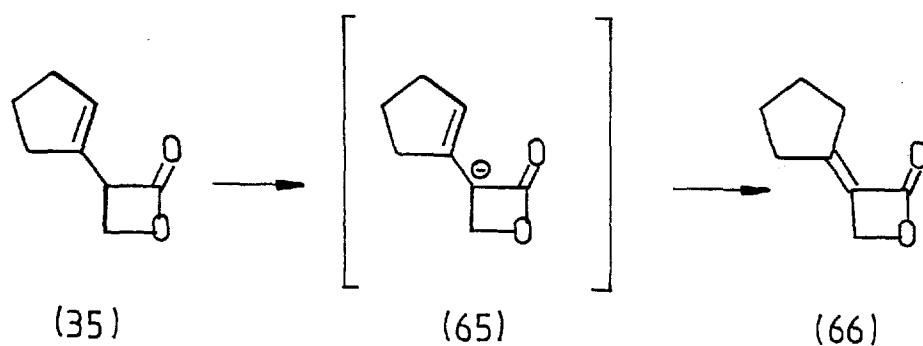
yielded on work-up an oil in excellent yield. The IR spectrum exhibited a broad absorption in the region $1780 - 1730\text{ cm}^{-1}$, but exhibited no absorption due to a hydroxyl moiety. The ^1H n.m.r. spectrum proved to be featureless, and of no use in the determination of the structure of the product.

Protonation of the epoxide could in principle be followed by two modes of cleavage, either giving rise

to a tertiary carbonium ion centre (pathway (b)) or via loss of the acidic proton α to the carbonyl moiety (pathway (a)) to give an intermediate α -methylene β -lactone. From the results here it is not clear as to the exact nature of the reaction pathway, but these rearrangements do look promising, and further work is required in order to determine the pathway of reaction.

(c) Approaches to α -Methylene β -Lactones

In view of the known biological activity of

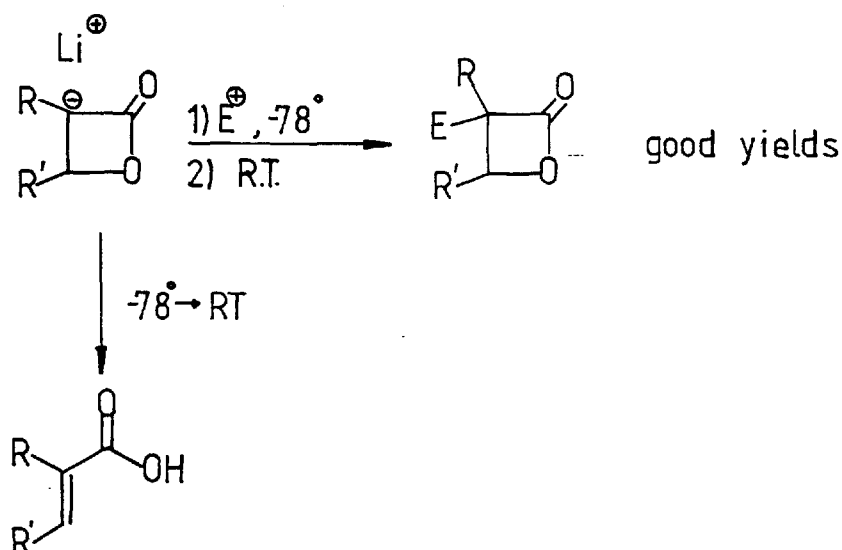


α -methylene γ -lactones,³³ we became interested in the preparation of α -methylene β -lactones. In principle this transformation involves migration of the β - γ carbon-carbon double bond in (37), into conjugation with the carbonyl group. We proposed that upon thermodynamic protonation, the enolate (65) could give rise to the α -methylene β -lactone (66). The enolate was easily formed by the reaction of the β -lactone (37) with lithium diisopropylamide

in THF at low temperature. However protonation under a variety of conditions failed to afford any of the desired lactone (66). In most cases reaction led only to variable amounts of recovered starting material (as shown by IR spectroscopy). It was noted however that quenching at 0°C or ambient temperatures resulted in less recovered β -lactone (37). Addition of hexamethyl phosphoric triamide to a solution of the enolate (65) at low temperature (HMPA enhances the reactivity of the enolate by complexation of the lithium counter ion) also failed to give the rearrangement product, (66), upon protonation. During the course of this work it has been reported that β - γ unsaturated amides can be alkylated in the γ -position, via their lithio-cuprate derivative.⁴¹ Therefore in an attempt to effect γ -protonation, the enolate (65) was treated with cuprous iodide at -78°C. The reaction mixture was allowed to warm until all the solid cuprous iodide had disappeared (approx. -30°C), and with the formation of the lithio cuprate complete, the reaction was cooled to -78°C, and quenched at this temperature with aqueous ammonium chloride. The IR spectrum of the crude product possessed absorptions at $\nu_{\max}$ 1720 and 1640 cm^{-1} . The product was found to be soluble only in polar solvents, the ^1H n.m.r. spectrum being recorded in d_5 -pyridine / d_1 -chloroform. The material appeared to be a carboxylic acid, and must have resulted from decomposition of the β -lactone, (37). The results obtained from these experiments indicate that (a) the

enolate (65) is thermally unstable and (b) α -protonation rather than γ -protonation is occurring.

It has recently been reported that the enolates derived from simple β -lactones undergo a forbidden β -elimination upon warming from -78°C to ambient temperatures.⁴² β -Eliminations require that the electron donating orbital and the electron accepting orbital adopt a syn- or anti-relationship. The structure of the enolate of a β -lactone is such that the two orbitals involved are orthogonal, and therefore in these systems β -eliminations are forbidden. Indeed the enolates have been shown to be remarkably stable at low temperature in THF, but upon warming to ambient temperature they slowly undergo the forbidden β - elimination to afford acrylic acid derivatives. However treatment with electrophiles at low temperature results in



good yields of α -substituted β -lactones. Therefore this explains why quenching at higher temperatures results in less recovered β -lactone. Quenching of the enolate (65)

at low temperature afforded products of α -protonation and decomposition. The lack of γ -protonation in this case must be due to the non-planarity of the enolate (65), there being no orbital overlap between the carbon-carbon double bond and the delocalised orbital system of the enolate.

Rearrangement of the β -lactone (37) via its enolate has proved unsuccessful. Therefore as an alternative to this procedure, the use of a transition metal catalyst to promote the desired transformation was investigated. Barton and co-workers have utilised the rhodium complex tris triphenylphosphine rhodium (I) chloride, to effect difficult exocyclic/endocyclic double bond rearrangements in a number of acid / base sensitive compounds.⁴³ It was hoped that this catalyst system might prove successful when applied to the β -lactone (37). Treatment of the β -lactone with the rhodium (I) complex (2.5 mole%) in d_6 benzene enabled the reaction to be followed by ^1H n.m.r. spectroscopy. However no trace of the isomeric (66) was observed, even after heating the sample to 70°C for twenty hours. The β -lactone (37) remained intact throughout this procedure, and no signs of decomposition were observed. This is remarkable in view of the known thermal instability of β -lactones, which readily undergo elimination of carbon dioxide to form the olefin. Due to the difficulties encountered in this work, further attempts at effecting the preparation of the α -methylene β -lactone (66) have been abandoned.

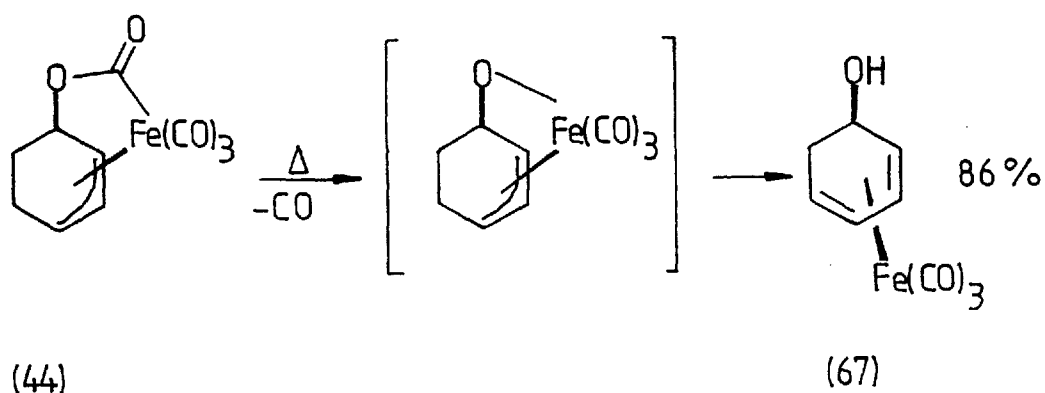
CHAPTER 4

THERMAL REARRANGEMENT OF TRICARBONYLIRON

LACTONE COMPLEXES

Introduction

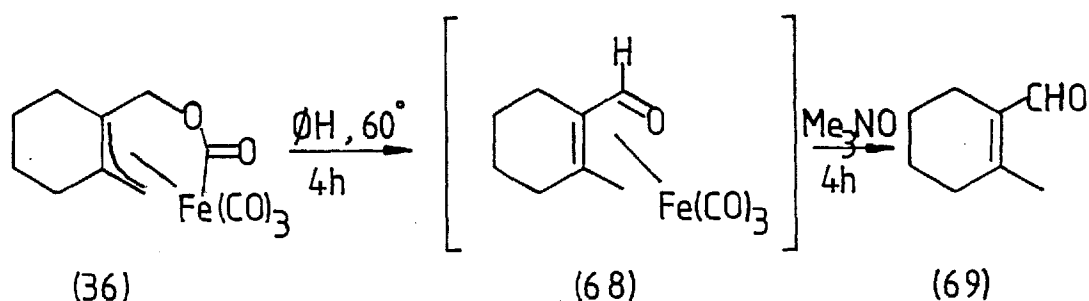
An isolated report suggested that thermal decomposition of tricarbonyliron lactone complexes occurs via initial decarbonylation and rearrangement; the



tricarbonyliron lactone complex (44), upon heating in benzene yielding the 5-endo-hydroxy cyclohexa-1,3-diene tricarbonyliron complex (67) in high yield.⁴⁴ In order to determine the generality, and possible synthetic application of this reaction, the thermolysis of a number of tricarbonyliron lactone complexes has been studied.

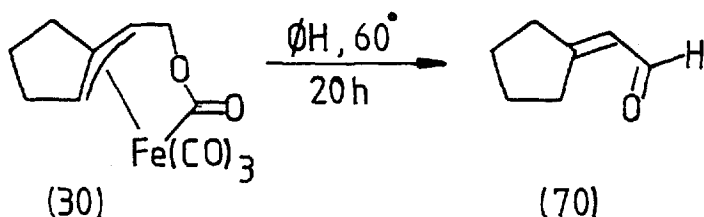
(a) Thermolysis of Tricarbonyliron Lactone Complexes

The tricarbonyliron lactone complex (36) upon heating in dry, degassed benzene at 60°C under argon, underwent smooth transformation to afford a single component (as indicated by t.l.c.). The intermediate formed by this process was UV active, and upon development of the t.l.c. plate with molybdate reagent, the characteristic yellow-green colouration associated with carbonyliron complexes was observed. Addition of the mild oxidant trimethylamine N-oxide,⁴³ afforded after p.l.c. the enal (69) in 69% yield, which was readily characterised by ¹H n.m.r.



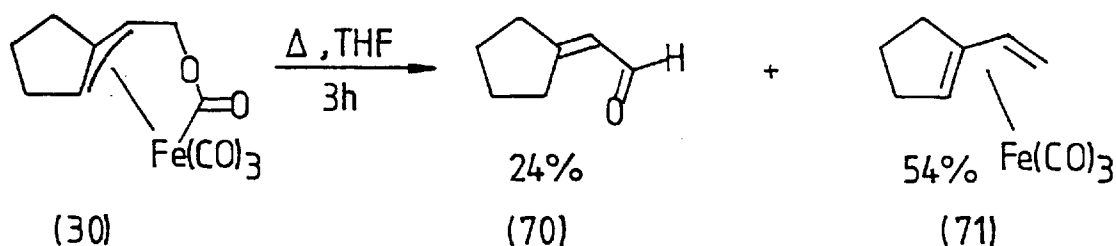
and IR spectroscopy. That reaction proceeds via an intermediate enal-tricarbonyliron complex (68) rather than a π -allyl tricarbonyliron complex (postulated as the intermediate in the thermal reaction of complex (44))⁴⁴ is supported by the results of reaction of trimethylamine N-oxide with various tricarbonyliron complexes.⁴⁵ The decomplexation accomplished by triethylamine-N-oxide has

been shown to be applicable to diene and heterodiene tricarbonyliron systems only. Attempted thermolysis of the tricarbonyliron lactone complex (30) proved to be more complex. In benzene at 60°C (30) was transformed over a period of 20 hours into a single component, however oxidative work-up with trimethylamine-N-oxide furnished uncharacterisable materials. Alternative oxidants such as cupric bromide and activated manganese dioxide also failed to give a clean reaction. IR analysis of the crude reaction



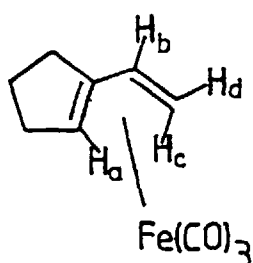
mixture after 20 hours at reflux (ν_{max} . 2040, 2020, 1995, 1980 and 1675 cm^{-1}) indicated that the new intermediate still maintained a lactone linkage. Removal of the solvent by distillation and p.l.c. of the residue afforded the enal (70) in poor yield. The ^1H n.m.r. exhibited characteristic resonances at δ 9.72 (d J8Hz) and 5.9 (dt J8, 2Hz) due to the aldehyde and olefin protons respectively. In order to improve the yield of reaction it was proposed that a lower boiling solvent would facilitate isolation of the volatile enal. When reaction was carried out in refluxing THF, two components (as shown by t.l.c.) were formed in a matter of a few hours. Both components were UV active, the

less polar component was identified as a carbonyliron complex by its behaviour upon visualisation with molybdate reagent. Therefore a change in solvent polarity has dramatically changed the course of reaction. The same complex (30) when heated at 60°C in THF appeared to be indefinitely stable, only upon reflux did reaction occur. This is extremely interesting, in THF it appears that reflux is required to cause irreversible decarbonylation of the tricarbonyliron lactone complex, whereas in benzene at 60°C isomerisation of the complex (30) occurred. The two components from the THF reaction were isolated by removal of solvent at atmospheric pressure and p.l.c. of the residue. On the basis of the spectral data the two components were identified as the enal (70) and the tricarbonyliron diene



complex (71). While the enal can reasonably be derived from decarbonylation, the diene complex (71) corresponds to a formal decarboxylation of the tricarbonyliron lactone complex (30). The structure of the diene complex (71) was confirmed by comparison to an authentic sample prepared by the action of enneacarbonyl diiron on the

uncomplexed diene.

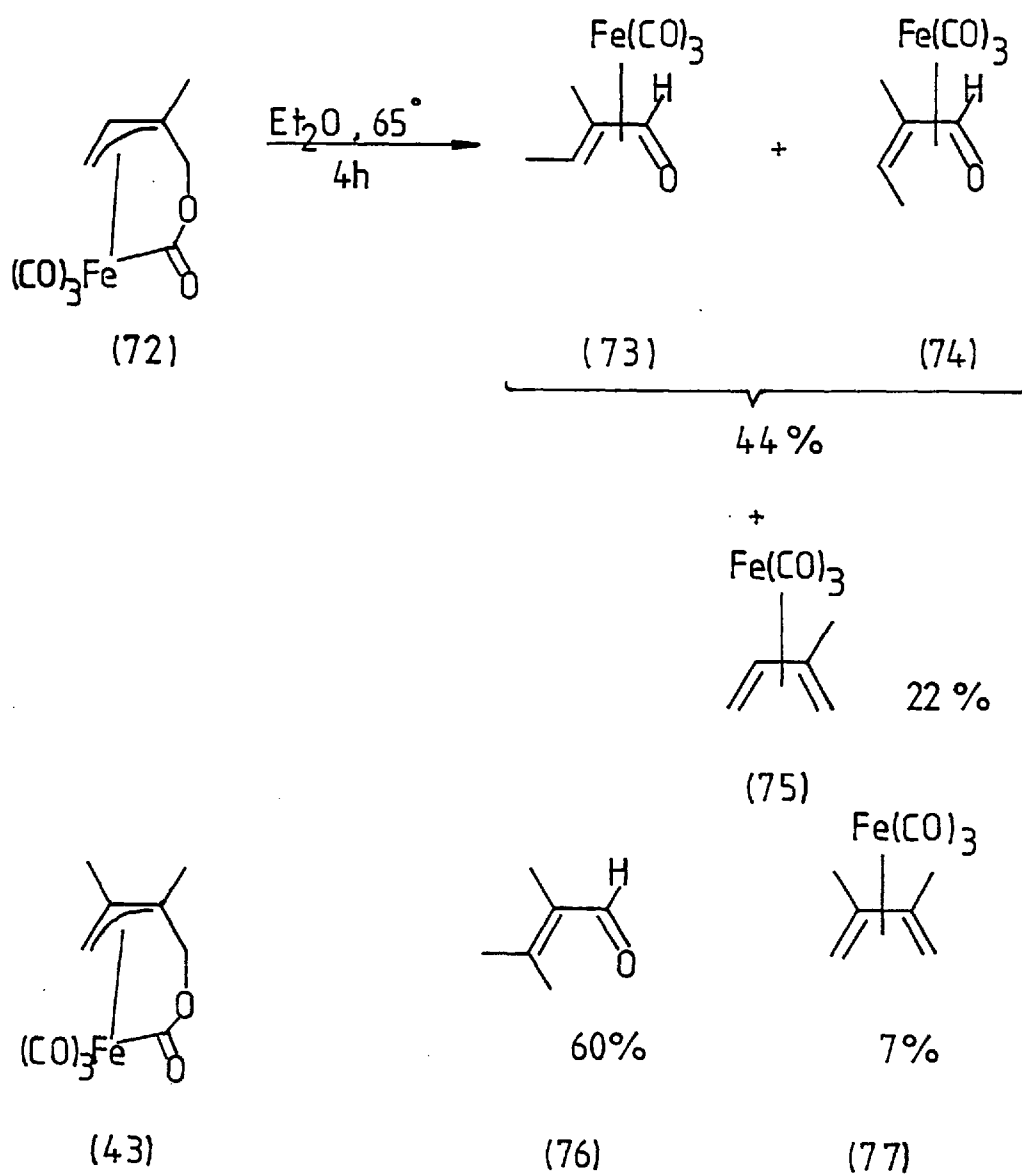


(71)

<u>nmr data</u>	<u>δ</u>
H_a +methylene	1.57-2.07 (7H,m)
H_b	5.25 dd J8.7,6.6 Hz
H_c	-0.23 dd J8.7,2 Hz
H_d	1.47 dd J6.6,2 Hz

The ^1H n.m.r. spectrum of the diene complex clearly shows the signals due to protons H_b , H_c and H_d . The chemical shift values for these protons (measured from TMS) are in accord with those of similar diene tricarbonyliron complexes,¹⁹ the inner proton H_c resonating at higher field than the corresponding outer proton H_d . Owing to the lability of such diene complexes a satisfactory microanalysis has not yet been obtained on the complex (71).

The tricarbonyliron lactone complexes (72) and (43)⁴⁶ were subjected to thermolysis in THF, reaction proceeding smoothly to afford products derived from decarboxylation and decarbonylation pathways. Isolation of the products however proved troublesome owing to their volatility. It was found that dry degassed diethyl ether could be used in place of THF, the reaction being then carried out in a sealed bomb. Removal of the solvent by distillation at atmospheric pressure and p.l.c. of the residue afforded the products shown in the scheme in

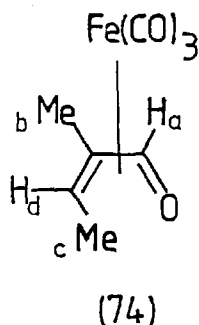
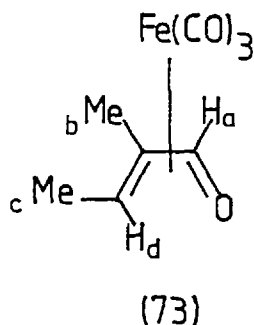


Scheme 1: Thermolysis of the Tricarbonyliron Lactone Complexes (72) and (43)

reasonable yields. The enal (76) was characterised by IR and 1H n.m.r. spectroscopy. The reaction yield was determined by glc analysis of the crude reaction product

using appropriate internal and external standards. The diene complexes (75) and (77) proved difficult to isolate on such a small scale, and were identified from their retention times upon gas chromatography under previously reported conditions.²⁹ The yields of these diene tricarbonyliron complexes were estimated by UV spectroscopy. Studies of such tricarbonyliron diene complexes have revealed that complexation has little effect upon the UV absorption characteristics of the parent diene (λ_{max} and extinction coefficients are close to those of the parent diene).⁴⁷ Therefore since no other component in the crude reaction product possessed an overlapping UV absorption, the data of the uncomplexed diene was used to estimate reaction yields.

The isolation and characterisation of the isomeric complexes (73) and (74) proved a little more complex. The complexes were easily separable by p.l.c. and structural



nmr data

H _a	7.28 s
H _b	1.46 d J 6.5 Hz
H _c	2.06 s
H _d	2.21 q J 6.5 Hz

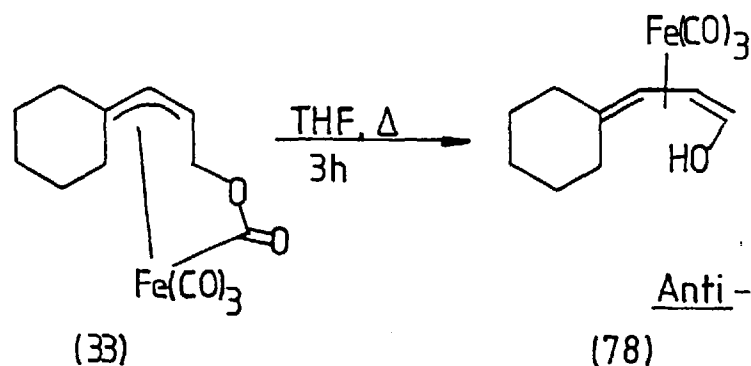
H _a	7.44 s
H _b	1.42 d J 6.5 Hz
H _c	1.28 d J 7.5 Hz
H _d	2.36 dq J 7.5, 6.5 Hz

assignment was based upon their spectral properties. The IR spectra of these complexes showed the absence of the enal carbonyl stretch in the normally observed region, an observation which is in accord with similar compounds reported in the literature.⁴⁸

The complexes were isolated in the ratio 2.2:1 (73):(74), and the geometry assigned on the basis of the ¹H n.m.r. spectra. The major isomer (73), exhibited a resonance due to methyl protons H_C at approximately 0.7 ppm lower field than the corresponding methyl group in (74), the shielding effect of the carbonyliron moiety being greater for the anti-methyl (H_C) in complex (74) than the syn-methyl (H_C) in complex (73). Photolysis of the parent enal tigaldehyde, with pentacarbonyliron in benzene afforded an enal tricarbonyliron complex which gave a satisfactory microanalysis and was identical in every respect to the complex (73).

