

IRON CARBONYLS
IN ORGANIC SYNTHESIS

A thesis presented by

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ABSTRACT

The review section of this thesis describes the occurrence of monocyclic δ -lactones in nature, and their biological activity if known. Specific attention is paid to parascorbic acid, massoia lactone, malyngolide, and the sex pheromones of the oriental hornet and the carpenter bee, and their various syntheses are described.

The results and discussion section describes the development of a new method for the preparation of π -allyltricarboxyliron lactone complexes, from allyl epoxides, using ultrasound, and their subsequent conversion into δ -lactones *via* a high pressure carbonylation reaction. These methods were then employed in the synthesis of several naturally occurring monocycle δ -lactones. A short synthesis of parascorbic acid and the sex pheromone of the carpenter bee are described. A model synthesis for the antibiotic malyngolide allowed a route to more complex δ -lactones to be developed, and malyngolide itself was synthesised. Attempted asymmetric syntheses of massoia lactone and the sex pheromone of the oriental hornet are also described.

Finally, the chemistry of π -allyltricarboxyliron lactone complexes was investigated, including the preparation of π -allyltricarboxyliron lactam complexes and their carbonylation to δ -lactams. The potential of nonacarbonyl diiron as a reagent in the synthesis of ureas is also described, and the formation of an iron carbonyl carbene complex as an intermediate is proposed.

A woman so various that she seem'd to be
Not one, but all mankind's epitome.
Stiff in opinions, always in the wrong;
Was everything by starts, and nothing long:
But, in the course of one revolving moon,
Was chemist, fiddler, statesman, and buffoon.

With apologies to John Dryden (1631-1700)

Absalom and Achitophel,

pt. i, l.1

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FOR JULES

CONTENTS

	<u>Page</u>
ABSTRACT	2
ACKNOWLEDGEMENTS	4
 1. Naturally Occurring Monocyclic δ -Lactones, A Review	
1.1 Occurrence and Activity	8
1.2 Synthesis	23
References	36
 2. Synthesis of Tricarbonyliron Lactone Complexes	42
2.1 Introduction	42
2.2 Sources of Iron: The Ultrasound reaction	47
2.3 Preparation of Epoxides	49
2.4 Preparation of Lactone Complexes	51
2.5 Preparation of Lactones	56
 3. Natural Product Synthesis	60
3.1 Synthesis of Parasorbic Acid	60
3.2 Synthesis of the Sex Pheromone of the Carpenter Bee	61
3.3 Model Synthesis for the Natural Product Malyngolide	66
3.4 Synthesis of Malyngolide	74
3.5 Attempted Synthesis of the Sex Pheromone of the Oriental Hornet	85
3.6 Attempted Synthesis of Massoia Lactone	90

CONTENTS continued

	<u>Page</u>
4. Chemistry of Tricarbonyliron lactone complexes and Iron carbonyls	93
4.1 Preparation of Lactam Complexes	93
4.2 Preparation of Lactams	97
4.3 Other Reactions of Nonacarbonyl Diiron	98
4.4 Reactions of Lactone Complexes	103
4.5 Attempted Use of Non-Iron Metal Carbonyls	105
5. Experimental Details	107
REFERENCES	136
PUBLICATIONS	140

REVIEW

Naturally occurring mono-cyclic δ -lactones

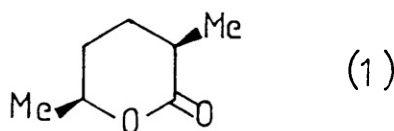
Introduction

Naturally occurring mono-cyclic δ -lactones can be divided into two broad groups, saturated and unsaturated, the former being mainly pheromones and flavour compounds in foods, the latter being antibiotics, toxins and various biologically active compounds derived from plants. This review will deal specifically with five of these lactones and generally with a number of others.