Thermolysis of the tricarbonyliron lactone complex (33) in THF, did not produce any of the expected diene complex or enal. Instead a single product, a tricarbonyliron complex, was obtained in excellent yield. The IR spectrum of which exhibited absorptions at $\nu_{\max}$ 3605, 2940, 2875, 2040 and 1980-1930cm⁻¹. These data indicated the presence of a hydroxy function and of a tricarbonyliron unit. The ¹H n.m.r. spectrum exhibited resonances at δ 5.12 (d J7.6Hz) and 3.52 (m D₂O exchangeable) attributable to an olefinic and hydroxy proton respectively. From this

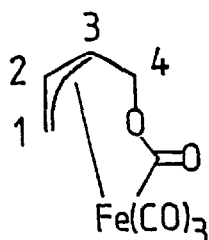
data, and comparison to literature examples,⁴⁹ the structure (78) was assigned. The configuration of the hydroxyl



group was proposed to be anti-, on the basis of its coupling constant (J 7.6Hz) with the neighbouring olefinic proton. The nomenclature anti- is used consistently in the literature to denote such a configuration, and will be used here to denote the configuration of a functional group. However in the case of methylene termini, this nomenclature becomes confusing and therefore throughout this work the terms inner- and outer- will be used to denote such protons. A trans- relationship between these protons would have been expected to give rise to a coupling constant in the order of 9-10Hz. The resonances due to the other two olefinic protons were shown by decoupling experiments to lie in the region δ 2.6 - 3.0, but no other information was obtainable by this method. Attempts to derivatise the dienol complex (78) failed, decomposition occurred upon treatment with alkyl lithiums at low temperature

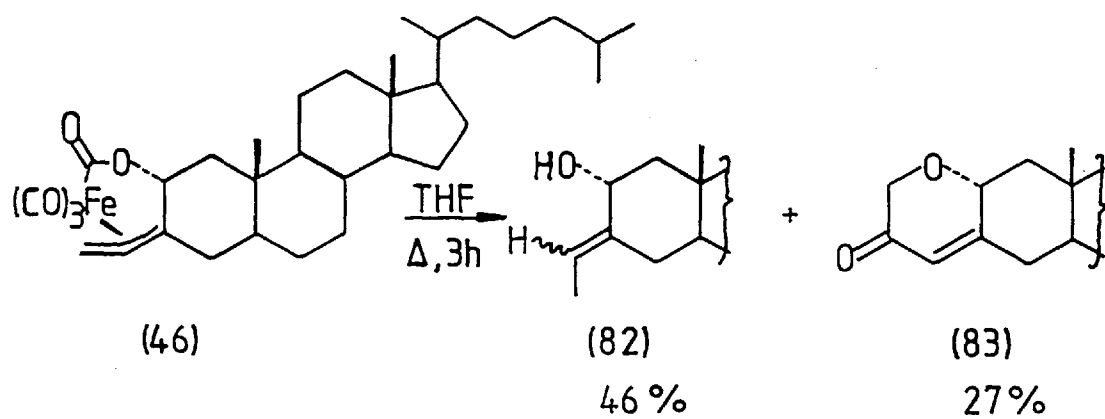
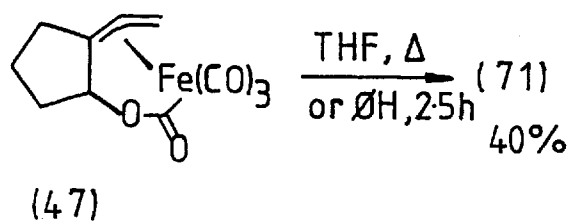
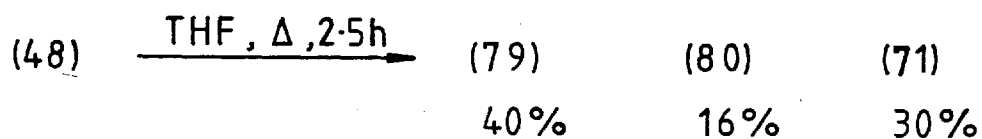
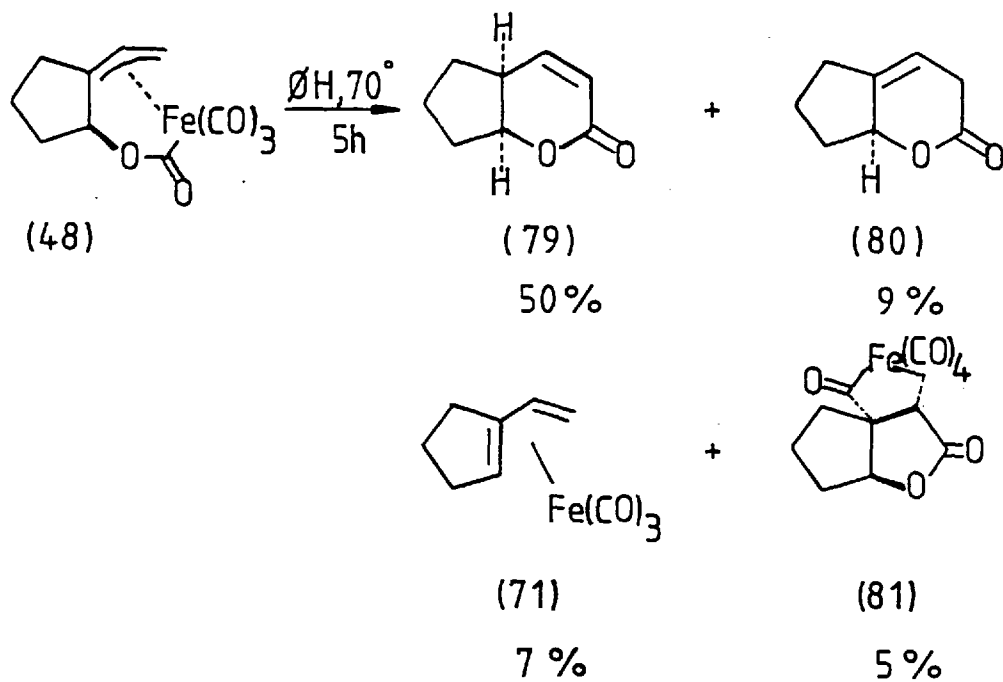
followed by reaction with benzoyl chloride. However a satisfactory microanalysis for the dienol complex (78) was obtained.

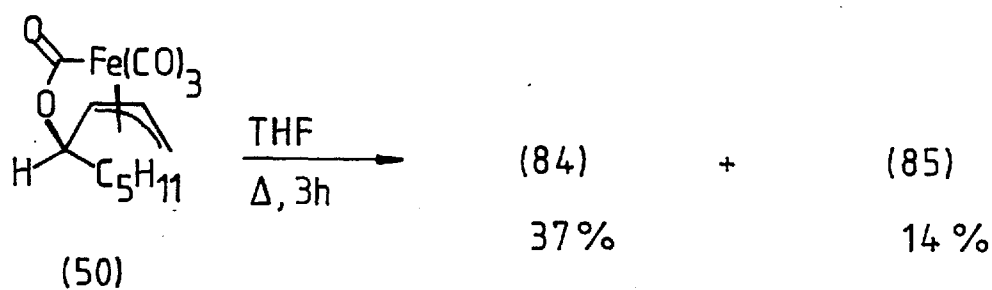
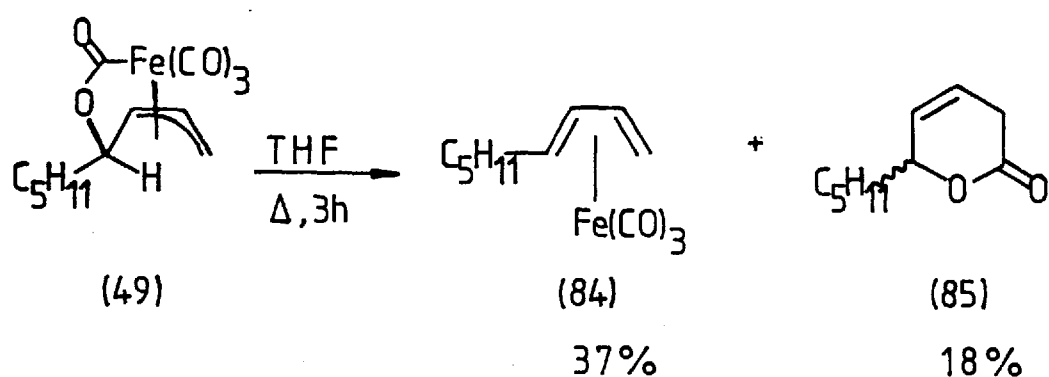
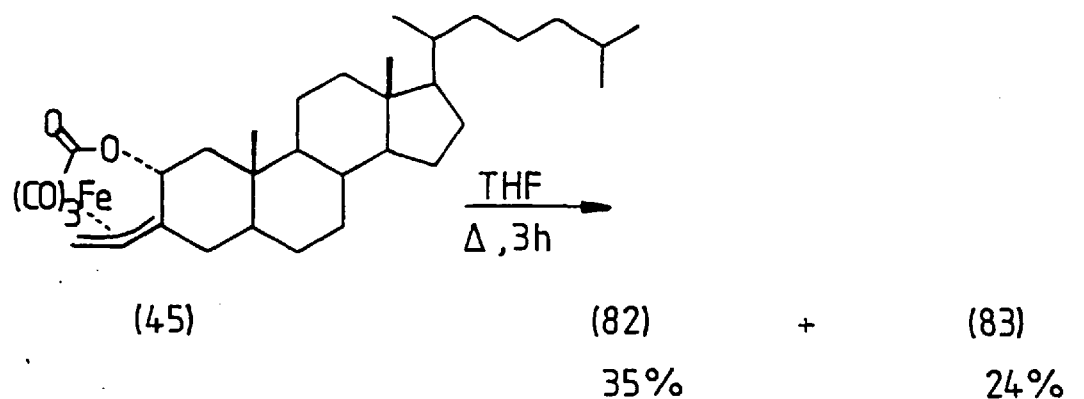
This result contrasts with previous findings, and indicates that a number of pathways are possible in the thermal reaction of tricarbonyliron lactone complexes. This study has been limited to tricarbonyliron lactone



complexes which are unsubstituted at the C-4 position; the complementary C-4 substituted complexes have been studied in our laboratories⁵⁰ and the results of these experiments are summarised in Scheme 2.

From these results it is clear that C-4 substituted tricarbonyliron lactone complexes behave differently towards thermolysis. No enals or enal-tricarbonyliron complexes have been isolated from these reactions, however it is apparent that δ -lactones are being formed in most cases. These results complement the oxidation of the complexes, where a preference for the formation of the smaller ring β -lactones was observed. The anti-tricarbonyliron lactone complex (48) gives as the major products the δ -lactones (79) and (80). It is not clear whether the α , β -unsaturated lactone (80) is a primary product of





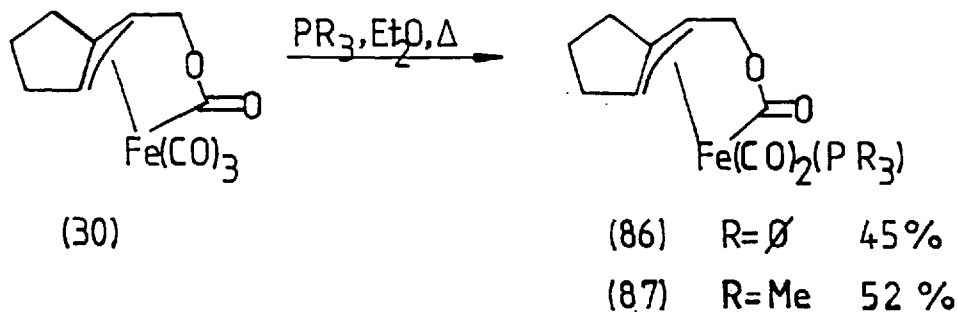
Scheme 2. Thermolysis of Tricarbonyliron Lactone Complexes

decarbonylation, or is formed by carbonyliron catalysed isomerisation of the β - γ unsaturated lactone (79). (Such an isomerisation in the case of the lactone (85) has been shown to require higher temperatures than refluxing THF.⁵⁰) Thermolysis of the anti-complex (48) in benzene proceeds much slower, and the formation of the novel compound (81) indicates that significant quantities of carbon monoxide remain in solution. The syn-complex (47) gives rise only to the diene complex (71) and no detectable δ -lactones. Of note is that thermolysis of the steroidal complexes (45) and (46) give rise to allylic alcohols, this type of rearrangement has not been observed in any of the other examples.

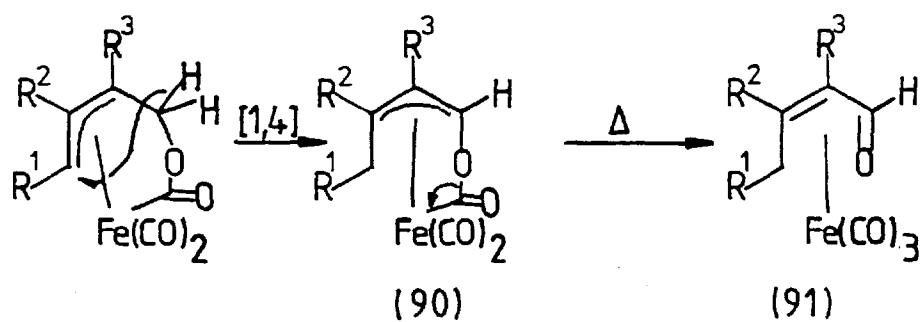
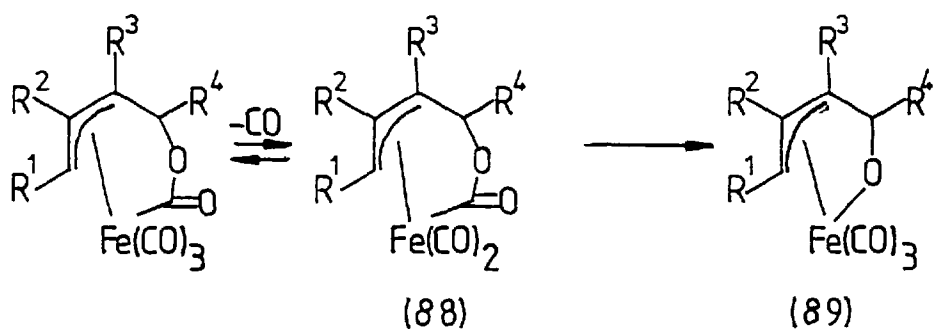
(b) Mechanism of Rearrangement

Any mechanism proposed must take into account the variation in reactivity and the distribution of products. It seems evident from all the results so far, that one of the major pathways of reaction is decarbonylation to give a coordinatively unsaturated intermediate. The ease with which ligand substitution occurs, that is replacement of carbon monoxide by another ligand has been demonstrated by the reaction of the tricarbonyliron lactone complex (30) with trimethyl and triphenylphosphine. Replacement of one molecule of carbon monoxide by a phosphine ligand was accomplished by refluxing in ether in the

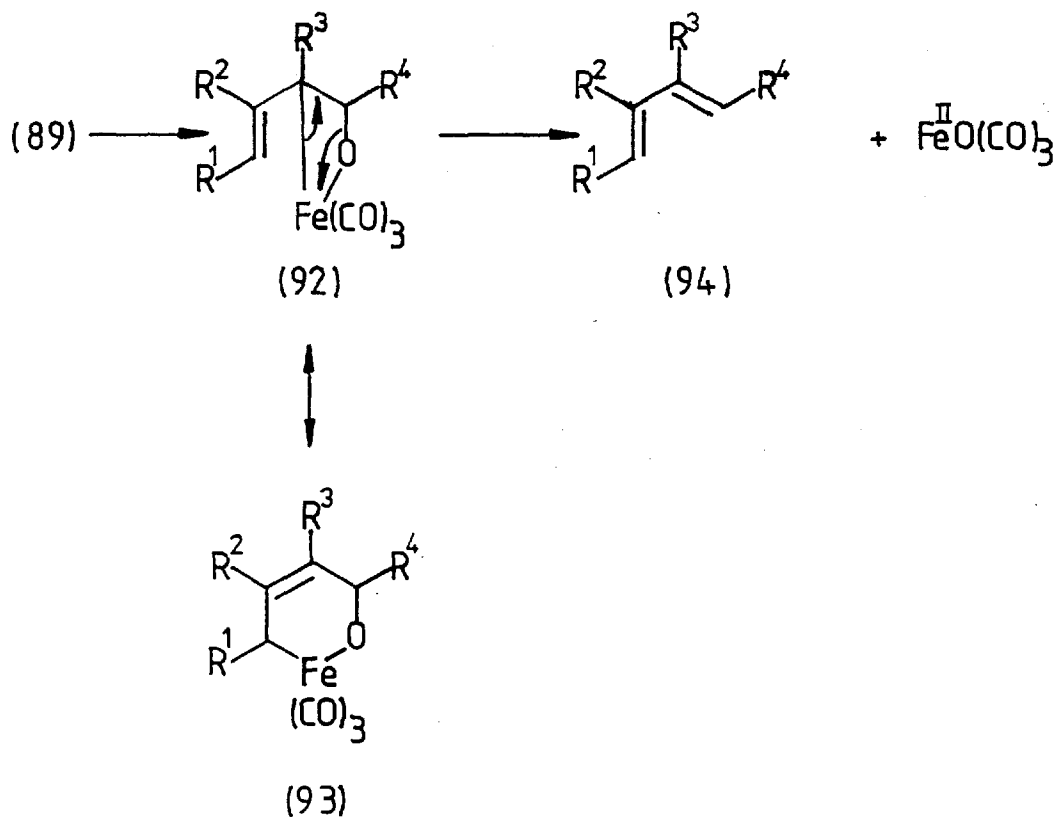
presence of one equivalent of the phosphine.



It is proposed that formation of all the non-lactonic products arises from initial decarbonylation of the tricarbonyliron lactone complexes to afford an intermediate (88) (this process could be assisted by the solvent, but whether this is the case is not clear). This intermediate is co-ordinatively unsaturated and therefore can undergo rearrangement. Intermediate (88) could become co-ordinatively saturated by collapsing to (89). The formation of an enal from either of these intermediates would require the equivalent of a 1,4-hydrogen shift to form (90), which further collapses to afford the enal - tricarbonyliron complex (91). Similar 1,4-hydrogen shifts have been reported,¹⁹ the tricarbonyliron lactam complex (95) giving rise to the heterodiene complex (96), upon reflux in methanol. When $\text{R}_4 \neq \text{H}$, this pathway becomes disfavoured

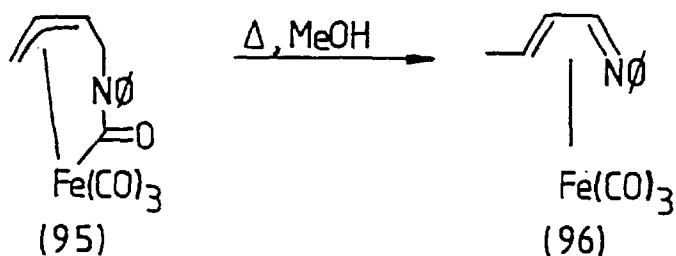


$\text{R}^4 = \text{H}$ Formation of Enal Complexes



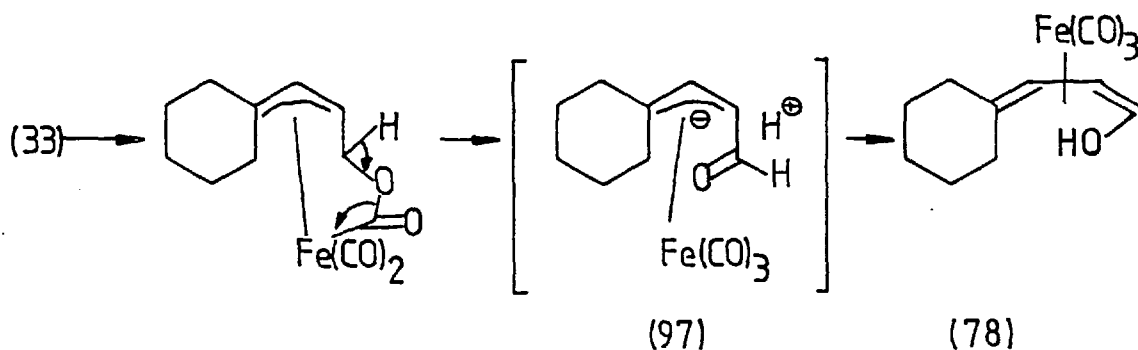
Formation of Dienes

Scheme 3:



and reaction proceeds via the other possible routes. It follows that there is a delicate balance between several competing pathways, substitution by an alkyl group at the methylene bearing oxygen being sufficient to favour alternative reaction pathways.

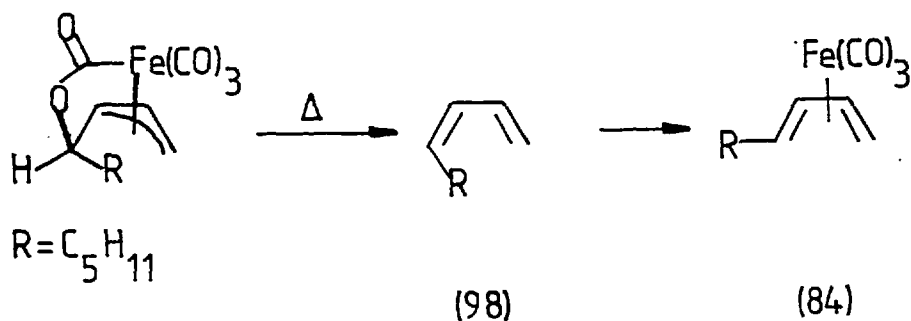
In the case of the tricarbonyliron complex (33), the dienol (78) was obtained as the sole product. It is very unlikely that this arose from trapping out of the



enol tautomer of the corresponding enal, its formation requires that the carbonyliron moiety remain attached to the molecule throughout the rearrangement process. From an examination of the molecular models, collapse of coordinatively unsaturated species such as (88) to (89) would be disfavoured due to severe steric interaction between the tricarbonyliron moiety and the cyclohexane ring. Therefore ^{with} this pathway effectively blocked, loss of a proton to form a π -allyl anion (97), as a tight ion pair, and reprotonation on oxygen would afford the dienol (78). Such π -allyl anionic complexes have been reported, and on protonation afford dienol complexes.⁵¹

The formation of tricarbonyliron diene complexes during thermolysis is common to a number of systems. This reaction results from extrusion of either carbon dioxide or an iron oxide. To determine which was the case, the tricarbonyliron lactone complex (30) was thermolysed under previously determined conditions in a sealed bomb which had been flushed extensively with dry argon. After several hours a sample of the gas phase in the bomb was analysed by IR spectroscopy. The result obtained from this experiment indicated that carbon monoxide (ν_{max} 2170, 2120 cm^{-1}) and not carbon dioxide (ν_{max} 2330 cm^{-1}) had been produced upon thermolysis. Examination of the solution phase by t.l.c. indicated that reaction had gone to completion to afford the enal (70) and the tricarbonyliron diene complex (71). Therefore it is proposed that

intermediates such as (92) and (93) could give rise to a diene. Loss of iron oxide however, reduces the quantity of carbonyliron species in solution, and therefore for the above mechanism to operate, yields of diene complex cannot be in excess of 50%. This is the case in all results, except that of the lactone complex (30), but here the observed yield of 54% is only marginally above the theoretical maximum and is within experimental error. The formation of tricarbonyliron diene complexes is easily rationalised, since in most cases enal tricarbonyliron or δ -lactone tetracarbonyliron complexes are also formed, and under the reaction conditions would transfer the tricarbonyliron moiety to afford the thermodynamically more stable product. In the case of the syn-complex (47), the tricarbonyliron diene complex (71) was the only isolated product. The yield of this reaction was below 50%, therefore it is difficult to comment on this result since the nature of any other material formed is not known.

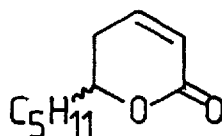


Interestingly, thermolysis of the tricarbonyliron lactone complexes (49) and (50) gives rise to only one diene tricarbonyliron complex. In view of the proposed mechanism, isolation of the diene complex (84) from complex (50) is anomalous. Either rearrangement of the expected diene (98) must occur, or there must be equilibrium of reaction intermediates prior to extrusion of iron oxide. Some reactions of simple acyclic dienes with carbonyliron complexes lead to rearrangements of this kind, however such reactions often require high temperatures.¹⁹ Although it is not clear as to the exact nature of the pathway leading to formation of dienes, equilibration of the intermediates prior to the loss of iron oxide seems more likely.

The formation of δ -lactones from tricarbonyliron lactone complexes has been accomplished previously by Aumman and co-workers.²⁹ The procedure involved subjecting tricarbonyliron lactone complexes to high pressures of carbon monoxide (typically 200 atmospheres and 80°C in benzene as solvent). The study was limited to complexes derived from simple methyl substituted butadienes, but simple thermal reactions of these complexes were not reported. We have shown by our studies that δ -lactones can arise from simple thermolysis of suitably substituted tricarbonyliron lactone complexes. Our results suggest that formation of δ -lactones occurs via thermal rearrangement of tricarbonyliron lactone complexes, decarbonylation being a competing pathway. Therefore if the decarbonylation

pathway is suppressed, δ -lactones would be expected to be the sole product. That such high pressures of carbon monoxide are not necessary for the formation of δ -lactones was shown by reaction of the complex (50) under milder conditions.

The tricarbonyliron lactone complex (50) was heated to 195°C in benzene under 60 atm of carbon monoxide for 3.5 hours, to afford upon work-up a crude product which consisted of the α , β -unsaturated δ -lactone (99) and 5-10% of the β , γ -unsaturated lactone (85) as the sole products.



($\pm$) Massoialactone
(99)

The α , β -unsaturated δ -lactone (99) was isolated in 65% yield by column chromatography of the crude reaction product. This material possessed identical spectral properties to the natural product massoialactone,⁵² first isolated in 1937 from the essential oil from the bark of Cryptocarya Massoi a L.

Other work in our laboratories has shown that the isomeric complex (49) also undergoes the same transformation. In this case more of the β , γ unsaturated lactone (85) was formed. The β , γ lactone has been shown to rearrange to massoialactone upon treatment with nonacarbonyl diiron in refluxing dibutyl ether.⁵⁰ These results indicate that the

initial product of reaction is the β , γ -unsaturated lactone, most probably as its tetracarbonyliron complex. Subsequent rearrangement to massioalactone although favoured by the high temperature, would be expected to be inhibited by the high pressure of carbon monoxide.

In conclusion therefore it has been shown that a number of pathways operate in the thermal reaction of tricarbonyliron lactone complexes, and it is hoped that further work will result in better control of such pathways, particularly for the preparation of lactonic products.

CHAPTER 5

HIGH FIELD ^1H N.M.R. STUDIES OF TRICARBONYLIRON LACTONE COMPLEXES

Introduction

The resonance position (chemical shift) of a proton in an organoiron molecule will depend on a number of factors such as screening by valence electrons and shielding by neighbouring magnetically anisotropic groups. Since none of these terms can be predicted with any great accuracy for complex organometallic molecules, it is unwise to draw far-reaching theoretical conclusions about electronic structure based upon comparison of chemical shifts. However, a great deal of empirical data is at hand which does allow the classification of various types of iron - organic ligand systems.

The first generalisation that can be made for iron organometallics is that protons on complexed ligands almost invariably resonate at higher field than in the free ligand. This is probably due to the diamagnetic anisotropy of the iron atom and attendant groups rather than to any major net flow of electron density onto the ligand. Also, the degree of proton shift upon complexation is characteristic of the different types of metal-ligand bonding system.

In tricarbonyliron π -allyl complexes the unique proton on the centre of the η^3 -allyl unit typically resonates at lower field, ca. δ 5-4, and the accompanying syn- and anti-protons invariably at higher field, δ 4-2.7 and δ 3.7-0.7, respectively. The higher field shift of the anti-proton with respect to the syn-proton is a general trend in these systems, and may reflect greater proximity to the iron atom. As might be expected, shielding and deshielding substituents have the same general effect on neighbouring protons in complexes as in the free ligand, though the exact magnitude of the induced shifts is unsystematic.

When interpreted with care, spin-spin coupling constants are often more reliable than chemical shifts for deducing structure and bonding in organic iron systems; geminal and vicinal H-H couplings being quite sensitive to modest changes in dihedral angles and hybridisation. Therefore from both chemical shifts and coupling constants it should be possible to build up a complete picture of the structural and bonding characteristics of an organo-iron complex.

Aumann has compiled ^1H and ^{13}C data on a number of tricarbonyliron lactone complexes, but his examples were limited to systems derived from methyl substituted butadiene moieties.²⁹ However, initial results obtained in our laboratories from both 60 and 100 MHz ^1H n.m.r. spectra proved to be of sufficient complexity as to defy their

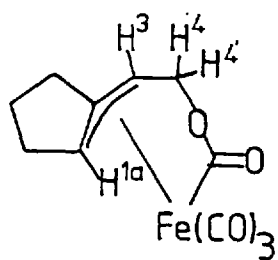
complete spectral arrangement.

Therefore a programme of high field n.m.r. experiments coupled with computer-aided spectral simulation techniques was carried out in order to characterise completely the tricarbonyliron lactone complexes produced in our laboratories. In the case of highly complex systems, X-ray crystallographic studies were carried out in order to confirm structures assigned by n.m.r. techniques.

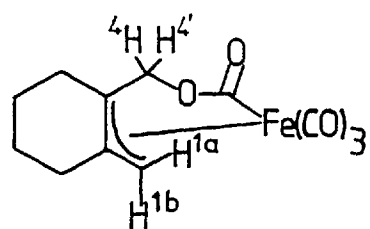
Discussion

The results obtained from the 250 MHz⁵³ and 400 MHz⁵⁴ ^1H n.m.r. spectra of the tricarbonyliron lactone complexes are presented in tables 1 and 2.

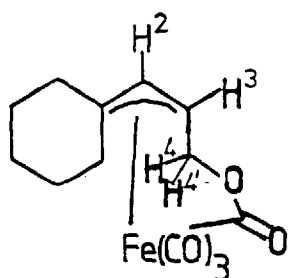
The 250 MHz ^1H n.m.r. spectra of complexes (30) and (36) were first order spectra and hence were readily assigned by inspection. ^1H n.m.r. spectroscopy of the crude tricarbonyliron lactone complex obtained from photolysis of epoxide (31), indicated that the material was a mixture of the Z- and E- complexes (33) and (34) respectively, in a 4:1 molar ratio. By inspection, and calculation, it was found possible to assign data to both isomeric complexes, the spectral assignments being verified by computer-aided simulation techniques.⁵⁵ Interestingly, in the case of complex (33) proton H-3 resonates at lower field than the centre proton H-2, of the allyl unit, a reversal of the normally observed trend. The resonance due



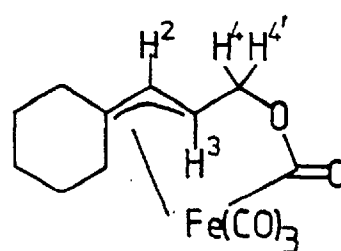
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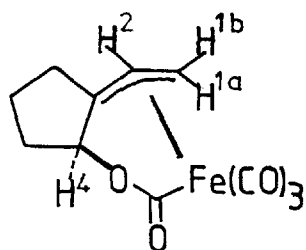
(36)

Z-

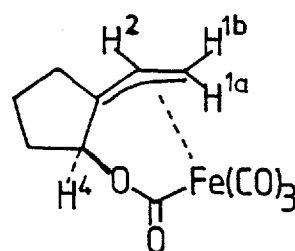
(33)

E-

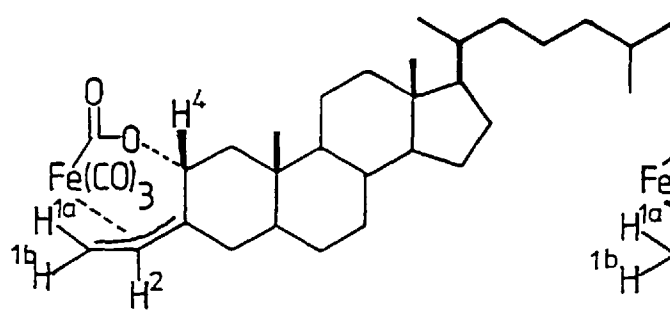
(34)

Syn-

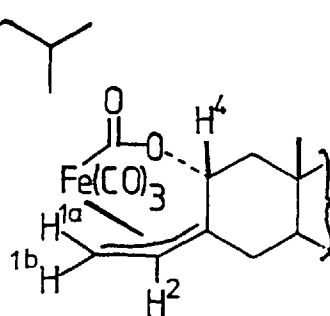
(47)

Anti-

(48)

Syn-

(45)

Anti-

(46)

TRICARBONYLIRON LACTONE COMPLEX	CHEMICAL SHIFT δ^a					
	INNER $H_1 - a$	OUTER $H_1 b$	H_2	H_3	H_4	H_4^1
(30)	4.39	-	-	4.72	4.17	4.03
(36)	2.59	3.23	-	-	4.12	3.89
(33)	-	-	4.46	4.98	4.13	4.06
(34)	-	-	4.47	3.52	4.65	4.24
(47) <u>syn</u> -	2.59 ^c	3.46	5.29	-	4.20	-
(48) <u>anti</u> -	2.96	3.47	4.57	-	4.29	-
(45) <u>syn</u> -	2.94	3.63	4.69	-	4.35	-
(46) <u>anti</u> -	3.03	3.57	4.57	-	4.37	-
(49)	3.08	3.78	4.94	4.65	4.04	-
(50) ^b	3.12	3.78	4.77	4.85	4.30	-
(100) ^b	3.98	-	4.78	4.62	4.06	3.96

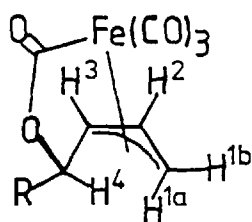
Notes: a. Measured downfield from TMS.

b. Results obtained from 400MHz $^1\text{H.m.r.}$ spectrum.

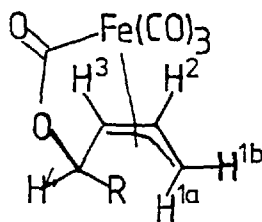
c. Overlapping resonance with ring methylene protons.

TRICARBONYLIRON LACTONE COMPLEX	COUPLING CONSTANT J (Hz)							
	J1a, 1s	J1a, 2	J1s, 3	J1s, 2	J2, 3	J3, 4	J3, 4'	J4, 4'
(30)	-	-	-	-	-	-	4.7	-11.9
(36)	0.21	-	-	-	-	-	-	-11.9
(33)	-	-	-	-	8.1	6.8	2.3	-11.8
(34)	-	-	-	-	9.4	0	3.2	-12.1
(47) <u>syn</u> -	1.6	12.2	-	7.9	-	-	-	-
(48) <u>anti</u> -	2.3	12.1	-	9.0	-	-	-	-
(45) <u>syn</u> -	1.9	12.9	-	8.8	-	-	-	-
(46) <u>anti</u> -	2.2	12.6	-	9.1	-	-	-	-
(49) a.	1.38	12.8	2.13	8.0	7.8	0	-	-
(50) a.	1.9	12.2	1.3	8.2	8.0	6.6	-	-
(100) a.	-	12.0	-	-	7.6	5.3	1.47	-12.0

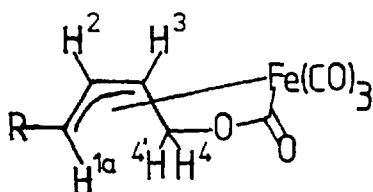
Note: a. In these cases all coupling constants were optimised by computer-aided simulation techniques.



(49)



(50)



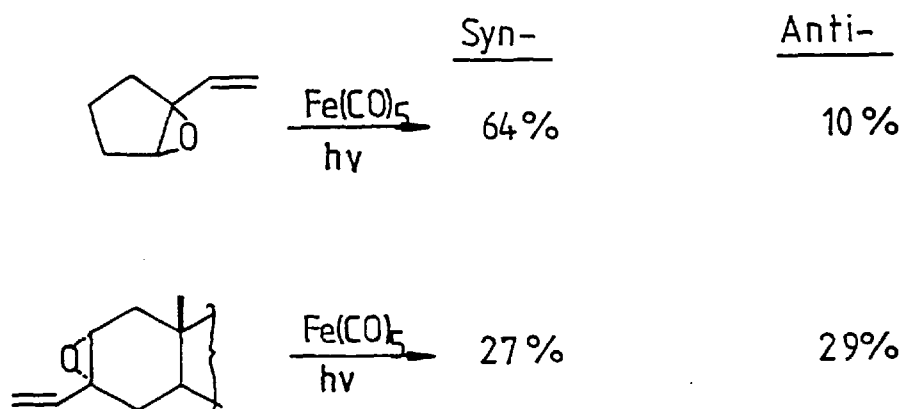
(100)

to proton H-3 in the complex (34), is shifted approximately 1.5ppm to higher field than the corresponding proton in the isomeric complex (33). This implies that proton H-3 is closer to the iron moiety in the E-isomer (34), than in the Z-isomer (33). The only other significant shift is that of the proton H-4, the low field shift presumably being due to an increased distance from the iron moiety.

The syn- and anti-complex pairs (47), (48) and (45), (46) were again assigned by detailed analysis of their 250MHz ^1H n.m.r. spectra (syn and anti referring to the position of the bridging oxygen with respect to the tricarbonyliron unit). The results, however, require further comment. The resonance due to proton H-2 of the anti complex exhibits a marked upfield shift, δ 4.57, with respect to the corresponding proton in the syn-complex,

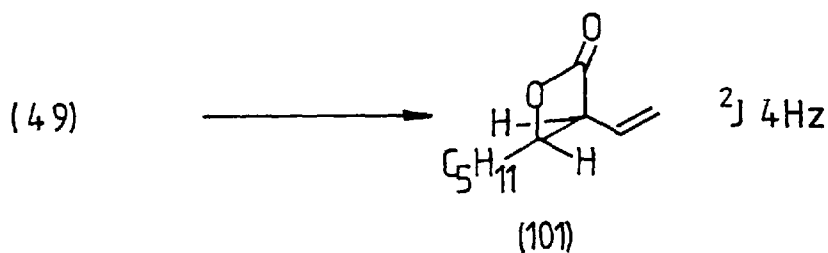
δ 5.29, and indicates a closer proximity to the iron moiety. This is confirmed from the X-ray data,³² the C_2 atom being $0.08\text{\AA}$ closer to iron in the anti-complex (48), than in the syn-complex (47). Similarly, iron is $0.03\text{\AA}$ closer to C_1 in the anti-isomer. This in turn implies that the distance between the iron moiety and proton H_1 -a is increased and hence deshielded. This is indeed the case, this proton resonating at δ 2.96, as opposed to δ 2.59 in the syn-complex. Also the greater proximity of the iron moiety to the cyclopentane methylene protons in the syn-complex is reflected in the observed high field shift of these protons in the ^1H n.m.r. spectrum.

However, in the case of the isomeric steroidal tricarbonyliron lactone complexes (45) and (46) no significant structure related shifts were observed. This indicates that the steroidal system is sterically much less demanding than the cyclopentane systems (47) and (48), being able to accommodate such isomerism without significant variation in the proximity of the π -allyl system to iron moiety. That the steroidal system is sterically less demanding is also illustrated by the yields of formation of the isomeric syn- and anti-complexes from the corresponding vinyl epoxide. The assignment of geometry in these systems could not be deduced from their ^1H n.m.r. spectra, but was based upon the oxidation behaviour of the complexes. The chemical shifts and coupling constants derived from these spectra fitted extremely well with the



general trends observed in all other examples of the tri-carbonyliron lactone complexes.

The 250MHz ^1H n.m.r. spectrum of the complex (49) was interpreted by inspection, and a tentative structural assignment was made based upon consideration of the chemical shift of proton H_4 . This resonated at δ 4.04, 0.26ppm to higher field than the corresponding proton of the isomeric complex (50), implying a closer proximity to the iron moiety. This assignment was confirmed by the oxidative

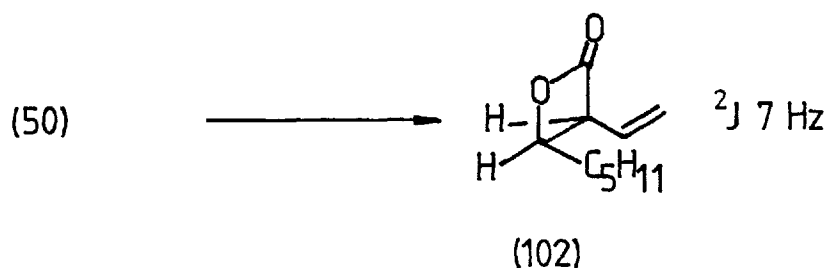


behaviour of complex (49), the trans- β -lactone (101) being obtained upon oxidation (J trans 4Hz, in agreement with literature examples⁴⁰).

The structure of tricarbonyliron lactone complex (49) has recently been corroborated by X-ray crystallographic studies (fig. 12). The structure determination was refined ($R_h = \text{factor}^5$) such that it was possible to determine the position of the C_3 proton. This was found to be $0.5\overset{\circ}{\text{A}}$ out of plane of the neighbouring carbon atoms. This illustrates the high degree of Sp^3 character at the C-3 carbon, and also explains why a near zero coupling between protons H_3 and H_4 is observed (the dihedral angle between protons H_3 and H_4 must approach 90°).

Complex (50) provided a similar spectrum, with the exception that resonances due to protons H_2 and H_3 overlapped. This made it extremely difficult to extract coupling constants and chemical shift data. This problem was overcome by use of an iterative procedure. Estimation of unknown chemical shifts and coupling constants provided a data set which was then optimised by calculation. This involved use of the estimated set of data to calculate a theoretical ^1H n.m.r. spectrum,⁵⁵ which upon comparison to the experimentally derived spectrum provided a new data set; the sequence being continually repeated until a convergence of the data was obtained. In this manner all coupling constants and chemical shift data have been optimised; the simulated spectrum based upon this data

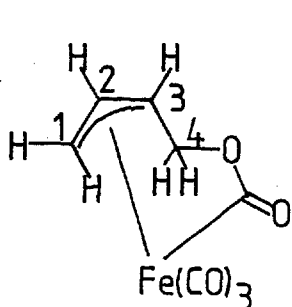
corresponding closely to the experimentally derived 250 MHz ^1H n.m.r. spectrum. As a further check, a 400 MHz ^1H n.m.r. spectrum⁵² was obtained for the complex (50), decoupling experiments also being carried out in order to determine the connectivity between the various protons. This data agreed very closely to the previously optimised data obtained from the 250 MHz n.m.r. experiments, the results of the decoupling being in total accord with the proposed structure. Further confirmation was obtained upon oxidation of complex (50), the cis β -lactone (102) being the sole product (J cis 7 Hz⁴²).



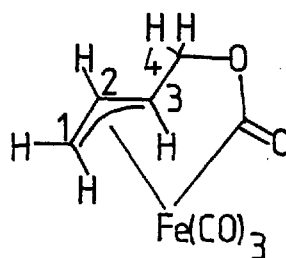
The tricarbonyliron lactone complex (100), although a simple compound produced the most complex n.m.r. spectrum recorded in our laboratories. Even at high field, (400 MHz) overlapping resonances caused significant problems in interpretation. With the aid of decoupling experiments, sufficient data became available to enable the calculation of an optimised set of chemical shifts and coupling constants. These values when used to calculate

a theoretical spectrum, provided an almost identical fit to the experimentally determined 400 MHz ^1H n.m.r. spectrum. It can be seen from tables 1 and 2 that protons H_1 , H_3 and H_4 are almost co-incident. This overlapping of resonances is just an unfortunate coincidence, the derived parameters fitting well with the general trends observed in the ^1H n.m.r. spectra of tricarbonyliron lactone complexes.

From these examples a general pattern does emerge, both in the magnitudes of the chemical shifts and coupling constants of the protons of the π -allyl tricarbonyliron lactone unit.



Z-



E-

<u>PROTON</u>	<u>RANGE OF CHEMICAL SHIFT δ</u>	
H_{1-a}	2.6 - 3.2	} C_1 alkyl substitution shift resonance $\approx$ 1ppm to lower field
H_{1-b}	3.2 - 3.8	
H_2	4.3 - 5.3	
H_3	4.6 - 5.0 (<u>Z</u> -)	1ppm upfield shift for <u>E</u> -isomer
H_4	3.8 - 4.4	

The inner-proton H_{1a} always resonates at higher field than the corresponding outer-proton H_{1b} . In general proton H_{1a} resonates to higher field of all the other protons of the π -allyl system. Alkyl substitution at the C_1 -carbon atoms has a profound effect upon the observed chemical shifts of both protons H_{1a} and H_{1b} , shifting their resonance approximately 1ppm downfield from their normally observed values. The unique central proton H_2 of the allyl system in general resonates at lower field than proton H_3 , but in certain examples this order has been found to be reversed. Various steric requirements of the remainder of the molecule can cause significant shifts of the H_2 resonance as has been discussed previously in the case of the syn and anti-complexes (47) and (48) respectively. The resonance due to proton H_3 , in the case of the Z-complexes occurs in the same region as that due to proton H_2 . However in the E-isomer, this proton resonates at higher field, the shift being in the order of 1ppm, due to closer proximity to the iron moiety. The protons on the carbon atom bearing oxygen exhibit little variation in the position of their n.m.r. resonances. Therefore, chemical shifts can provide useful information as to the structure of tricarbonyliron lactone complexes.

An examination of the proton spin-spin coupling constants in these systems reveals a more consistent pattern, and therefore should prove a more reliable method for arrangement of structure. The geminal coupling constant

between protons H_{1a} and H_{1b} is low in the order of a few Hz. This is in agreement with other examples and theoretical calculations on the magnitude of coupling constants

<u>COUPLING CONSTANT</u>	<u>RANGE OF VALUES OBSERVED</u>
$J_{1a, 1b}$	1 - 2 Hz
$J_{1a, 2}$	11 - 13 Hz (<u>trans</u> coupling)
$J_{1b, 2}$	6 - 8 Hz (<u>cis</u> coupling)
$J_{2, 3}$	7 - 9Hz
$J_{4a, 4b}$	- (11.8 - 12.2Hz)

in systems with similar bonding schemes. The trans coupling between protons H_{1a} and H_2 (11 - 13 Hz) is greater than the corresponding cis coupling ($J_{1b,2}$ 6 - 8 Hz), the two ranges not overlapping. These coupling constants are therefore extremely useful in determining the geometry about the terminus of the π -allyl system. In the case of the coupling between protons H_2 and H_3 , little variation is observed in the magnitude of the coupling constant of both Z- and E-isomers (cis and trans-relationship between protons H_2 and H_3 respectively). This contrasts the large difference observed between the cis and trans coupling constants at the other terminus of the allyl unit (C_1 terminus). It is known that slight changes in the hybridisation can cause large effects in the magnitude of coupling constants in such systems. The results obtained here indicate that the hybridisation at the C_3 terminus is

somewhat different to that at the C_1 terminus of the allyl system. This result being in agreement with those obtained from X-ray crystallographic structure determinations of complexes (47), (48) and (49). These data also indicate that the C_3 terminus of the π -allyl system possesses a significant amount of Sp^3 character. This fact has been shown to have significant effects upon the reactivity of these complexes (cf: behaviour towards oxidation).