1. Occurrence and Activity

1.1 Carpenter Bee Pheromone

Male Carpenter Bees (*Xylocopa hirsutissima*) have been shown to secrete a substance from their mandibular glands which is used both as a territory marker and as a 'sex attractant'.¹ In the high mountains of Brazil male bees hover over trees which they mark as their territory with this secretion which also attracts females from a large surrounding area. The active component of this secretion has been shown² to be the lactone (1) and its production is limited to this

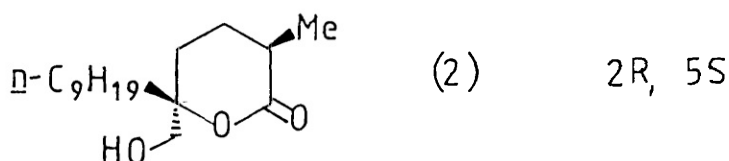


species as smaller Carpenter Bees (genus *Ceratina*) do not produce it. Experiments with the synthetic lactone were inconclusive³ but as it was not stated to be chiral, the use of a racemic mixture must be presumed; it is known that the presence of an isomer other than the naturally occurring one can act as a strong inhibitor.⁴

1.2 Malyngolide

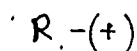
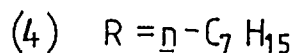
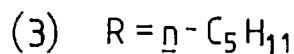
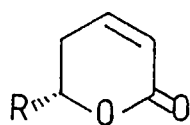
Burkholder⁵ has shown that methanolic extracts from Hawaiian Marine Blue-Green Algae (*Lyngbya Majuscula*) exhibit seasonal anti-bacterial activity against *E. coli* and *C. albicans*. Starr⁶ has shown that extracts are active against *Ps. fluorescens*, *M. pyrogenes* (var *aureus*) and *M. smegmatis*, but not against *E. coli*. This may be because Burkholder used algae collected in May-June (which is strongly active) and in January (which has little activity) whereas Starr used algae collected in October. Starr also showed that extracts were cytotoxic and antiviral, in that viral maturation in host cells was prevented by addition of the extracts (mouse meningopneumonitis virus, human synovial cells).

Potent antifungal inhibitor effects have also been noted,⁷ and the algae has been implicated in outbreaks of a skin complaint called 'swimmers itch'.⁶ The δ -lactone (2), Malyngolide was identified as the active component of the algae.⁸



1.3 Massoia Lactone

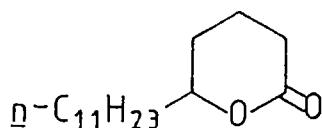
Massoia Lactone (3), isolated from Massoia Bark oil⁹ has long been used as a native medicine in New Guinea.¹⁰ It has also been found in two species of formicine ant (*Camponatus*),¹⁰ in *Polianthus Tuberosa*¹¹ and in cane molasses.¹² It is a powerful skin irritant, produces systolic standstill in frog heart muscle,⁹ and has been shown to have a sedative action on mice.¹³ The analogue lactone (4) has been shown to be a minor constituent of the bark oil. In formicine ants, the lactone



is found in the large mandibular gland and it is thought to form part of the defensive and/or pheromone secretions.¹⁰

1.4 Oriental Hornet Pheromone

The Oriental Hornet (*Vespa Orientalis*) occurs in tropical and subtropical climates and is a pest to fruit farmers as it attacks the honey bee and various summer fruits.¹⁴ Extracts from the Queen hornets' heads contain a pheromone, identified as δ -lactone (5).

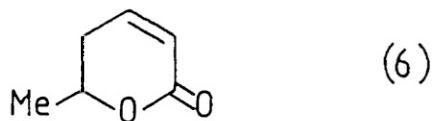


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It is stated¹⁴ that the effects of the synthetic lactone are the same as for the natural one, but no details are given of the stereochemistry of either.