Therefore it is possible from 1H n.m.r. spectroscopy to characterise completely a tricarbonyliron lactone complex. The structure of such complexes can easily be assigned from examination of the spin-spin coupling constants, which have been shown to exhibit little variation between different tricarbonyliron lactone complexes. Where resonances overlap, high field 1H n.m.r. spectroscopy can provide enough data to calculate hidden parameters, and hence lead to assignment of structure. The general trends in the magnitudes of both chemical shifts and coupling constants observed in the cases studied here, should provide sufficient data to enable any new tricarbonyliron lactone complexes to be characterised with ease.

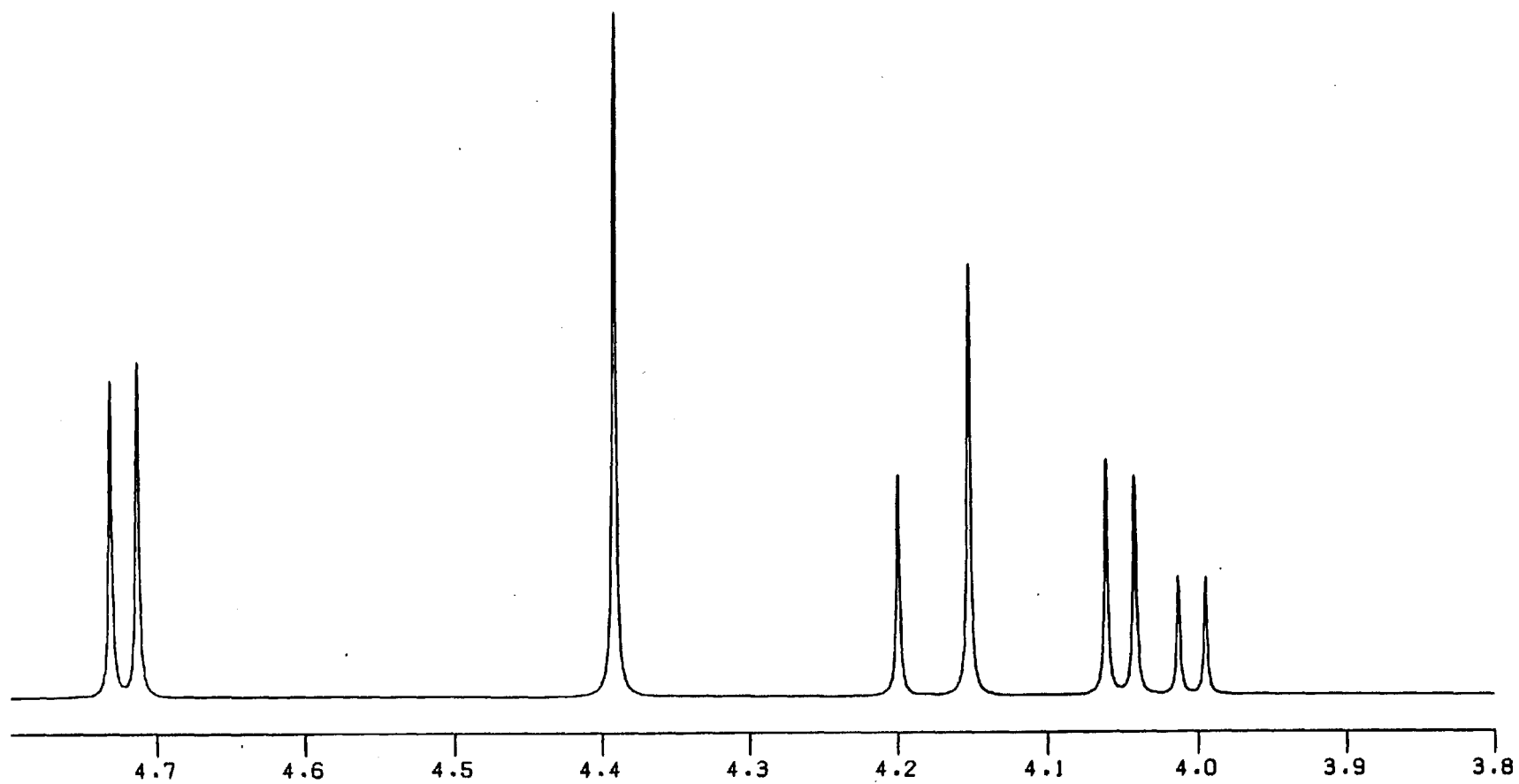


Fig 1. Simulated ^1H nmr Spectrum of Complex(30).

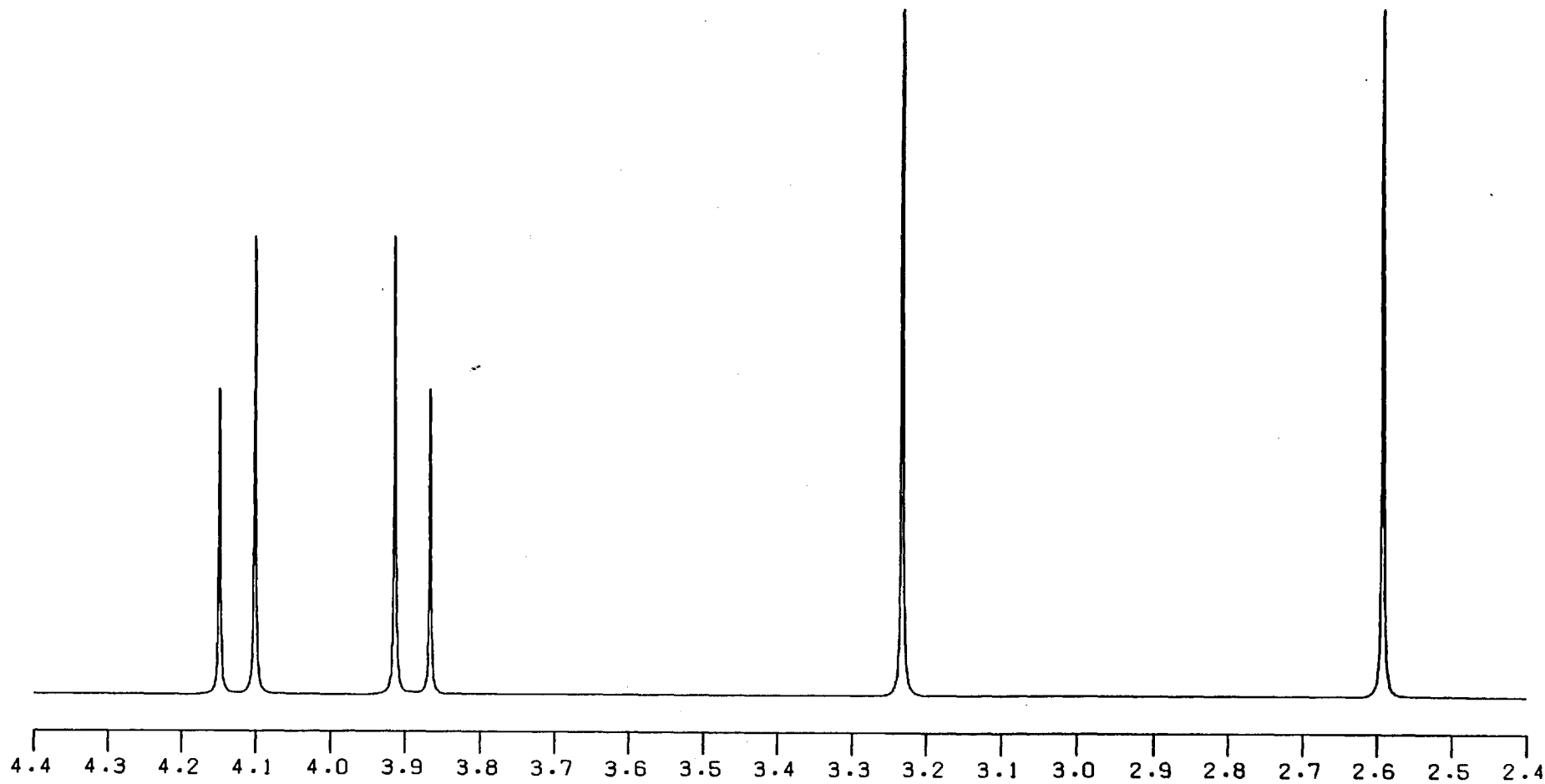


Fig2. Simulated ^1H nmr Spectrum of Complex(36).

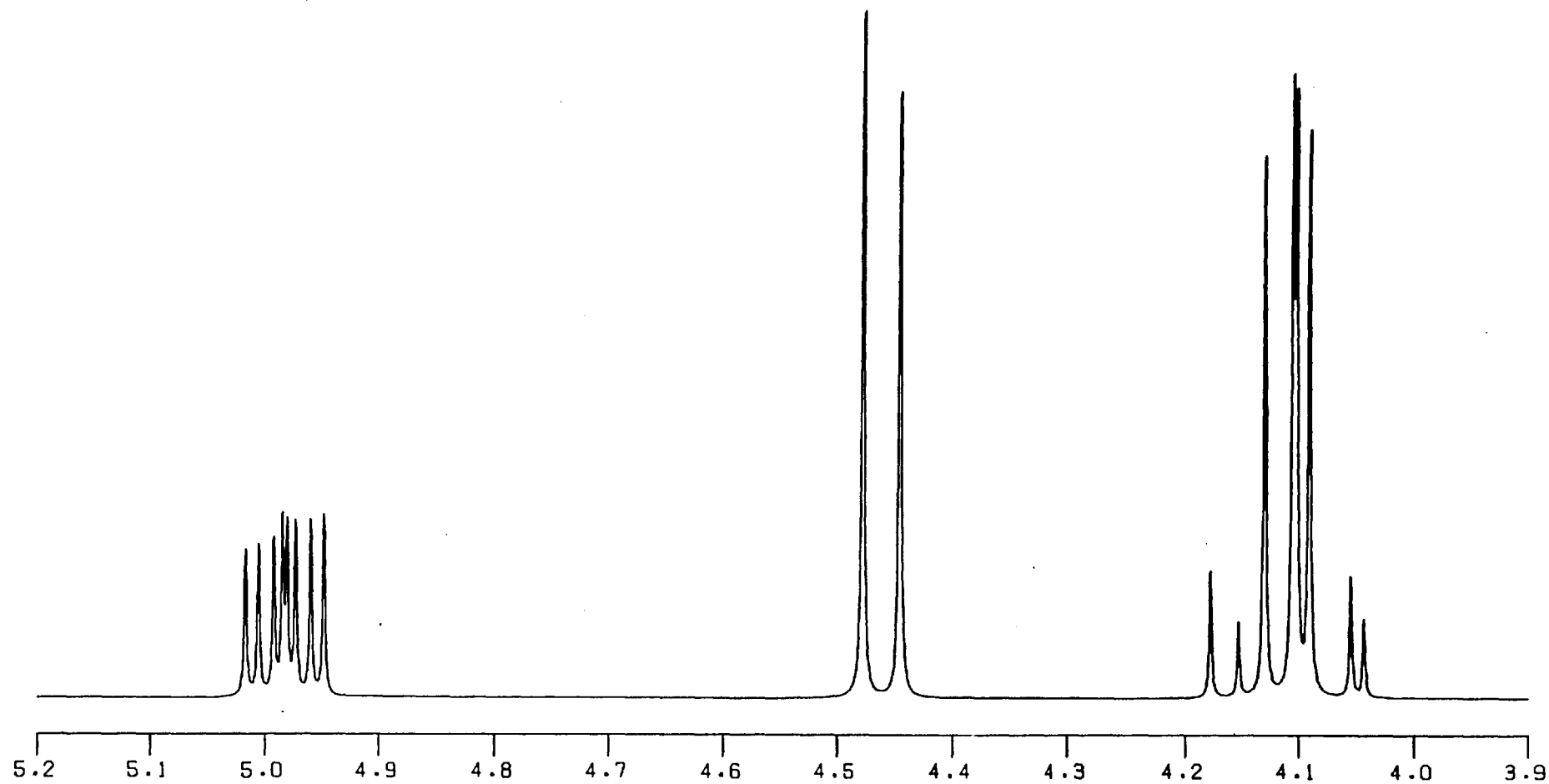


Fig 3. Simulated ^1H nmr Spectrum of Complex (33).

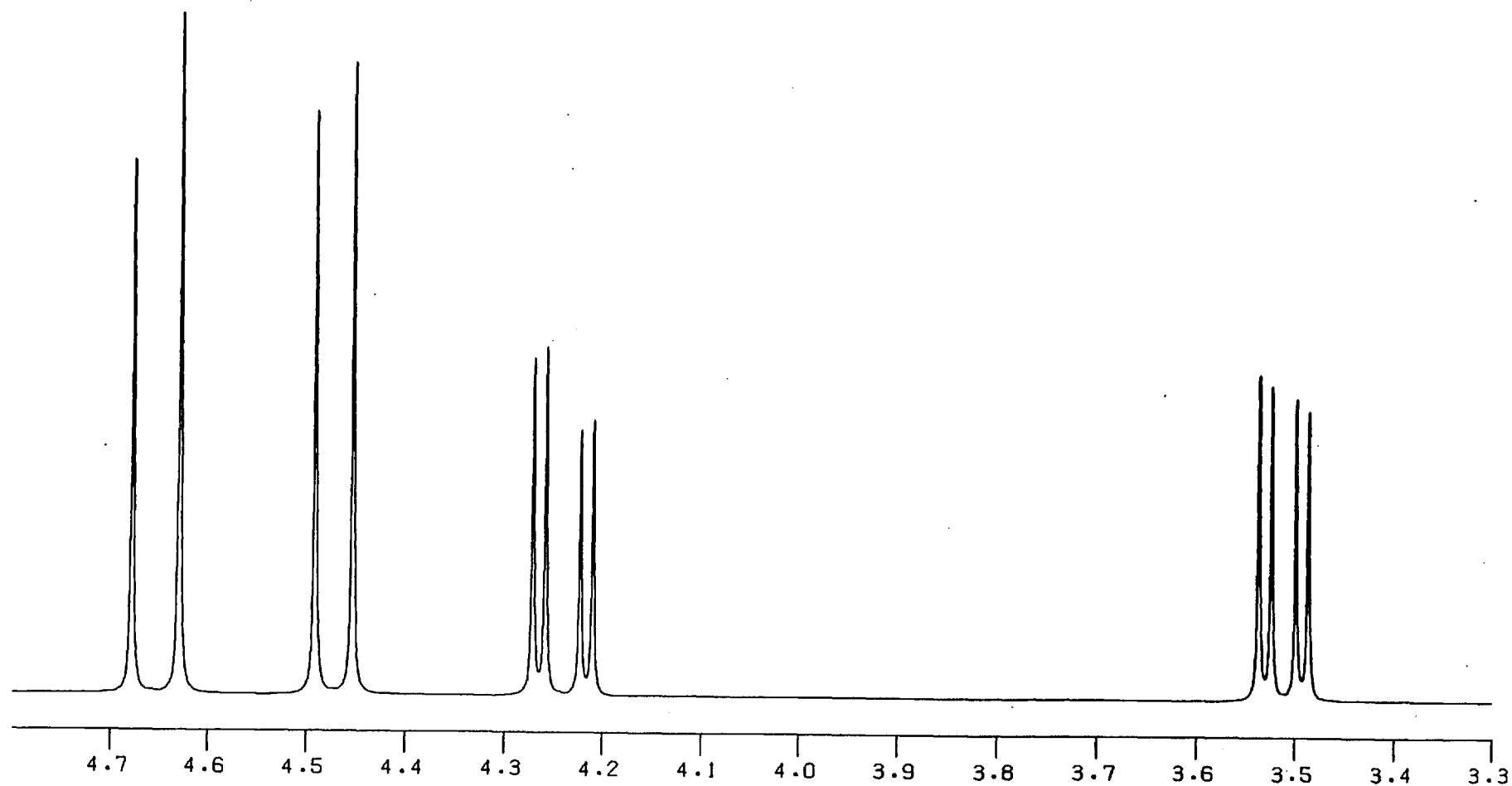


Fig4. Simulated ^1H nmr Spectrum of Complex(34).

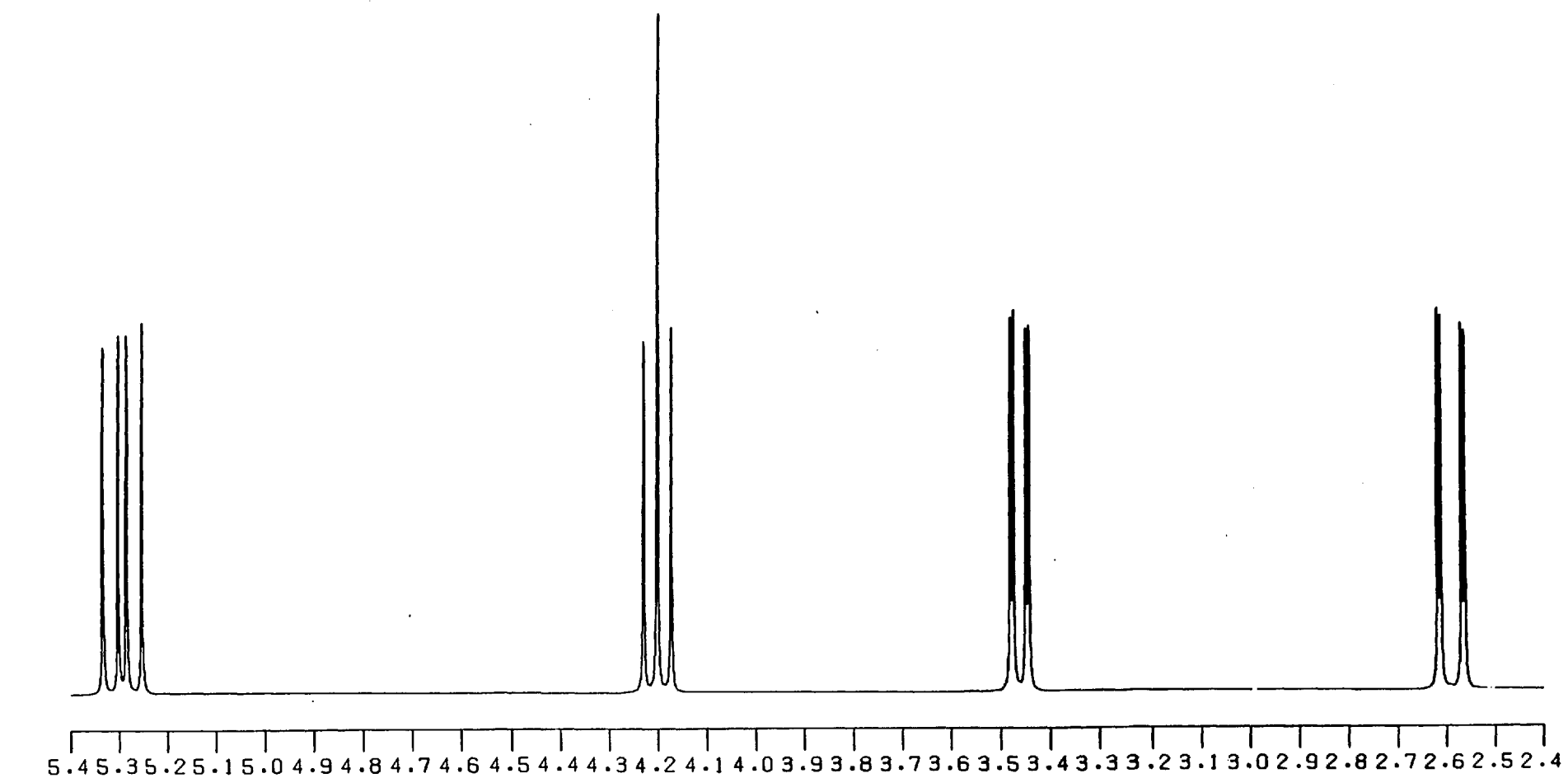


Fig5. Simulated ^1H nmr Spectrum of Complex (47)

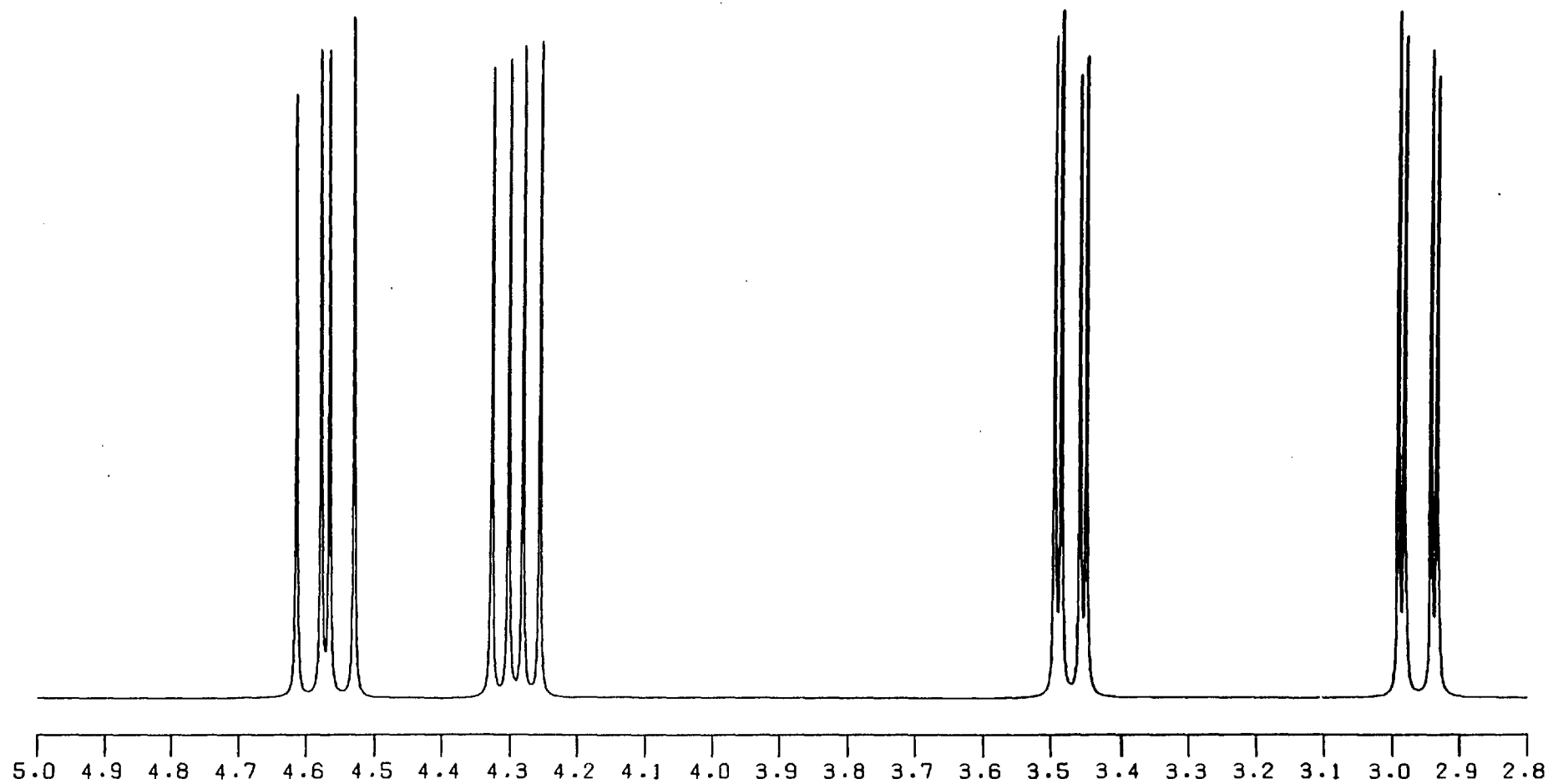


Fig 6. Simulated ^1H nmr Spectrum of Complex(48)

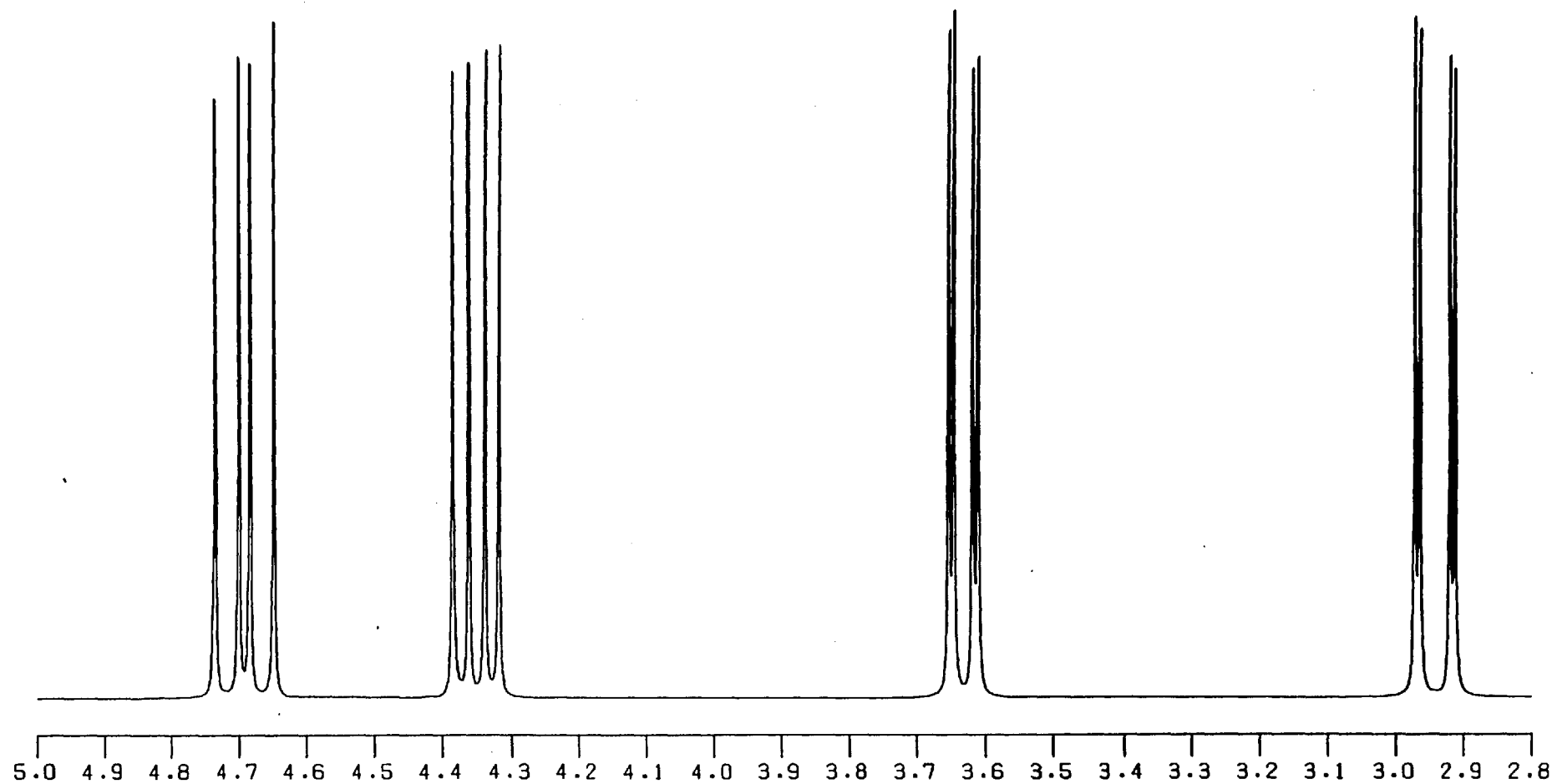


Fig7. Simulated ^1H nmr Spectrum of Complex(45)

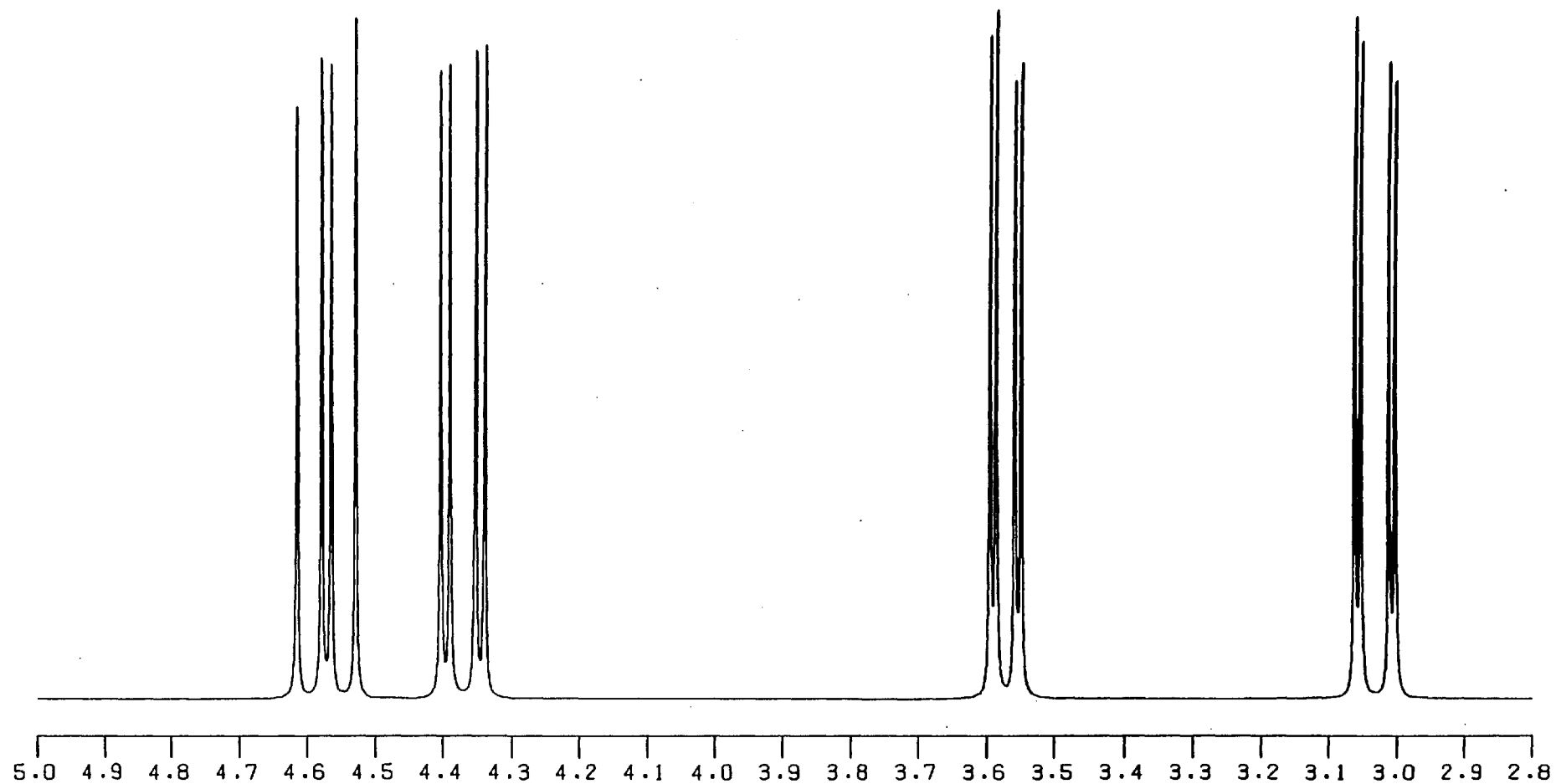


Fig8. Simulated ^1H nmr Spectrum of Complex(46).

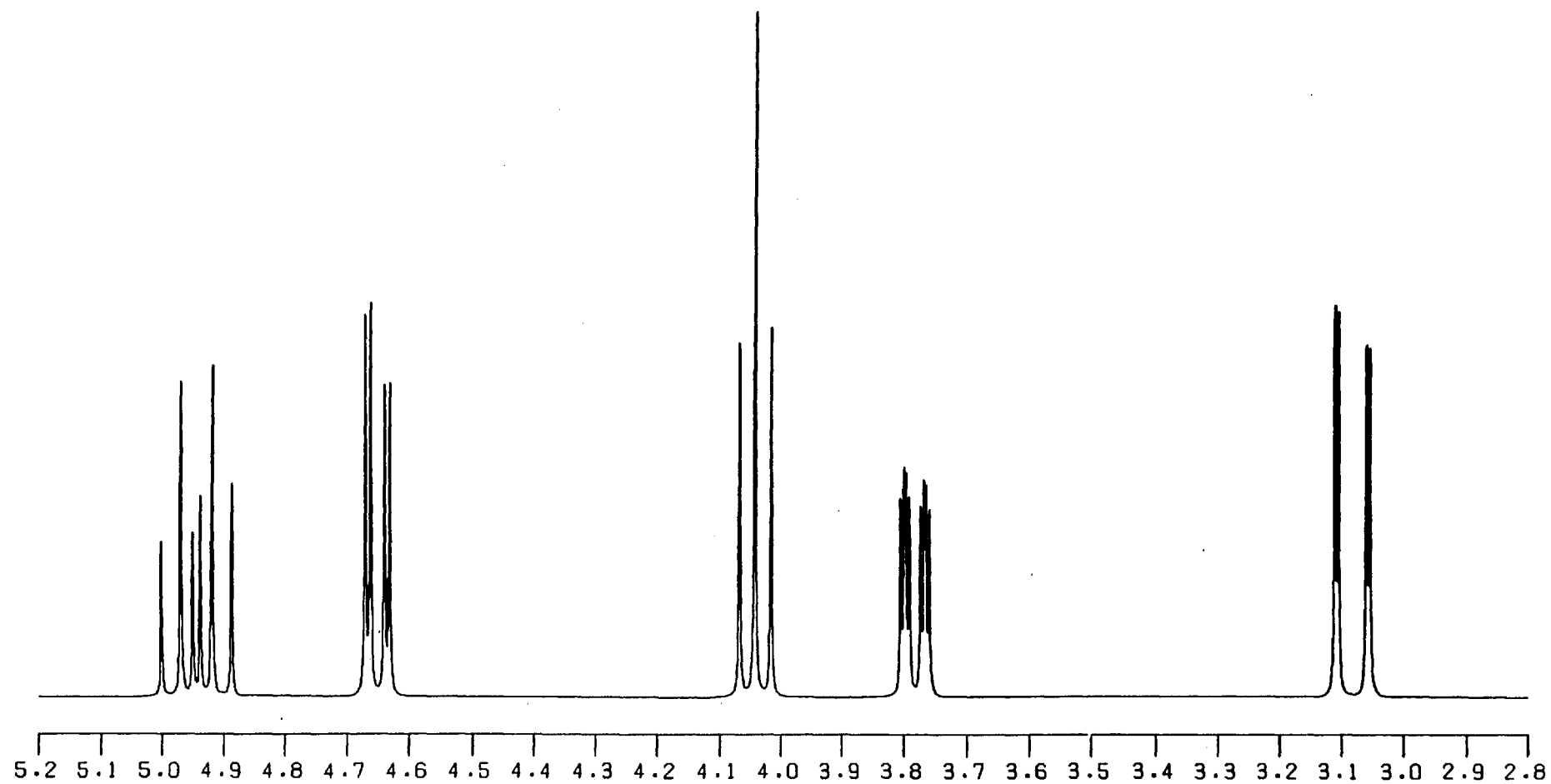


Fig 9. Simulated ^1H nmr Spectrum of Complex(49).

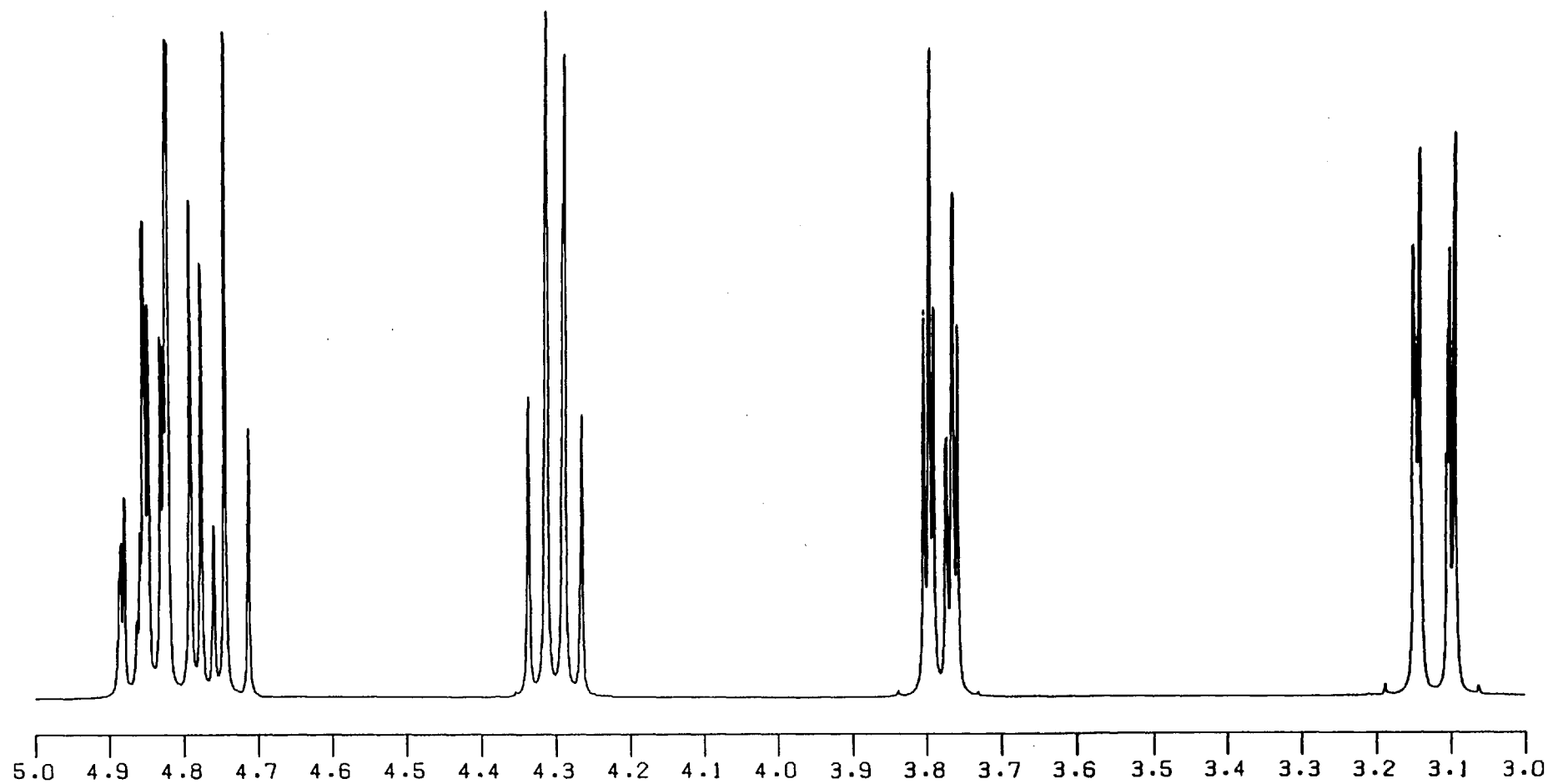


Fig 10. Simulated ^1H nmr Spectrum of Complex(50)

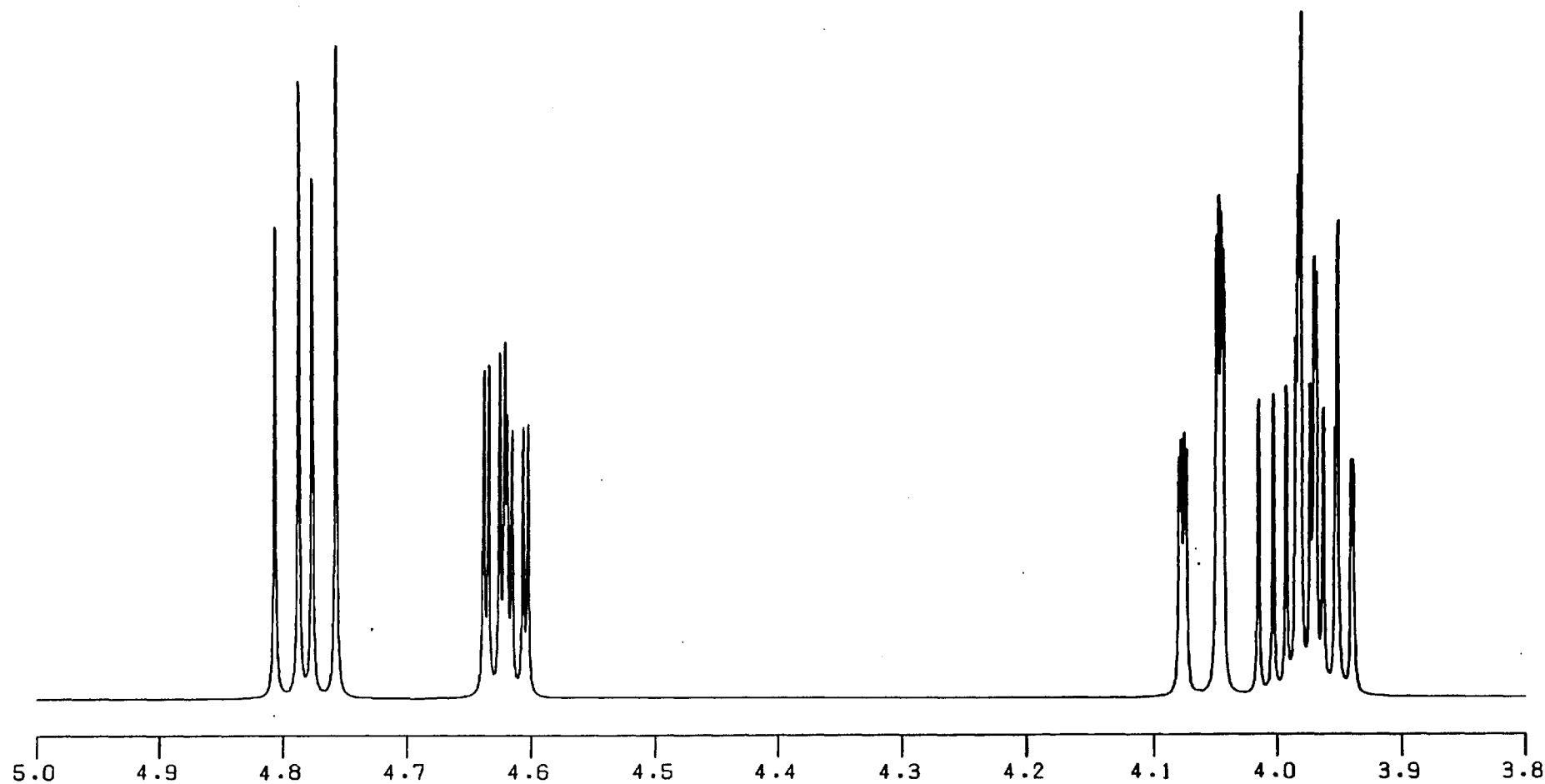


Fig 11. Simulated ^1H nmr Spectrum of Complex(100)

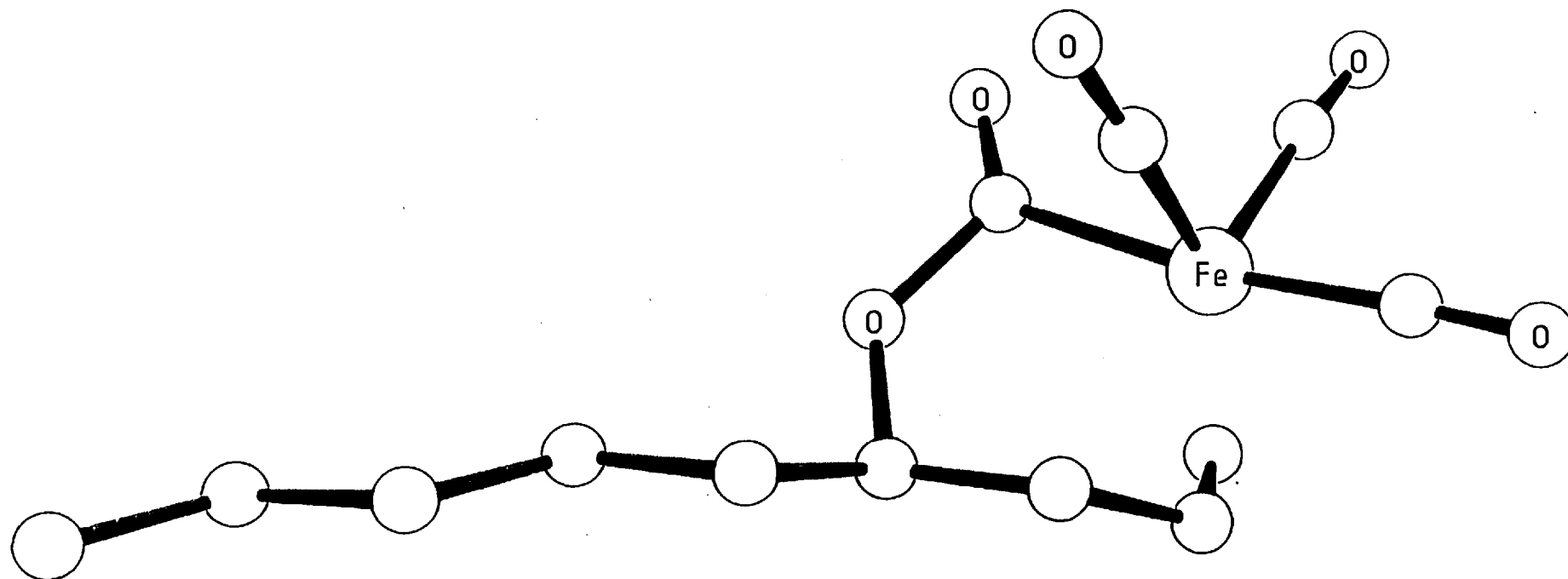


Fig 12. The Molecular Structure of the Tricarbonyliron Lactone Complex (49).