1.5 Parascorbic Acid

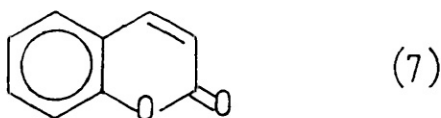
Parascorbic acid (6) has been isolated from berries of the Mountain Ash or Rowan tree (*Sorbus aucuparia*)¹⁵ from which it derives its name. It has been found to have inhibitory effects on cell division in a wide variety of plants, animals and bacteria. It is cytotoxic in plants and adversely affects the germination of mustard seed at a concentration of 3.5×10^{-3} M,¹⁶ and inhibits the growth of tomato¹⁷



and onion roots.¹⁸ This general effect would be expected to be beneficial to germinating Rowan tree berries as it would prevent the germination and growth of other plants, thus giving the Rowan tree berry a greater chance to germinate and grow itself. Parascorbic acid is also found in wheat middlings (presumably for the same reason), orange rind, malt and yeast.¹⁹

In onion and tomato roots it causes inhibition of mitosis by blocking it at metaphase, so that the metaphasic cells accumulate. No abnormalities occur and these retarded cells eventually continue normal development,²⁰ (anaphase and telophase) especially if the source of parascorbic acid is removed. This effect is observable at concentrations of 1 in 5,000 in onions and 1 in 10,000 in tomatoes with D or DL forms,²¹ as is the case with most of its activity. It has been shown²² that it is antagonistic to β -indole acetic acid, the chemical growth promoter in germinating seedlings.

The chemically related lactone coumarin (7) has similar effects²⁰



but disrupts rather than blocks metaphase and causes abnormal cells which cannot continue their cycle of cell division when the coumarin

source is removed. These results agree with previous evidence¹⁸ that the benzene ring disrupts mitosis while the lactone ring inhibits growth.

Plant inhibitors generally have broad effects on animal cells, but parascorbic acid is very selective. It causes inhibition of growth in frog embryos²³ particularly in the heart muscles and central nervous system and has similar effects on chick embryos.²⁴ The effect on flat worms²⁵ (*Dugesia Teigrina*) is to cause a partial evisceration (as the fibroblasts are inhibited in their production of collagen). This is followed by disintegration of the gut and finally by the appearance of lesions in the dorsal epithelium. The effect was very specific to parascorbic acid and could not be produced by a variety of other toxic compounds. It was also noted that well-fed worms incurred more damage than starved worms. Growth of chick fibroblasts *in vitro* is also inhibited when epithelial cells proliferate as normal.

By far the most interesting effect is the arrest of growth and sometimes complete reabsorption of Jensen Sarcoma in rats treated with parascorbic acid.²⁶ This work does not seem to have been followed up, possibly due to the discovery of more effective anti-cancer agents and also because the dose required to arrest the tumour growth is almost that which arrests normal growth in rats. (There is also another report stating that parascorbic acid is carcinogenic!²⁷)

In animals parascorbic acid acts as a growth inhibitor²⁸ and is said to inhibit a growth factor more specifically required by fibroblasts than by epithelial cells. This is reflected in bacteria where some are responsive to inhibition²⁹ (*S. aureus*) and others are unresponsive (*Streptobacterium plantarum*). Cysteine is antagonistic to parascorbic acid,²⁹ possibly due to the interaction of the -SH

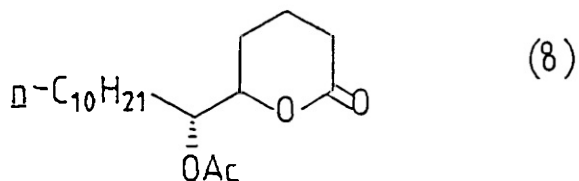
groups with the lactone ring. In general reports of antagonists are confused and contradictory.

All these effects are opposite to those of β -lactones, many of which are carcinogenic.³⁰ δ -Valerolactone (dihydroparascorbic acid) is non-toxic and non-inhibitory, where as acrolein and crotonaldehyde are known inhibitors,²³ all of which suggest that it is the α,β -unsaturated carbonyl unit which is responsible for the activity of parascorbic acid.