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. I.R. spectra were recorded with Perkin-Elmer 237 and 298 grating spectrometers. Spectra of solids were obtained from nujol mulls, and oils from thin films or solution in chloroform. ^1H n.m.r. spectra were recorded with a Varian E.M. 360A or XL100 spectrometer. High field ^1H n.m.r. spectra were obtained on Bruker WH-250 or WH400 FT spectrometers with 16K and 32K transforms respectively. Spectra were obtained for solutions in deuteriochloroform with tetramethylsilane as internal standard unless otherwise stated. Apparent J values are quoted throughout. Mass spectra were recorded with a V.G. Micromass 7070 spectrometer. Reaction solvents were purified and dried by literature methods, product solutions being dried over sodium sulphate unless otherwise stated. Chromatography was performed on Merck-Kieselgel 60 (0.04 - 0.063mm) and plc carried out on Merck-Kieselgel GF 254.

Cyclohexene 4,5-cis diol (6).

(a) Cyclohexene 4,5-cis diol was prepared from 1,4-cyclohexadiene mono epoxide (12.5g, 130mmol) according to a literature procedure.⁶ The product was recrystallised from diethyl ether/40-60 petroleum ether, to afford the cryst-

alline diol (6) (10.2g, 57%), m.p. 80-81°C (lit⁶, 80.3 - 81.1°C), δ 1.87 - 2.7 (6H, M), 3.7 - 4.1 (2H, brs) and 5.47 - 5.63 (2H, t J $\approx$ 1Hz).

(b) Cyclohexene 4,5-cis diol was prepared from 1,4 cyclohexadiene (47.5g, 59.4 mmol) according to a literature procedure.⁷ The product was recrystallised from diethyl ether/40-60 petroleum ether, to afford the crystalline diol (6) (33.2g, 49%), m.p. 80-81°C (lit⁷ 80.5 - 81.5°C), δ 2.3 (4H, m), 2.78 (2H, brs D₂O exchangeable), 3.92 (2H, brs) and 5.57 (2H, t).

Cyclohexene 4,5-cis diol diacetate (7)

(a) To a stirred solution of cyclohexene 4,5-cis diol (0.85g, 7.46mmol), in pyridine (5.4ml) at -25°C, was slowly added over a period of 30 min, acetyl chloride (1.17g, 14.9mmol). The reaction mixture, after 1h at ambient temperature was diluted with ether (20ml) and the pyridine hydrochloride removed by filtration. The organic phase was washed respectively with dilute hydrochloric acid (2 x 50ml of 2M HCl), saturated aqueous sodium chloride (20ml) and dried. Removal of the solvent at reduced pressure afforded the diacetate (7) (0.92g, 62%), δ 1.97 (6H, s), 2.27 (4H, m), 4.93 (2H, m) and 5.47 (2H, brs).

(b) Cyclohexene 4,5-cis diol monoacetate (0.5g, 74.6mmol) was combined with pyridine (30ml) and acetic anhydride (7.6g,

7.45mmol) for 36h at 0°C, followed by partition between diethyl ether (500ml) and water (200ml). The aqueous phase was continually extracted with diethyl ether (4 days), the combined ethereal solutions dried, and the solvent removed at reduced pressure. Residual pyridine was removed under high vacuum to yield the diacetate (7) (7.65g, 77%), $\nu_{\max}$ 3040, 2950, 2870, 1740, 1660, 1250 and 1170 cm^{-1} , δ 2.04 (6H, s), 3.37 (4H, m), 5.03 (2H, m) and 5.62 (2H, brs).

1,2-Dibromo cyclohexan 4,5-cis diol diacetate (8)

To a stirred solution of cyclohexene 4,5-cis diol diacetate (4g, 20.2mmole) in anhydrous chloroform/20ml) and methylene chloride (20ml) at -30°C, was added bromine (3.15g, 20.2mmole) in chloroform (5ml). The rate of addition was such that the solution never became orange in colour. On completion of addition the reaction was allowed to attain ambient temperature, and the solvent removed at reduced pressure to afford the dibromide (8) (7.2g, 100%), δ 1.93 (3H, s), 2.07 (3H, s), 2.17 - 2.77 (4H, m) and 3.67 - 5.5 (4H, m).

General Procedure for Dehydrobromination of 1,2-Dibromides and Allylic Bromides

Method A

The substrate was combined with lithium fluoride, lithium carbonate and powdered soft glass in anhydrous hexamethylphosphoric triamide, and heated at 90°C with stirring under dry argon. The reaction was followed by tlc and UV spectroscopy and on completion the cooled reaction mixture was partitioned between 40-60 petroleum ether and saturated aqueous sodium chloride. The organic phase was washed respectively with distilled water, saturated aqueous sodium chloride, and dried. Removal of solvent at reduced pressure afforded crude product.

Method B

The substrate was combined with dry lithium chloride and lithium carbonate in anhydrous hexamethyl phosphoric triamide, and heated at the appropriate temperature, with stirring under dry argon. Upon completion (as shown by tlc and UV spectroscopy) the cooled reaction mixture was worked up as above.

Dehydrobromination of 1,2-dibromo cyclohexan 4,5-cis diol diacetate (8)

Reactions were carried out under the conditions shown in table 1. The crude reaction product was analysed

by UV spectroscopy ($\lambda_{\text{max}} = 257\text{nm}$, $\log_{10} \epsilon = 3.62$) to estimate the yield of diene produced by reaction.

The material from reaction (d) was subjected to short path distillation at reduced pressure (82°C at 0.4 mmHg) to afford 1-bromo cyclohex-1-ene 4,5-cis diol diacetate (10) (1.24g, 41%), ν_{max} 1740, 1650, 1360, 1240 and 1045cm^{-1} , δ 2.0 (6H, s), 2.17 - 2.5 (2H, m), 2.45 - 2.83 (2H, m), 5.0 - 5.22 (2H, m) and 5.77 - 6.0 (1H, m), and m/e . 278, 276 (M^+), 218 and 216.

DIBROMIDE (7)	REACTION CONDITIONS	CRUDE PRODUCT	ESTIMATED DIENE CONTENT
(a) 300 mg s, 0.84mmol	LiF 200mgs, 7.7 mmol Li ₂ CO ₃ 600mgs 8.1mmol HMPA 2ml, glass 40mgs 10h at 90°C	δ 2.05(s), 2.17 - 2.5 (m), 2.58 - 2.87(m), 5.0 - 5.33(m) 5.5 - 5.67 (m) and 5.7 - 6.0(m)	37mgs, 22%
(b) 1.5g, 4.19mmol	LiF 1g, 38.5mmol Li ₂ CO ₃ 3g, 40.6mmol HMPA 5ml, glass 0.2g 12h at 90°C	0.62g, δ 2.08(s), 2.14 - 2.88(m) and 5.0 - 6.0(m)	0.1g, 12.5%
(c) 1.5g, 4.19mmole	LiF 1g, 38.5mmol Li ₂ CO ₃ 3g, 40.6mmol HMPA 5ml (freshly distilled) glass 0.2g, 12h at 90°C	0.595g, δ 2.1(s), 2.28 - 2.89(m) and 4.95 - 5.94(m)	87.6mgs, 10.5%
(d) 3.9g, 10.9mmole	LiF 2.6g, 10mmol Li ₂ CO ₃ 7.8g, 10.5mmol HMPA 13ml, glass 0.5g, 10h at 90°C	1.8g, subject to distillation at reduced pressure	-

TABLE 1: DEHYDROBROMINATION OF DIBROMIDE (8) VIA METHOD A

(e) 1,2-Dibromo cyclohexan 4,5-cis diol diacetate (1.3g, 3.6mmol) was combined with lithium chloride (0.3g, 7.1mmole), lithium carbonate (0.6g, 8.1mmole) in anhydrous hexamethyl phosphoric triamide (8ml), and heated at 100°C with stirring under argon. The reaction was followed by UV spectroscopy (table 2) and upon work up afforded an oil, 0.43g, δ 2.1(s), 2.2 - 2.8(m), 4.9 - 5.4(m), 5.5 - 5.8(m), 5.8 - 6.05(m) and 6.5 - 7.5(m).

TABLE 2

TIME t(min)	% DIENE BY UV SPECTROSCOPY, $\lambda_{\max} 257\text{nm}$
75	61
105	25
135	20
180	18

3-Bromo Cyclohex-1-ene 4,5-cis diol diacetate (12)

Cyclohexene 4,5-cis diol diacetate (3.1g, 15.6 mmol) and N-bromosuccinimide (3.1g, 17.4 mmol) in carbon tetrachloride (50ml) was refluxed under irradiation from a tungsten lamp for 2h. The cooled mixture was filtered and the solvent removed under reduced pressure to give the bromide (12) (4.3g, 98.8%), δ 2.05(6H, m), 2.2 - 2.67 (2H, m) and 4.43 - 5.23 (5H, m) and m/e 279 and 277, 219

and 217, and 175 and 173.

Dehydrobromination of 3-bromo cyclohex-1-ene 4,5-cis diol diacetate (12)

The dibromide (12) (0.27g, 0.97mmole) was combined with lithium fluoride (0.15g, 5.8mmol), lithium carbonate (0.5g, 6.8mmole) and powdered soft glass (0.02g) in anhydrous hexamethylphosphoric triamide (1ml) at 90°C for 12h. Reaction was followed by UV spectroscopy, and work up in the normal manner afforded an oil, 0.081g, δ 2.03(s), 2.17 - 2.45(m), 5.0 - 5.28(m), 5.33 - 5.63(m), 5.78 - 6.22(m) and 6.83 - 7.67(m).

Cyclohex-1-ene 4,5-cis diol isopropylidene (15)

Cyclohexene 4,5-cis diol (20g, 175mmol), was combined with anhydrous copper sulphate (56g, 350mmol), anhydrous acetone (410ml, 50eqvs) and concentrated sulphuric acid (1ml) and shaken continuously for 48h. The reaction mixture was neutralised by the addition of excess dry calcium hydroxide and filtered. Removal of the solvent by distillation at atmospheric pressure, followed by distillation of the residue at reduced pressure gave the isopropylidene derivative (15) (27g, 100%), b.p. 65 - 69°C at 20mm Hg (lit.⁷, 67-69°C at 22 mmHg), δ 1.23(3H, s), 1.33 (3H, s), 2.2 (4H,m), 4.17 (2H,m) and 5.68 (2H, t).

1,2-Dibromo cyclohexan 4,5-cis diol isopropylidene (16)

1,2 Dibromo cyclohexan 4,5-cis diol isopropylidene was prepared by reaction of cyclohexene 4,5-cis diol isopropylidene (27g, 175mmole) and bromine (20.8g, 175mmol) in the presence of sodium carbonate (21g) at -30°C in chloroform. Yield, 38.8g (95%), δ 2.33 (3H, s), 1.53 (3H, 5), 1.73 - 3.0 (4H, m) and 4.2 (2H, t).

Dehydrobromination of 1,2-dibromo cyclohexan 4,5-cis diol isopropylidene (16)

(a) The dibromide (16) was treated with a variety of bases, the reaction being followed by UV spectroscopy. The results of reaction are summarised in table 3.

Dehydrobromination of 1,2-dibromo cyclohexan 4,5-cis diol Isopropylidene (16)

(a) The dibromide (16) (300mgs, 0.96 mmol), lithium fluoride (200mgs, 7.6mmol), lithium carbonate (600mgs, 8.1mmol) and hexamethylphosphoric triamide (1.5ml) were heated at 90°C under argon, the reaction being followed by UV spectroscopy (λ_{max} . 274nm, $\log_{10} \epsilon \approx 3.6$). The results of this experiment are summarised in table 4.

DIBROMIDE (16)	REACTION CONDITIONS	ISOLATED PRODUCT	ESTIMATED DIENE CONTENT
(a) 500mgs, 1.6mmol	DBU 395mgs, 3.2mmol 60-80° petroleum ether, Δ 7h.	754mgs, δ 2.0-3.0(m), 3.03-3.5(m), 3.67-4.67(m) and 5.67-6.0(m)	5%
(b) 500mgs, 1.6mmol	tetramethylguanidine 366mgs, 3.2mmol, 60-80 petroleum ether, Δ 7h	679mgs, 1.33(s), 1.53(s), 1.87-3.03(m), 3.67-4.67(m), 5.0(s) and 5.67-6.0(m)	5%
(c) 2.75g, 8.75mmol	110°C, sodium isopropoxide 30.5mmol, triglyme ¹²	no characterisable material obtained.	-
(d) 500mgs, 1.6mmol	sodium methoxide 344mgs, 6.4mmol, diethylether, Δ, 2h.	dibromide (16) (421mgs, 77%) δ 1.3(3H,s), 1.5(3H,s), 1.67-3.0 (4h,m) and 3.67-4.57 (4H,m)	20%
(e) 500mgs, 1.6mmol	potassium t-butoxide, 360mgs, 3.2mmol, 1h 0°C, 6h, RT.	265mgs, δ 1.25(s), 1.47(s), 1.67-3.0(m), 3.67-4.83(m) and 5.4-6.0(m)	4%
(f) 1g, 3.2mmol	potassium t-butoxide, 1.06g, 9.6mmol, -15°C, 2h, Et ₂ O.	812mgs, δ 1.1-1.6(m), 1.67-2.73(m), 4.27(m) and 5.6-6.27(m). Integral ratio 6:3:8:2	-

TABLE 3: REACTION OF THE DIBROMIDE (16) WITH VARIOUS BASES

TABLE 4

TIME t (min)	% DIENE
30	47
60	55
90	47
120	45

(b) The dibromide (16) (300mgs, 0.96 mmol), lithium chloride (100mgs, 2.36mmol), lithium carbonate (150ml, 2mmol) and anhydrous hexamethylphosphoric triamide (2.5ml) were heated at 100°C under argon, the reaction being followed by UV spectroscopy. The results of this experiment are summarised in table 5.

TABLE 5

TIME t (min)	% DIENE
30	63
60	63
90	74
120	67
150	64

(c) This procedure was repeated on a larger scale, the results being summarised in table 6.

DIBROMIDE (16)	REACTION CONDITIONS	ISOLATED PRODUCT	ESTIMATED DIENE CONTENT
260 mgs	LiCl, 100mgs Li ₂ CO ₃ , 160mgs HMPA, 2.6ml, 100°C, 2h.	-	38mgs, 30%
1.98g	LiCl, 0.76g Li ₂ CO ₃ , 1.2g HMPA, 20ml, 100°C, 2.5h.	1.5g, δ 1.13-1.5(6H,m), 2.03-2.7(4H,m), 3.03-4.53(4H,m) and 6.53-7.3(m)	270mgs, 28%
1g	LiCl, 0.4g Li ₂ CO ₃ 0.6g HMPA, 10ml, 100°C, 2h.	0.8g, δ 0.77-1.17(m), 1.33-2.83(m), 3.97-4.77(m) and 5.0-6.67(m)	68mgs, 14%
5g	LiCl 2g Li ₂ CO ₃ 3g HMPA, 50ml, 100°C, 2h.	3.2g, δ 1.2-2.76(m), 4.1-7.35(m).	290mgs, 12%

TABLE 6

3,6-Dibromocyclohex-1-ene 4,5-cis diol diacetate (20)

A solution of cyclohexene 4,5-cis diol diacetate (1.22g, 6.16mmol) and N-bromosuccinimide (2.2g, 1.3mmol) in dry carbon tetrachloride (10ml) was brought to reflux and irradiated with a 500W tungsten lamp, the reaction being followed by tlc. On completion of reaction (2h), the cooled mixture was filtered, and the solvent removed at reduced pressure to yield (20) (2.19g, 100%), ν_{max} . 1740, 1225, 1050, 800 and 780cm^{-1} , δ 2.0 (6H, m), and 4.23 - 6.2 (6H, m).

3,6-Dibromo cyclohex-1-ene 4,5-cis diol bis methoxy ethyl methyl ether (21)

A solution of cyclohexene 4,5-cis diol bis methoxy ethyl methyl ether (200mgs, 0.69mmol) and N-bromo-succinimide (245.5mgs, 1.38mmol) in dry carbon tetrachloride (10ml) was brought to reflux and irradiated with a 500W tungsten lamp, the reaction being followed by tlc. On completion of reaction (0.5h), the cooled mixture was filtered and the solvent removed at reduced pressure to afford (21) (286.3mgs, 92%), δ 3.0 - 3.83 (12H, m), 4.8 (4H, m) and 5.67 (2H, m).

Reaction of 3,6-dibromo cyclohex-1-ene 4,5-cis diol diacetate with disodium tetracarbonylferrate

To a stirred solution of the dibromide (20) (500mgs, 1.4mmol) in dry degassed THF (20ml) at -15°C , was

added, portionwise, disodium tetracarboxylferrate (806mgs, 3.76mmol), the reaction being followed by tlc. On completion (4h), the reaction mixture was diluted with ether (50ml), filtered under argon and the solvent removed at reduced pressure. Chromatography on silica gel (eluted with 40-60 petroleum ether) afforded a yellow oil which was subjected to short path distillation, 331.4mgs, b.p. 20-100°C 10.5mmHg, ν_{max} . 3400, 2900, 1750, 1600, 1240, 1060 and 760 cm^{-1} , and δ 2.0(m), 2.43(m), 4.33 - 6.17(m) and 6.67 - 7.33(m).

Reaction of 3,6-dibromo cyclohex-1-ene 4,5-cis diol bis-methoxy ethyl methylether with disodium tetracarboxylferrate

In a similar manner the dibromide (21) (286mgs, 0.64mmol) was treated with disodium tetracarboxylferrate (425mgs, 1.98mmol) at -15°C in THF (10ml). The residue from work-up was subjected to plc (8:2 diethyl ether/40-60 petroleum ether as eluant) to give three major components.

Component 1. 172mgs, δ 1.22(s) and 7.17 - 7.33(m), and m/e 240, 210, 184, 182, 165, 149 and 105.

Component 2. 46.4mgs, δ 1.27(s), 3.3 - 4.37(m), 4.77(d) and 5.13 - 6.0(m), and m/e 288, 219, 147, 89 and 59.

Component 3. 14.3mgs, δ 1.23(s), 3.27 - 4.33(m) and 4.75(d) and m/e 495, 467, 439, 383, 367, 339, 311, 257, 224, 183, 167, 149 and 89.

Reaction of 3,6-dibromo cyclohex-1-ene 4,5-cis diol diacetate with zinc dust

The dibromide (20) (200mgs, 0.56mmol) was combined with activated zinc dust (42mgs, 0.62mmol) and acetic acid (1 drop) in THF (10ml), and heated to reflux. On completion (as indicated by tlc) the solvent was removed at reduced pressure and the residue subjected to plc (1:1 diethyl ether/40-60 petroleum ether as eluant) to yield two components.

Component 1. 15.8mgs, δ 1.87(brs), 2.22(s), 4.71(brs) and 6.68 - 7.26(m).

Component 2. 39.9mgs, 2.0(m), 6.0 - 6.5(m) and 6.8(m).

Pyran-2-one (22)

Pyran-2-one was prepared according to a literature procedure¹⁵ by thermal decarboxylation of coumalic acid, b.p. 78-80°C at 0.75mmHg, δ 6.13 - 6.47(2H, m) and 7.23 - 7.63 (2H, m).

Vinylene carbonate (24)

Vinylene carbonate was prepared by radical chlorination, dehydrochlorination of ethylene carbonate according to a literature procedure,¹⁶ b.p. 70°C at 30mmHg, $\nu_{\max}$. 3120, 2100, 1980, 1920, 1900-1700, 1560 and 1160cm⁻¹, and δ 7.17(s).

Diels Alder reaction between Pyran-2-one (22) and Vinylene carbonate (24)

Pyran-2-one was combined with vinylene carbonate and a few crystals of hydroquinone (table 7) in a small carius tube sealed under vacuum. The tubes were heated at constant temperature, and upon completion the contents were analysed by ^1H n.m.r. spectroscopy.

1,2-Isopropylidene dioxycyclohexane 4,5-epoxide

1,2-Isopropylidene dioxycyclohexane 4,5-epoxide was prepared from cyclohexene 4,5-cis diol isopropylidene (15) (5g, 32.5mmol) and m-chloroperbenzoic acid (6.58g, 85% technical grade, 1 eqv) according to a literature procedure.⁷ Yield, 4.43g, (80%), b.p. 58°C at 0.05 mmHg (lit⁷., b.p. 53-55°C at 0.2mmHg), δ 1.2(2h, s), 1.35(3H,s), 2.08(4H, m), 2.98(2H, m) and 4.08(2H,m).

4,5-Isopropylidene dioxycyclohex-2-en-1-ol (26)

4,5-Isopropylidene dioxycyclohex-2-en-1-ol was prepared from 4,5-isopropylidene dioxycyclohexane-4,5-epoxide (1.1g, 6.49mmol) and lithium diethylamide (16.22mmol) in diethylether (20ml) according to a literature procedure.⁷ Yield, 1.1g (100%), ν_{max} . 3600-3100, 3030, 2980, 2875, 1235, 1220 and 1060 cm^{-1} , and δ 1.37(6H, s), 1.3 - 1.8(2H, m), 3.0(1H, brs), 4.42(3H, m) and 5.73(2H, m).

Wt. PYRAN-2-ONE	Wt. VINYLENE CARBONATE	REACTION CONDITIONS	RESULT
1.43g, 14.9mmol	3g, 34.8mmol	160°C, 24h	δ 5.48 (s, D ₂ O exchangeable), 7.13(s) and 6.67 - 7.67(m)
90.6mgs, 0.94mmol	172.5mgs, 2mmol	80°C, 12h	δ 6.12(m), 7.2(s) and 7.42(m)
143.4mgs, 1.5mmol	151.3mgs, 1.76mmol	100°C, 12h	δ 6.13(m)
112.7mgs, 1.17mmol	158mgs, 1.83mmol	120°C, 12h	δ 6.2(m), 7.17(s) and 7.43(m)
126.6mgs, 1.32mmol	200mgs, 2.32mmol	140°C, 12h	δ 5.57 (brs, D ₂ O exchangeable), 7.15(s) and 6.68 - 7.6(m)
110mgs, 1.14mmol	190mgs, 2.2mmol	140°C, 5h	34.3mgs (32%), δ 5.21 (1H, s, D ₂ O exchangeable), and 6.75 - 7.45 (5H, m).
186mgs, 1.93mmol	176mgs, 2.04mmol	140°C, 4h	(a) Pyran-2-one (identical by tlc and n.m.r.) (b) 27.8mgs, δ 6.78 - 7.07(m) and 7.17 - 7.46(m). Integral ratio 2:3.
100mgs, 1.04mmol	85mgs, 1mmol	140°C, 4h	(a) Pyran-2-one (identical by tlc and n.m.r.) (b) 26.3mgs, δ 6.74 - 7.04(m) and 7.09 - 7.32(m). Integral ratio 1:1

TABLE 7

1,2-Isopropylidenedioxycyclohex-3-en-5-ol acetate (27)

4,5 Isopropylidenedioxycyclohex-2-en-1-ol (1.1g, 6.49mmol) was combined with dry pyridine (10ml), N,N-dimethyl 4-aminopyridine (79mgs, 0.65mmol), acetic anhydride (664mgs, 6.49mmol), stirring overnight at room temperature. The reaction was partitioned between ether (200ml) and water (50ml), the organic phase washed with water (3 x 50ml), and dried. Removal of the solvent afforded the monoacetate (27), 1.48g (100%), δ 1.38(6H, s), 2.07(3H, s), 1.8 - 2.6(2H, m), 4.45(2H, m), 5.43 (1H, m) and 5.8 (2H, brs). (Found: C, 62.44; H, 7.85. $C_{11}H_{16}O_4$ requires C, 62.25; H, 7.58%).

Exo-5,6-Isopropylidene dioxy cyclohexa-1,3-diene tricarbonyliron (19)

The acetate (27) (500mgs, 2.2mmol) was combined with tetrakis(triphenylphosphine) palladium (127mgs, 5mole%), triethylamine (244mgs, 2.42mmol) and dry THF (20ml) in a sealed bomb. Heating at 85-90°C for 8h, followed by removal of solvent at atmospheric pressure yielded crude diene. Palladium salts were removed by short path distillation at reduced pressure. This material was combined with enneacarbonyl diiron (1.2g, 3.3mmol), p-methoxybenzylidene acetone (41.5mgs, 0.23mmol) in dry degassed diethyl ether (10ml) and heated at reflux. On completion (4½h) the cooled material was subjected to plc to afford the yellow crystalline diene tricarbonyliron complex (19) (100mgs, 14.5%) m.p. 152.5°C, ν_{max} . 2930, 2060, 2000, 1980, 1970, 1605(w), 1420, 1370, 1005 and 910cm⁻¹.

and δ 1.16(3H, s), 1.33(3H, s), 2.88(2H, ddd J 7.8, 2.6, 2.5Hz), 4.54(2H, t) and 5.55(2H, dd J 7.8, 2.6Hz).
(Found: C, 49.64; H, 4.17. $C_{12}H_{12}FeO_5$ requires C, 49.34; H, 4.14%).

1-Epoxyethylcyclopent-1-ene (29)

Sodium hydride (4.4g, 50%, 92mmol) was combined with dry dimethyl sulphoxide (60ml) and heated at 70-75°C under nitrogen until effervescence ceased. The solution was diluted with dry THF (100ml) and cooled to -2°C. To this stirred solution was added over a period of 3min trimethyl sulphonium iodide (18.7g, 92mmol) in dry dimethyl sulphoxide (70ml). The solution was stirred for 1min. further, and formyl cyclopentene (8g, 83mmol) in dry THF (10ml) added, such that the internal temperature of the reaction vessel did not rise above -2°C. The reaction was allowed to attain room temperature, water (100ml) added and extracted with dimethyl ether (3 x 200ml). The ether-eal extracts were dried (K_2CO_3), the solvent removed at reduced pressure, and distillation at reduced pressure yielded the vinyl epoxide (29) (7.58g, 83%), b.p. 80° at 20mmHg, δ 1.70 - 2.80(6H, m), 2.83(2H, m), 3.52(1H, t) and 5.85(-H, t J 1.5Hz). (Found: M^+ 110.0723. $C_7H_{10}O$ requires M 110.0732).

2', 3'-Epoxy propenylidene cyclohexane (32)

Sodium hydride (1.47g, 50%, 31mmol) was combined with dry dimethyl sulphoxide (30ml) and heated at 70-75°C under nitrogen, until effervescence ceased. The solution was diluted with dry THF (30ml), and cooled to -2°C. To this stirred solution was added, over a period of 3min, trimethyl sulphonium iodide (6.32g, 31mmol) in dry dimethyl sulphoxide (25ml). The solution was stirred for 1 min further, and the enal (31) (3.45g, 28mmol) in dry THF (5ml) added, such that the internal temperature of the reaction vessel did not rise above -2°C. The reaction was allowed to attain room temperature, water (50ml) added, and extracted with diethyl ether (3 x 100ml). The ethereal extracts were dried (K_2CO_3), the solvent removed at reduced pressure, and distillation of the residue at reduced pressure afforded the vinyl epoxide (32) (3.17g, 83%), b.p. 65°C at 2mmHg, δ 1.33 - 2.40(10H, m), 2.42(1H, dd J 5, 4Hz), 2.77(1H, dd J 5, 3Hz), 3.32(1H, ddd J 8, 4, 3Hz) and 4.77(1H, d J 8Hz), (Found: M^+ 138.1052. $C_9H_{14}O$ requires M 138.1045).

1,2-Dimethylenecyclohexane

1,2-Bis acetoxymethyl cyclohexane (89.4g) was slowly distilled over 1.5h into a quartz tube packed with quartz chips (2M x 0.025m) maintained at 580°C, the pyrolysate being collected on a cold finger maintained at

-78°C. The material collected on the cold finger was diluted with water (500ml), extracted with ether (5 x 200ml), and dried. Removal of solvent by distillation, and distillation of the residue gave 1,2-dimethylenecyclohexane, 18.3g, 43%, δ 1.58(4H, m), 2.22(4H, m), 4.57(2H, m) and 4.82(2H, m).

2-Methylenecyclohexane spiro-2'-(epoxide) (35)

1,2-Dimethylenecyclohexane (17.6g, 160mmol) on oxidation with peracetic acid (32g, 38%, 160mmol) in methylene chloride (300ml) containing sodium carbonate (42g) afforded the vinyl epoxide (35) (11.2g, 55%) b.p. 75°C at 47mmHg, δ 0.7 1 2.48(δ H, m), 2.67(2H, s), 4.73 (1H, s), and 4.88(1H, s).

General Procedure for Tricarbonyliron Lactone Complex Formation

Method A

A solution of the vinylepoxide ($\approx$ 0.01M) and pentacarbonyliron in dry degassed benzene was irradiated at room temperature under an argon atmosphere with external 2 x 450W Hanovia medium pressure Hg lamps through Chance OXI filters. The reaction was followed by IR spectroscopy until formation of the complex was maximised (2-6h). Removal of the benzene and excess pentacarbonyliron by freeze-drying gave crude product. The product was stirred

with ether and filtered through a pad of celite. Trituration with petroleum ether afforded the crystalline complex.

Method B

A solution of the vinyl epoxide ($\approx 0.01M$) and pentacarbonyliron in dry degassed benzene was irradiated (10-15 min) using a 450W Applied Photophysics lamp in an internal well system and circulating sodium bromide filter solution.³¹ The product was worked-up as above.

Preparation of tricarbonyl-(1,1',2- η -ethylcyclopent-1-ene-1-yl) -2'-oxycarbonyliron (30)

Using Method B (29) (1.53g, 13.9mmol), $Fe(CO)_5$ (15.3g, 78.1mmole) in benzene (11t) gave tricarbonyl - (1,1',2- η -ethylcyclopent-1-ene-1-yl) -2'-oxycarbonyliron (30) (2.77g, 72%) m.p. 88.5 - 89.5°C (decomp.), ν_{max} . 2970, 2100, 1990 and 1670 cm^{-1} , δ 1.12 - 3.24(6H, m), 3.94 - 4.38(3H, m) and 4.73(1h,d J 4Hz) (Found: C, 47.52; H, 3.65. $C_{11}H_{10}FeO_5$ requires C, 47.48; H, 3.6%).

Preparation of tricarbonyl-1,1',2'- η -1,1-propylidenecyclohexane-1-yl) -3'-oxycarbonyliron (33)

Using Method B (32) (1.23g, 8.9mmol), $Fe(CO)_5$ (15.3g, 78.1mmol) in benzene (11t) gave tricarbonyl- (1,1', 2'- η -1,1-propylidenecyclohexane-1-yl) -3'-oxycarbonyliron (33) (1.27g, 46%), m.p. 51-53°C (decomp.), ν_{max} . 2938, 2855,

2075, 2015, 1660 and 1100 cm^{-1} , δ 1.24 - 2.76(10H, m), 3.86 - 4.70(3H, m) and 4.98(1H, m) (Found: C, 50.88; H, 4.60. $\text{C}_{13}\text{H}_{14}\text{FeO}_5$ requires C, 51.01; H, 4.61%).

Preparation of tricarbonyl-(2,3,4- η -2,3-(tetramethylene)-2-buten-2-yl)-1-oxycarbonyliron (36)

Using method A (35) (1.46g, 11.8mmol), $\text{Fe}(\text{CO})_5$ (17.5g, 89.2 mmol) in benzene (750ml) gave tricarbonyl-(2,3,4- η -2,3-(tetramethylene)-2-buten-2-yl)-1-oxycarbonyliron (36) (1.12g, 32.4%), m.p. $83-84^\circ\text{C}$ (decomp.), ν_{max} . 2900, 2050, 1990, 1650, 1380, 1045, 995, 950, and 660cm^{-1} , and δ 1.33 - 2.5(8H, m), 2.53(1H, d J 3Hz), 3.15(1H, d J 3Hz), 3.77(1H, ABq J 11.5Hz) and 4.13(1H, ABq J 11.5Hz).

General Procedure for Oxidation with Ceric Ammonium Nitrate

The complex was added in one portion to a stirred solution of ceric ammonium nitrate at low temperature in an appropriate solvent. After complete oxidation (2-6h) (as indicated by tlc) solvent was removed under reduced pressure. The residue was dissolved in the minimum amount of water and extracted with ether. The combined extracts were dried, and solvent removed under reduced pressure to afford the lactones which were purified by chromatography.

Oxidation of Tricarbonyliron Lactone complex (30)

Tricarbonyliron Lactone complex (30) (500mgs, 1.8mmol) with ceric ammonium nitrate (4.93g, 9mmol) in absolute ethanol at -15°C , gave after colour chromatography at 0°C on silica gel (1:1 diethyl ether/40-60 petroleum ether as solvent) 3-(cyclopenten-1-yl) oxetanone (3) (198mgs, 100%), ν_{max} . 2950, 2860, 1825, 1635, and 1115cm^{-1} , δ 1.92(2H, m), 2.36(4H, m), 4.21(1H, dd J 3.8, 3.7Hz), 4.42(1H, dd J 10.7, 3.7Hz), 4.52(1H, dd J 10.7, 3.8Hz) and 5.5(1H, brs) (Found: M^+ 138.0677, $\text{C}_8\text{H}_{10}\text{O}_2$ requires M, 138.0681).

Oxidation of tricarbonyliron lactone complex (33)

Tricarbonyliron lactone complex (33) (300mgs, 0.98mmol) with ceric ammonium nitrate (2.16g, 3.94mmol) in methanol at -78°C gave after column chromatography on silica gel at 0°C an oil (ν_{max} . 2940, 1820cm^{-1}) which was immediately reduced to the diol (40) with lithium aluminium hydride in diethyl ether (see later).

General Procedure for the Reduction of the Lactones with Lithium Aluminium Hydride

A solution of the lactone in dry THF or diethyl ether was added dropwise to a slurry of lithium aluminium hydride in the same solvent at low temperature. The reaction was stirred overnight at room temperature, and

saturated aqueous sodium sulphate added to the mixture to produce a white precipitate. The mixture was filtered and the precipitate washed with copious amounts of ether. The combined organic phases were dried and upon removal of solvent afforded the crude diol.

Reduction of β -Lactone (37)

β -lactone (37) (100mgs, 0.73mmol) with lithium aluminium hydride (100mgs, 2.6mmol) in diethyl ether (10ml) gave 2-(cyclopenten-1'-yl)-propan-1,3-diol (38) (36.2mgs, 35%), m.p. 45-46°C, δ 1.62 - 2.48(8H, m), 2.66(1H, t J 5Hz), 3.76(2H, d J 5Hz), 3.86(2H, d J 5Hz) and 5.46(1H, brs) (Found: C, 67.41; H, 9.90. $C_8H_{14}O_2$ requires C, 67.57; H, 9.92%).

Reduction of β -Lactone (39)

The crude product from oxidation of complex (33) with lithium aluminium hydride (200mgs) in diethyl ether (25ml) gave 2-(cyclohexylidene)-isopropane 1,3-diol (40) (72.1mgs, 43.2%), δ 1.35 - 2.5(10H, m), 3.7 - 3.9(2H, m exch. D_2O), 3.66(2H, t J 6Hz) and 4.05(2H, s) (Found: C, 69.11; H, 10.24. $C_9H_{16}O_2$ requires C, 69.19; H, 10.32%).

Reaction of the β -Lactone (37) with Dimethylamine

(a) Anhydrous dimethylamine gas was slowly bubbled through a stirred solution of the β -lactone (37) (50mgs,

0.36mmol) in dry diethyl ether (2ml) at -5°C , until the ether became saturated. After warming to room temperature the solvent was removed at reduced pressure to yield an oil, 66 mgs, ν_{max} . 3380, 2900 and 1625cm^{-1} , δ 1.5 - 2.53(m), 2.98(s), 3.2 - 4.27(m) and 5.47(brs).

(b) To a stirred solution of the lactone (37) (50mgs, 0.36mmol) in dry diethyl ether (1ml) at -30°C was slowly added dimethylamine (32.4mgs, 0.72mmol) in diethyl ether (3ml). The reaction was stirred for 1h at 0°C , allowed to reach ambient temperature and the solvent removed at reduced pressure to give as white crystals 2-(cyclopentene-1'-yl) propan-3-ol carboxcyclic dimethylamide (52) (65mgs, 98%), ν_{max} . 3400, 2900 and 1625cm^{-1} , δ 1.38 - 2.45(6H, m), 2.98(6H,s), 3.35 - 4.22(3H, m) and 5.45(1H, brs).

Reaction of the β -lactone (37) with Sodium n-Butyl Thiolate

(a) To the β -lactone (37) (50mgs, 0.36mmol) at 5°C was added over 1h an aqueous solution of sodium n-butyl thiolate (0.36mmol). The resulting mixture was allowed to warm to room temperature, the reaction being followed by tlc. On completion (2h) the reaction was acidified with p-toluene sulphonic acid monohydrate (75.7mgs, 0.4mmol), stirred for 30min and extracted with ether (2 x 50ml). The ethereal solution was dried, and upon removal of the solvent 2-(cyclopentene-1'-yl)-3-thio n-butyl-propanoic acid (53) was obtained (70.8mgs, 85.7%), ν_{max} . 3400, 2850 and

1710cm^{-1} , δ 0.6 - 3.0 (15H, m), 3.57 (3H, m), 5.6 (1H, brs) and 7.0 (1H, brs).

(b) The above procedure was repeated with β -lactone (37) (78.5mgs, 0.57mmol) and an aqueous solution of sodium n-butylthiolate (0.57mmol) to yield after plc two components.

Component 1. 35.3mgs, ν_{max} . 2950, 1750 and 1635cm^{-1} .

Component 2. 52.4mgs, ν_{max} . 3600-3000, 2900 and 1750-1680 cm^{-1} .

Reaction of the β -Lactone (37) with Sodium Thiophenoxide

To a stirred solution of the β -lactone (37) (500mgs, 0.36mmol) in dry acetone (1ml) at 0°C was slowly added over 1h, sodium thiophenoxide (47.8mgs, 0.36mmol) in the same solvent (1ml). The reaction mixture was allowed to attain room temperature overnight acidified (HCl) and diluted with methylene chloride (20ml). The organic phase was extracted with saturated aqueous sodium carbonate (2 x 10ml). These washings were acidified (HCl), saturated with sodium chloride, and extracted with ether (3 x 50ml). The ethereal layer was dried and upon removal of the solvent at reduced pressure the desired adduct 2-(cyclopentene-1'-yl)-3-thio phenyl-propanoic acid (55) was isolated, 3.7mgs (35.3%), ν_{max} . 3600-3000, 2900 and 1710cm^{-1} , δ 1.38 - 1.92 (6H, m), 3.08 - 3.8 (3H, m), 5.62 (1H, m) and 7.32 (5H, m).

(b) The above procedure was repeated using ethanol as solvent, to yield after plc, 2-(cyclopentene-1'-yl)-3-thiophenyl propanoic acid (55) (33.2mgs, 37%), δ 1.53 - 2.57(6H, m), 3.0 - 3.6(3H, m), 5.6(1H, m) and 7.25(5H, m).

Attempted Cyclisation of adduct (53)

(a) The adduct (53) (70.8mgs, 0.31mmol) was combined with anhydrous *p*-toluenesulphonic acid (5.3mgs, 10 mole%) in dry benzene at reflux, the reaction being followed by tlc. After 2.5h, the solvent was removed and the residue subjected to plc to afford as the major component (53) 22.1mgs (31.2% recovery).

(b) The acid (53) (22.1mgs, 0.1mmol) was with tri-fluoroacetic acid (51mgs, 0.45mmol) in dry benzene (5ml), the reaction being followed by tlc. After 1h, the reaction mixture was partitioned between diethyl ether (100ml) and water (100ml). The organic layer was washed with water (2 x 25ml), dried, and the solvent removed at reduced pressure to yield an oil, 15.3mgs, $\nu_{\max}$. 3600-3000 and 1710 cm^{-1} , m/e 105, 91, 85, 83 and 61.

Attempted Cyclisation of the adduct (55)

(a) To a stirred solution of the adduct (55) (33.2mgs, 0.14mmol) in dry benzene (1ml) was added *p*-toluenesulphonic acid monohydrate (25.4mgs, 0.16mmol) and the mixture brought to reflux. After 40h, the cooled solution was

subjected to plc on silica gel (1:1 diethyl ether/40-60 petroleum ether as eluant) to give two major components.

Component 1. 14.8mgs, ν_{max} . 2900, 1740, 1600 and 1100cm^{-1} , and δ 1.07 - 2.33(m), 3.0 - 4.2(m) and 7.17(m).

Component 2. Uncharacterisable baseline material.

(b) To a stirred solution of the adduct (55) (15.8mgs, 0.064mmol) in d_6 benzene (1ml) was added trifluoroacetic acid (36.4mgs, 0.32mmol), the reaction being followed by tlc and ^1H n.m.r. spectroscopy. After 24h, the material was subjected to plc on silica gel (1:1 diethyl ether/40-60 petroleum ether as eluant) to yield an oil, 15.9mgs, ν_{max} . 3600-3000, 2900, 1750 and 1710cm^{-1} , δ 1.33 - 2.58(m), 2.97 - 3.73(m), 5.63(brs) and 7.3(m), m/e. 218 and 123.

Reaction of the β -Lactone (37) with Tin Tetrachloride

To a stirred solution of the lactone (37) (88.2 mgs, 0.64mmol) in dry methylene chloride (10ml) at 123°C under argon, was added tin tetrachloride (333mgs, 1.28mmol) in the same solvent (1ml) (reaction being followed by tlc). After 2.5h, the solvent was removed (at -23°C) the residue taken up into ether (100ml), washed with saturated aqueous sodium hydrogen carbonate (2 x 10ml), and dried. Removal of the solvent and column chromatography at 0°C on silica gel afforded three components.

Component 1. 7.8mgs, ν_{max} . 2920, 2860, 1825, 1725 (bd),

1640 and 1100cm^{-1} .

Component 2. 9.9mgs, ν_{max} . 2970, 1825, 1725(bd), 1650, 1225 and 1150cm^{-1} .

Component 3. 7.5mgs, ν_{max} . 2940, 1825, 1765, 1725, 1640, 1275 and 1100cm^{-1} .

Reactions of the β -Lactone (37) with Titanium Tetrachloride

(a) To a stirred solution of β -lactone (37) (50mgs, 0.36mmol) in dry methylene chloride (10ml) under argon at -78°C was added titanium tetrachloride (75.6mgs, 0.4mmol). The solution was stirred for 1h at -78°C , allowed to warm to 0°C over 1.5h and quenched with saturated aqueous sodium hydrogen carbonate (3ml). The reaction mixture was extracted with ether (3 x 50ml), dried, and the solvent removed to give an oil, 50mgs, ν_{max} . 3600-3100, 2950, 1825(w), 1765(s), 1725(s), 1645 and 1100cm^{-1} . Plc of the crude product yielded two components.

Component 1. 1.8mgs, ν_{max} . 2920, 2760 and 1100cm^{-1} .

Component 2. 4.5mgs, ν_{max} . 2920, 2760, 1645(w) and 1100cm^{-1} .

(b) The above procedure was repeated with (37) (70 mgs, 0.51mmol) and titanium tetrachloride (106mgs, 0.56mmol); the Lewis acid being added as a solution in methylene chloride. Work-up with saturated aqueous ammonium chloride yielded an oil, 73.1mgs, ν_{max} . 2930, 2870, 1825(w), 1775, 1730, 1645 and 1100cm^{-1} . Plc of the crude product afforded as the major product an oil, 53.2mgs, δ 1.2 - 2.4(m),

3.2 - 2.4(m), 3.2 - 4.5(m) and 4.85(m).

3-(1',2'-epoxy cyclopentan-1'-yl) oxetanone (61)

To a stirred solution of the β -lactone (37) (95 mgs, 0.69mmol) in methylene chloride (10ml) was added m-chloroperbenzoic acid (118.8mgs, 0.69mmol), the reaction being followed by tlc. On completion (18h), the cooled solution was filtered, the filtrate washed with saturated aqueous sodium hydrogen carbonate (2 x 10ml) and dried (K_2CO_3). Removal of the solvent at reduced pressure and plc of the crude product led to isolation of a diastereoisomeric mixture of epoxides, 54.6mgs, 51.5%, $\nu_{max.}$, 3015, 2945, 2920, 2840, 1825, 1350, 1315, 1300, 1110 and $890cm^{-1}$, δ 1.27 - 2.2(6H, m), 3.18 and 3.52(1H, s), 3.67 - 4.33 (3H, m).

3-(epoxy cyclohexylidene) oxetanone (63)

To a solution of the β -lactone (39) (19.5mgs, 0.12mmol) in chloroform (10ml) was added m-chloroperbenzoic acid (44.6mgs, 0.26mmol), the reaction being followed by tlc. On completion (96h), the reaction mixture was washed with saturated aqueous sodium hydrogen carbonate (2 x 10ml) and dried (K_2CO_3). Removal of the solvent and plc of the crude product gave the epoxide (63), 10.4mgs, 48.6%, $\nu_{max.}$ 2935, 1830, 1640 and $1250cm^{-1}$, δ 1.0 - 1.8(m) and 3.1 - 3.45 (m).

Acid Catalysed Rearrangement of (61)

To the epoxy lactone (61) (54.6mgs, 0.35mmol) in dry benzene (1.5ml) was added methane sulphonic acid (0.35ml). The mixture was heated at reflux for 1.5h, cooled, neutralised with ammonium hydroxide (38% aqueous solution) and extracted with chloroform (3 x 50ml). The organic layer was washed with water (2 x 25ml), dried and the solvent removed at reduced pressure. Plc of the residue on silica gel (1:1 diethyl ether/40-60 petroleum ether as eluant) yielded a single product, 15.1mgs, ν_{max} . 3040, 2960, 1750, 1640 and 1050cm^{-1} , δ 0.93 - 1.43 (2H,m), 1.72 - 2.4 (4H,m), 3.5 (2H,brs) and 4.88 (1H,m)

Acid Catalysed Rearrangement of (63)

The epoxy lactone (63) (10.4mgs, 0.06mmol) was combined with benzene (1ml) and methane sulphonic acid (0.25ml) and heated at reflux for 1h. On cooling, the reaction was neutralised with ammonium hydroxide (28% aqueous solution) and extracted with chloroform (100ml) and dried. Removal of the solvent furnished an oil, 10.3 mgs, ν_{max} . 2960, 2925, 1780-1660(br) and 1100cm^{-1} , δ 0.63 - 1.0 (m), 1.23 (S) and 1.03 - 2.27 (m).