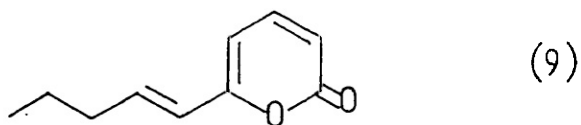
1.6 Other δ -Lactones

1.6.1 Pheromone Sources

The saturated lactone (8) has been identified³¹ as the major

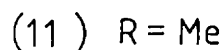
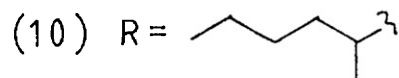
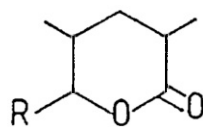


component of a mosquito oviposition attractant pheromone, which influences egg-laying of the female.³² It differs from the hormone of the oriental hornet by only the acetate group. Surprisingly for a pheromone, substance (9) is fully unsaturated and is one of the



substances responsible for queen recognition in the red imported fire ant³³ (*Solenopsis invicta*). It has also been found in ants of the genus *Camponatus*.³⁴ Another constituent of the red fire ants'

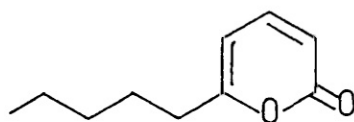
pheromone is lactone (10).³⁵ These ants are known for their painful persistent stings, which ties in well with the known skin irritant



properties of Massoia lactone and Malyngolide. Lactone (11), very similar to that produced by the carpenter bee, has been isolated from male Australian formicine ants of the genus *Calomyrex*,³⁶ but no details of stereochemistry are available.

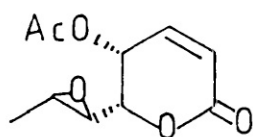
1.6.2 Microbial Sources

The unsaturated lactone (12) identical to lactone (9) except for one double bond, has been isolated as the major aroma constituent of

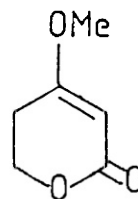


(12)

the fungus *Trichoderma viride*³⁷ and has a coconut-like odour. It has also been found in peach essence;³⁸ further reports³⁹ show that lactone (9) itself is also present. Both lactones are said to be biologically active. Asperlin (13) isolated from *Aspergillus nidulans*



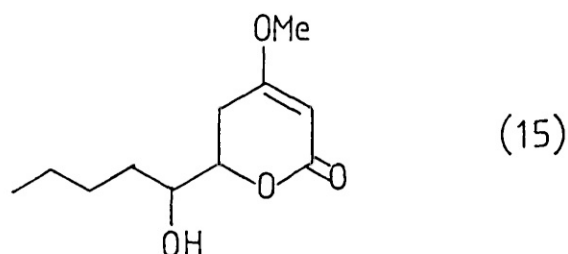
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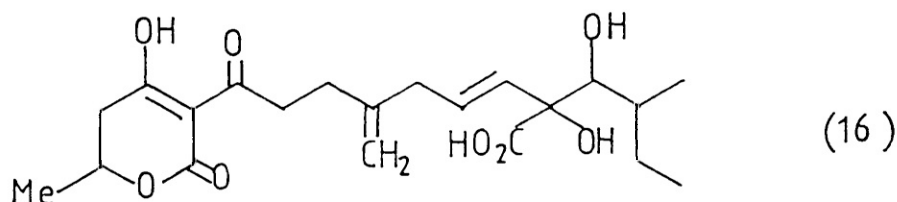
(14)

shows antibacterial activity *in-vitro*,⁴⁰ as does lactone (14) isolated from *Penicillium italicum*.⁴¹