Reaction of the β -Lactone (37) with Lithium Diisopropylamide

(a) To a stirred solution of the β -lactone (37) (60mgs, 0.44mmol) in dry THF at -78°C , under argon, was

added lithium diisopropylamide (0.44mmole) in THF (0.75ml). The reaction was stirred for 1h at -78°C , allowed to attain room temperature and quenched with diisopropylamine hydrochloride (68.1mgs, 0.49mmol). The reaction mixture was diluted with water (25ml), extracted with ether (3 x 50ml) and the combined organic layers dried. The solvent was removed at reduced pressure to yield (37), 60mgs (100%), ν_{max} . 2950, 2840, 1825, 1720(w) and 1635cm^{-1} , and δ 0.57 - 1.63(6H, m), 4.17(3H, m) and 5.63(1H, brs).

(b) To a stirred solution of lithium diisopropylamide (2.55mmol) and hexamethyl phosphoric triamide (47.7mgs, 2.66mmol) in THF (20ml) at -23°C under argon, was added over 30min the β -lactone (37) (244.5mgs, 1.77mmol) in the same solvent (5ml). After 30min at -23°C , the reaction was warmed to 0°C , stirred for a further 30min and quenched with saturated aqueous ammonium chloride (10ml). After dilution with ether (200ml) the organic phase was washed respectively with water (20ml), brine (2 x 50ml) and dried. On removal of the solvent at reduced pressure, the residue was immediately reduced with lithium aluminium hydride (450mgs) in diethyl ether (2)ml) at -78°C , and then overnight at room temperature. The reduction was worked-up with saturated aqueous sodium sulphate, the resultant precipitate washed with copious amounts of ether and the combined organic extracts dried. Removal of the solvent and plc of the residue afforded an oil, 24.3mgs, δ 0.8 - 1.41(m), 1.70(m), 2.20(m), 2.60(m), 3.71(d J 6Hz) and 5.37(m).

(c) To a solution of lithium diisopropylamide (0.73 mmol) and diisopropylamine (220mgs, 0.22mmol) in THF (10ml) at -20°C , under argon, was added the β -lactone (37) (100mgs, 0.73mmol) in THF (5ml) over a period of 30min. The resulting solution was allowed to attain room temperature and quenched with ammonium chloride (78mgs, 1.46mmol). Removal of the solvent at reduced pressure and extraction with ether (2 x 50ml), afforded after removal of solvent an oil, 42.8mgs, δ 0.76 - 2.56(m), 3.26 - 4.2(m), 4.9(d) and 5.46 - 6.06(m).

(d) To a stirred solution of lithium diisopropylamide (0.8mmol) in dry THF (10ml) at 0°C , under argon, was added the β -lactone (37) (100mgs, 0.73mmol) in THF (5ml). The resultant solution was cooled to -78°C , and copper (I) iodide (152mgs, 0.8mmol) added. The suspension was allowed to warm until a homogenous solution was obtained (-30°C), whereupon reaction was cooled to -78°C and stirred for 1h. Quenching with excess ammonium chloride and work-up in the normal manner, led to isolation of an oil, 77mgs, ν_{max} . 3500-3200, 2950, 2870, 1720, 1640 and 1270cm^{-1} , δ (CDCl_3 1 d_5 Pyridine) 0.9 - 2.6(m), 3.4-4.1(m) and 5.5(m).

Rhodium (I) catalysed isomeration of (37)

The β -lactone (37) (60mgs, 0.43mmol) was combined with deuteriochloroform (1ml) and tris triphenylphosphine rhodium (I) chloride (10mgs, 2.5mmol%) in an n.m.r.

tube. The reaction mixture was warmed to 70°C, and the reaction followed by ^1H n.m.r. spectroscopy.

General Procedure for Thermolysis of Tricarbonyliron Lactone Complexes

The tricarbonyliron complex was combined with a suitable dry degassed solvent (benzene or THF) and heated, under argon, at an appropriate temperature (reaction being followed by tlc). On completion, solvent was removed by distillation at atmospheric pressure and the products isolated by plc on silica gel.

Thermolysis of complex (36)

The tricarbonyliron lactone complex (36) (100mgs, 0.34mmol) was heated at 60°C in benzene. On completion (4h), trimethylamine N-oxide (205mgs, 2.74mmol) was added, and the resulting mixture refluxed (4h). Plc of the crude product yielded, 1-formyl-2-methylcyclohexene (69) (29.2mgs, 69%), ν_{max} . 2850, 1660, 1635, 1360, 1275, 1240, 1140, 1060 and 740cm^{-1} , and δ 1.23 - 1.7(4H, m), 1.72 - 2.28(7H, m) and 9.98(1H, s).

Thermolysis of complex (30)

(a) Complex (30) (160mgs, 0.58mmol) in benzene (16ml) at 60°C for 20h afforded (70) (12mgs, 19%) ν_{max} . 2960, 2870, 2840, 2760, 1670, 1650, 1610, 1150 and 1095cm^{-1} , and δ 1.5

- 2.0(4H, m), 2.33 - 3.0(4H, m), 5.9(1H, dt) and 9.73(1H, d J 8Hz).

(b) Complex (30) (200mgs, 0.72mmol) in THF (20ml) at reflux for 3h gave after plc (i) 1-Vinylcyclopentene tricarbonyliron (71) (90.2mgs, 54%) ν_{max} . 2950, 2860, 2020, 1980-1930, 1420, 1190 and 1160cm^{-1} , δ -0.23(1H, dd), 1.47(1H, dd), 1.57 - 2.07(6H, m) and 5.25(1H, dd); and (ii) 3,3-tetramethylene prop-2-en-1-ol (70) (17.8mgs, 23%), ν_{max} . 2940, 2860, 2750, 1670, 1615, 1175, 1155 and 840cm^{-1} , δ 1.47 - 2.93 (8H, m), 5.9(1H, dt J 8, 2Hz) and 9.72(1H, d J 8Hz).

(c) Complex (30) (200mgs, 0.72mmol) in THF (20ml) at 60°C for 24h gave no evidence of reaction (as indicated by tlc). On refluxing for 3h, and work-up in the normal manner there was obtained (i) 1-Vinyl cyclopentene tricarbonyliron (71) (67.6mgs, 40%), ν_{max} . 2950, 2860, 2020, 1980-1930, 1420, 1190 and 1160cm^{-1} , δ -0.23(1H, dd), 1.47(1H, dd), 1.57 - 2.07(6H, m) and 5.25(1H, dd), and (ii) 3,3-tetramethylene prop-2-en-1-al (70) (18.7mgs, 23.6%), ν_{max} . 1670 and 1650cm^{-1} , and δ 1.53 - 2.2(4H, m), 2.23 - 3.0(4h, m), 5.97(1H, dt J 8 2Hz) and 9.83(1H, d J 8Hz).

Thermolysis of complex (33)

(a) Complex (33) (114mgs, 0.37mmol) in benzene (10ml) at 60°C for 4h gave a single component, 25.2mgs, ν_{max} . 2980, 2940, 2870, 2060, 2000, 1995, 1960, 1675 and 1210cm^{-1} , and

δ 0.92 - 2.83(m), 5.1(m), 5.75(m) and 9.2(d).

(b) Complex (33) (100mgs, 0.33mmol) in benzene (10ml) at 60-65°C for 21h, upon plc gave rise to three components.

Component 1. 1.2mgs, ν_{max} . 2850, 2000(w), 1970(w) and 1675cm⁻¹.

Component 2. 5.3mgs, ν_{max} . 2020, 1900 and 1975cm⁻¹.

Component 3. 2.8 mgs, ν_{max} . 2900, 2010, 1990 and 1360cm⁻¹.

(c) Complex (33) (100mgs, 0.33mmol) in THF (10ml) at reflux for 3h furnished exclusively anti-1,1-penta-methylene buta-1,3-dien-4-ol tricarbonyliron (78) (74mgs, 82%), ν_{max} . 3605, 2940, 2875, 2040 and 1990-1930cm⁻¹, δ 1.2 - 2.3(6H, m), 2.3 - 3.38(6H, m), 3.53(1H, m D₂O exch.) and 5.12 (1H, d J 7.6Hz). (Found: C, 52.05; H, 5.05. C₁₂H₁₄Fe O₄ requires C, 51.83; H, 5.07%).

Thermolysis of complex (43)

(a) Complex (43) (200mgs, 0.75mmol) in THF (20ml) was heated at reflux for 30min to yield after plc:

Component 1. 10.7mgs, ν_{max} . 2960, 2920, 2870, 2080, 2040, 2020, 2000-1940, 1725(w) and 1560cm⁻¹.

Component 2. 1,2,2-Trimethylpropenal (76) (35.7mgs, 48.5%), δ 1.75(3H, d J 1.5Hz), 1.96(3H, s), 2.18(3H, d J 1.5Hz) and 10.13(1H, d J 1.5Hz).

(b) Complex (43) (100mgs, 0.38mmole) in THF (10ml) was heated at reflux for 30min, trimethylamine-N-oxide (2 (226mgs, 3mmol) added and the mixture refluxed for a further 30min. Plc of the crude product gave three components.

Component 1. $\nu_{\max}$. 2050 and 200-1940 cm^{-1} .

Component 2. $\nu_{\max}$. 2080, 2040, 2020, 2000-1960 and 1720-1600 cm^{-1} .

Component 3. 1,2,2-Trimethylpropenal (76) (8.3mgs, 22.5%), $\nu_{\max}$. 1678 and 1640 cm^{-1} .

(c) Complex (43) (100mgs, 0.38mmol) in diethyl ether (10ml) was heated at 80°C (in a sealed bomb) for 4h. Solvent was removed by distillation at reduced pressure and the residue analysed by Glc and Uv spectroscopy using internal and external standards.

2,3-Dimethylbutadiene tricarbonyliron (77), 6.9% by UV spectroscopic analysis, $\lambda_{\max}$. = 226nm, $\log_{10} \epsilon = 4.33$ ⁵⁶ and Glc retention time under previously reported conditions.²⁹ 1,2,2-Trimethylpropenal (76), 59.7% by Glc analysis, with authentic material as external standard.

Thermolysis of complex (72)

(a) Complex (72) (200mgs, 0.79mmol) in THF (20ml) was heated at reflux for 4h. and after plc afforded two components.

Component 1. 34mgs, $\nu_{\max}$. 2060 and 2000-1930 cm^{-1} .

Component 2. 8.9mgs, $\nu_{\max}$. 2070, 2050, 2005, 1995, 1980, 1690(w) and 1680(w) cm^{-1} , δ 1.1 - 1.6(m), 2.1(s), 2.2(s), 1.98 - 2.78(m), 7.29(s) and 7.44(s).

(b) Complex (72) (100mgs, 0.39mmol) in diethyl ether (10ml) was heated at reflux for 24h to give after plc two components.

Component 1. minor component, δ 1.11 - 1.51(m), 2.07(s) and 7.44(s).

Component 2. major component, δ 1.49(d), 2.09(m) and 7.28(s).

(c) Complex (72) (200mgs, 0.79mmol) in diethyl ether (20ml) was heated at 80°C (in a sealed bomb) for 4h. Work-up by distillation at atmospheric pressure, Glc and UV of the residue followed by isolation of the components gave:

Isoprene tricarbonyliron (75) 22% by UV spectroscopic analysis, $\lambda_{\max}$. = 220nm, $\log_{10}\epsilon = 4.38^{56}$ and Glc retention time under previously reported conditions.²⁹ Anti-2-methyl but-2-en-1-al tricarbonyliron (74) and Syn-2-methyl but-2-en-1-al tricarbonyliron (73), 44%^a combined yield, by Glc analysis.

NOTE: (a) The enal-tricarbonyliron complexes (73) and (74) were found to partially decompose on the injector block of the gas chromatograph to the parent enal, Tigaldehyde.

Therefore conditions were chosen such that the tricarbonyliron complexes underwent total decomplexation to give, on the injector, Tigaldehyde. The overall yield of this enal as determined by Glc was used to calculate the combined yield of complexes (73) and (74).

Glc parameters: Perkin-Elmer SIGMA3 Gas Chromatograph: Column: 4m 10% Carbowax on chromsorb; Oven temperature = 130°C; Injector/detector temperature = 220°C; Flow rate N₂ = 40ml min⁻¹. FID detector.

Plc of the remaining material afforded

- (i) Anti-2-methyl but-2-en-1-al tricarbonyliron (74)
(14.2mgs, 8%) δ 1.28(3H, d J 7.5Hz), 1.42(3H, d J 6.5Hz), 2.36(1H dq J 7.5, 6.5Hz) and 7.44(1H, s).
- (ii) Syn-2-Methyl but-2-en-1-al tricarbonyliron (73)
(30.7mgs, 17.3%) δ 1.46(3H, d J 6.5Hz), 2.06(3H, s), 2.21(1H, q J 6.5Hz) and 7.28(1H, s).

1-Vinyl cyclopentene tricarbonyliron (71)

1-Vinylcyclopentene (500mgs, 5.3mmol) was combined with enneacarbonyl diiron (2.13g, 5.9mmol) in dry degassed THF (20ml), and heated at reflux, under argon (the reaction being followed by tlc). On completion (2h) the cooled solution was filtered, the solvent removed by distillation at atmospheric pressure, and 1-Vinyl cyclopentene tricarbonyliron (71), isolated by plc yield, 200mgs (16%), δ -0.23(1H, dd J 8.7, 2Hz), 1.47 (1H, dd J 6.6, 2Hz), 1.57 -

2.07(7H, m) and 5.25(1H, dd J 8.7, 6.6Hz).

Syn-2-methyl but-2-en-1-al tricarboxyliron (73)

Tigaldehyde (500mgs, 5.95mmol) was combined with pentacarbonyliron (1.6ml, 11.9mmol) in dry degassed diethyl ether (25ml), under argon. The solution was irradiated with the radiation from a Philips HPK 125W Hg discharge lamp until reaction was complete (as indicated by tlc). Removal of the solvent by distillation at atmospheric pressure afforded a single enal complex in low yield. δ 1.44 (3H, d J 6.5Hz), 2.15(1H, q J 6.5Hz), 2.09(3H, s) and 7.28(1H, s). (Found: C, 42.87; H, 3.82. $C_8H_8FeO_4$ requires C, 42.90; H, 3.60%).

Triphenylphosphinedicarbonyl-(1,1',2-n-ethylcyclopent-1-ene-1-yl)-2'-oxycarbonyliron (86)

To a stirred solution of the complex (30) (100 mgs, 0.36mmol) in dry degassed diethyl ether (10ml) was added triphenylphosphine (94.4mgs, 0.36mmol). The solution was brought to reflux, and the reaction followed by tlc. After 7.5h the solution was cooled and the product isolated by filtration. Recrystallisation from benzene afforded (86) (83.7mgs, 45.4%), ν_{max} . 2850, 2000, 1960, 1625, 1090, 980 and $950cm^{-1}$, δ 1.3)6H,m), 3.4 - 3.77(2H, m), 3.93(1H, brs), 4.33(1H, m) and 7.03(15H, m). (Found: C, 65.66; H, 4.91; P, 5.89. $C_{28}H_{25}FeO_4P$ requires C, 65.64; H, 4.84; P, 6.05%).

Trimethylphosphinedicarbonyl-(1,1',2- η -ethylcyclopent-1-ene-1-yl) (87)

In a similar manner the complex (30) (100mgs, 0.36mmol) was combined with trimethylphosphine (27.9mgs, 0.36mmol) in dry degassed diethyl ether (10ml). After 24h at reflux, removal of the solvent afforded the crude phosphine complex, which was recrystallised from diethyl ether/40-60 petroleum ether. Yield 61.4mgs (52%) m.p. 114-115°C, ν_{max} . 3000-2800, 2080, 2000, 1960, 1660, 1285, 1090 and 950 cm^{-1} , δ 1.573 (d J 9.3Hz) and 1.671 (d J 9.5Hz) [9H, equatorial and axial phosphine isomers], 1.72 - 3.08 (5H, m) and 3.56 - 4.50 (4H, m). (Found: C, 48.01; H, 5.88. $\text{C}_{13}\text{H}_{19}\text{FeO}_4\text{P}$ requires c, 47.88; H, 5.87%).

Thermolysis of tricarbonyliron Lactone Complex (30):
determination of mechanism

The complex (30) (100mgs, 0.36mmol) was combined with dry degassed THF (10ml) and introduced into a bomb, which had previously been flushed with argon. The bomb was heated at 80°C for 2h, cooled, and a sample of the gaseous phase taken for IR spectroscopic analysis.

Carbon monoxide ν_{max} . 2170 and 2120 cm^{-1} .

Carbon dioxide ν_{max} . 2330 cm^{-1} .

The ratio of extinction coefficients was found by experiment to be 9:1 $\epsilon_{\text{CO}_2}:\epsilon_{\text{CO}}$.

Only carbon monoxide was detected in the gaseous phase from the sealed bomb reaction; no carbon dioxide was detectable.

(±) Massioalactone (99)

The tricarbonyliron lactone complex (49) (100 mgs, 0.32mmol) was combined with dry degassed benzene (10ml) and sealed in a bomb under 60 atmospheres of carbon monoxide. The bomb was heated at 195°C for 4h, the pressure released and the crude product isolated by removal of the solvent. Column chromatography on silica gel (1:1 diethyl ether/40-60 petroleum ether as eluant) to afford (±) Massioalactone (99) (35.6mgs, 65%), ν_{max} . 2920, 2865, 1725 and 1630 cm^{-1} , δ 0.87(3H, s), 1.07 - 1.93(8H, m), 2.3(2H, m), 4.33(1H, m), 5.95(1H, dt J 10, 1.5Hz) and 6.83(1H, dt 10, 4.7Hz). (Found: C, 71.45; H, 9.87. $\text{C}_{10}\text{H}_{16}\text{O}_2$ requires C, 71.39; H, 9.87%).

Tricarbonyl-(1,1',2- η -ethylcyclopent-1-ene-1-yl)-2'-oxycarbonyliron (30) δ (250MHz) 1.51(1H, m), 1.98(1H, m), 2.13(1H, m), 2.49(2H, m), 3.19(1H, m), 4.03(1H, dd, J-11.9, 4.7Hz), 4.17(1H, ABq J-11.9Hz), 4.39(1H, d J 2.8Hz) and 4(1H, d J 4.7Hz).

Tricarbonyl-(2,3,4- η -2,3-[tetramethylene]-2-buten-2-yl)-1-oxycarbonyliron (36) δ (250MHz) 1.78(4H, m), 2.23(2H, m), 2.49(2H, m), 2.98(1H, m), 3.22(1H, d J 0.2Hz), 3.89(1H, ABq J-11.9Hz) and 4.12(1H, ABq J-11.9Hz).

Z-Tricarbonyl-(1,1',2'- η -1,1-propylidenecyclohexane-1-yl)-3'-oxycarbonyliron (33) δ (250MHz) 1.33 - 2.47(10H, m), 4.05(1H, dd J-11.8 and 2.3Hz), 4.15(1H, dd J-11.8 and 6.8 Hz), 4.46(1H, d J 8.1Hz) and 4.97(1H, ddd J 8.1, 6.8 and 2.3Hz).

E-Tricarbonyl-(1,1',2'- η -1,1-propylidenecyclohexane-1-yl)-3'-oxycarbonyliron (34) δ (250MHz) 1.33 - 2.47(10H, m), 3.51(1H, dd J 9.4 and 3.2Hz), 4.24(1H, dd J-12.1 and 3.2Hz), 4.47(1H, d J 9.4Hz) and 4.65(1H, ABq J-12.1Hz).

Syn-tricarbonyl-(1,1',2'- η -1-vinyl-cyclopentan-1-yl)-2-oxycarbonyliron (47) δ (250MHz) 1.7 - 2.3(4H, m), 2.52 - 2.7(3H, m), 3.43(1H, dd J 8 and 1.5Hz), 4.16(1H, t, J 7Hz), and 5.26(1H, dd J 12 and 8Hz).

Anti-tricarbonyliron-(1,1',2'- η -1-vinylcyclopentan-1-yl)-2-oxycarbonyliron (48) δ (250MHz) 1.3 - 1.52(1H, m), 2.0 - 2.35(4H, m), 2.5 - 2.71(1H, m), 2.96(1H, dd, J 12 and 2Hz), 3.46(1H, dd, J 9 and 2Hz), 4.29(1H, dd, 11.5 and 6Hz) and 4.56(1H, dd, J 12 and 9Hz).

Syn-tricarbonyl-(3,1',2'- η -3-vinyl-5 α -cholestan-3-yl)-2 α -oxycarbonyliron (45) δ (250MHz) 0.64(3H, s), 0.83(3H, s), 0.9 - 2.3(36H, m), 2.1(1H, dd, J 13 and 5Hz), 2.6(1H, dd, J 13 and 11Hz), 2.90(1H, dd, J 13 and 2Hz), 3.60(1H, dd, J 9 and 2Hz), 4.32(1H, dd, J 11 and 5Hz) and 4.66(1H, dd, J 13 and 9Hz).

Anti-tricarbonyl-(3,1',2'- η -3-vinyl-5 α -cholestan-3-yl)-2 α -oxycarbonyliron (46) δ (250MHz) 0.67(3H, s), 0.78 - 2.05 (39H, m), 2.35(1H, dd, J 12 and 3.5Hz), 2.5(1H, t, J 12Hz), 3.03(1H, dd, 12 and 2Hz), 4.37(1H, dd, J 12 and 3.5Hz), and 4.56(1H, dd, J 12.5 and 9Hz).

Trans-tricarbonyl-(1,2,3- η -1-nonen-3-yl)-4-oxycarbonyliron (49) (δ 250MHz) 0.87(3H, t, J 7Hz), 1.7 - 2.1(8H, m), 3.08(1H, dd, J 13 and 1Hz), 3.78(1H, ddd, J 8, 2 and 1Hz), 4.04(1H, t, J 6.5Hz), 4.65(1H, dd, J 7.5 and 2Hz) and 4.98(1H, ddd, J 13, 8 and 7.5Hz).

Cis-tricarbonyl-(1,2,3- η -1-nonen-3-yl)-4-oxycarbonyliron

(50) (δ 400MHz) 0.9(3H, t, J 7Hz), 1.7 - 2.15(8H, m), 3.12(1H, dd, J 13 and 2Hz), 3.78(1H, ddd, J 8.4, 2 and 1.5 Hz), 4.3(1H, dt, J 7 and 6Hz), 4.77(1H, ddd, J 13, 8.4 and 7.2Hz) and 4.85(1H, ddd, J 7.8, 7.8 and 1.5Hz).

Trans-tricarbonyl-(2,3,4- η -2-nonen-4-yl)-1-oxycarbonyliron

(100) (δ 400MHz) 0.92(3H, t, J 7Hz), 1.2 - 1.6(6H, m), 1.77(1H, dt, J 9 and 5Hz), 2.27(1H, d, J 5Hz), 3.96(1H, ddd, J 12, 5 and 0.5Hz), 3.98(1H, ddd, J 12, 10 and 5Hz), 4.06(1H, ddd, J 12, 15 and 0.5Hz), 4.62(1H, ddd, J 7.5, 5 and 1.5Hz) and 4.78(1H, dd, J 12 and 7.5Hz).

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