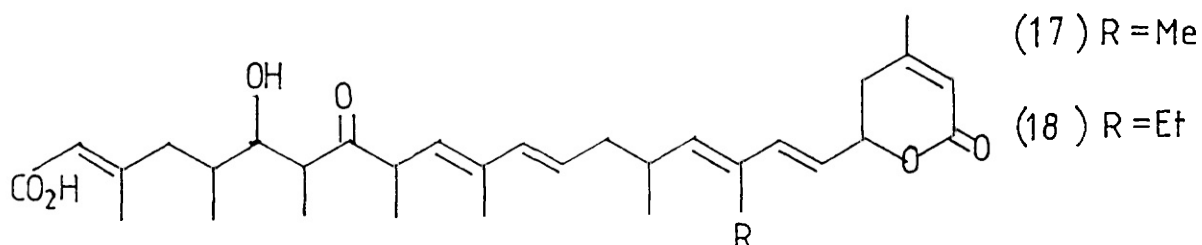
Pestatolin (15) a gibberellin synergist has been isolated from *Pestalotia Cryptomeriaecolo*, a fungus which is pathogenic for the Japanese Cedar.⁴²



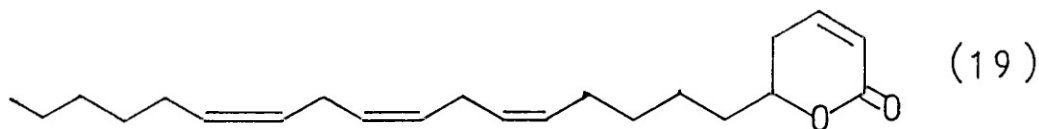
Lactones with very long side chains have also been isolated from microbial sources; lactone (16), alternic acid, from *Alternaria solani*,¹⁵ has weak antibacterial activity, specific potency against fungi, and is unusual in that its long chain is α - to the carbonyl group.



Leptomycins A and B, (17) and (18) are antifungal antibiotics from

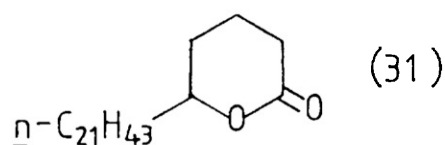
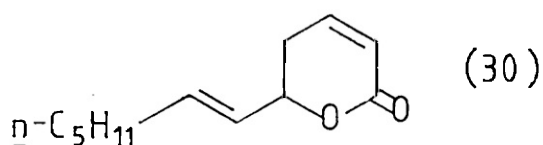


Streptomyces spATS 1287.⁴³ Lactone (19), from red algae *Phacellocarpus labillardieri* is a metabolite which may be responsible for the neuromuscular blocking activity of dichloromethane extracts of the algae.⁴⁴



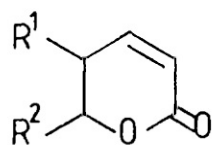
1.6.3 Plant Sources

Various species of plants of the genus *Hyptis* produce unsaturated lactones, (20)-(23), the leaves of *Iboza riparia* produce lactones (24)-(27) and *Eupatorium pilosum* produces lactones (28) and (29). (Table 1). Only structure and spectral data have been reported. Similar to these is Argentilactone (30), another skin irritant isolated from *Aristolochia argentina*,⁵² while lactone (31) has been isolated from the herb *Heliotropium curvassavicum* linn, along with 10% of the C₂₃ form.⁵³

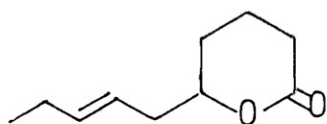
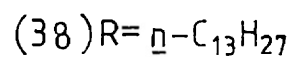
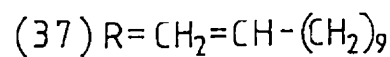
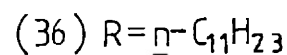
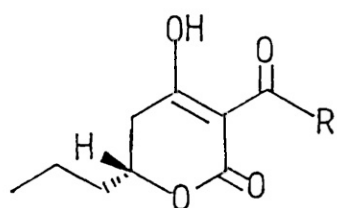
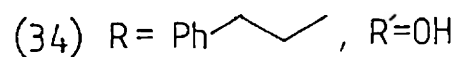
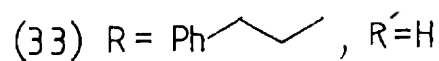
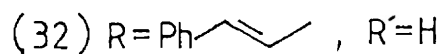
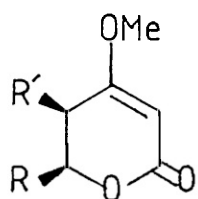


Kawain (32), which has been used in the treatment of gonorrhoea, and Marindinin (33) have both been isolated from the kawa root,¹⁵ the oil of which was once confused with Massoia bark oil. The 5-hydroxy form (34) has also been reported.⁵⁴ Similar to Argentilactone is lactone (35) which has been isolated from Jasmine oil, *Jasminum Grandiflorum*.⁵⁵ Podoblastins A, B and C (36)-(38) have been isolated from *Podophyllum peltatum*,⁵⁶ a plant known for its medicinal properties.⁵⁷ It has shown very strong antifungal activity against *Pyricularia oryzae*,

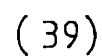
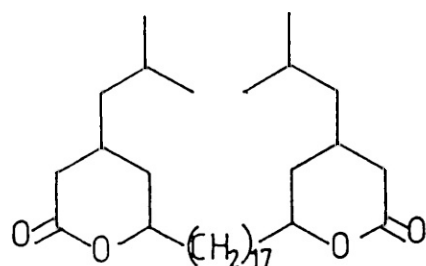
TABLE 1



No.	R ¹	R ²	Ref.
20	H		45
21	H		45
22	H		46
23	H		46
24	H		47
25	H		48
26	H		47
27	OAc		49
28	OAc		50
29	H		51

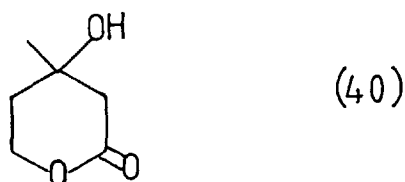


which attacks rice. Cadabalone (39) isolated from pods of *Cadaba fruticosa*⁵⁸ and although not strictly speaking monocyclic, is the only example of a bicyclic lactone which does not contain fused rings.



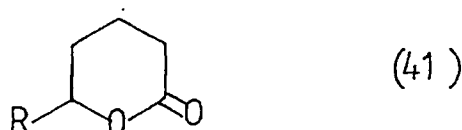
1.6.4 Other Sources

Mevalolactone⁵⁹ (40) a simple saturated lactone which is the biogenetic precursor of terpenes and steroids is one of the few naturally occurring δ -lactones to have a chiral carbon atom other than at C-5.



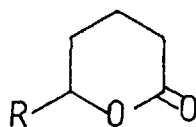
1.6.5 Saturated Lactones as Odour and Flavour Compounds

Lactones of the type (41) where R- is a saturated straight carbon chain occur in a wide variety of foods, principally fruits and animal fats and are responsible for a major part of their flavour (Table 2).



The predominant lactones have $R = n\text{-C}_3\text{H}_7$, $n\text{-C}_5\text{H}_{11}$ and $n\text{-C}_7\text{H}_{15}$ and have been described as having fruity/buttery/coconut-like odours.⁸³ Branched chains are much rarer (42)-(44) but as most of these compounds are identified by mass spectral and gas chromatographic means only, all the structural isomers may not have been observed or resolved. There is also a problem of decomposition of the lactones under the fairly vigorous chromatographic conditions sometimes employed. An example is Bartlett pear brandy - the most typical specific flavour compound is destroyed and therefore not observed when running gas chromatograph - mass spectral analysis.⁸⁴

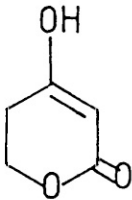
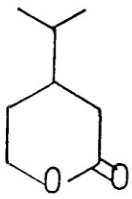
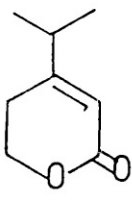
TABLE 2



R	Source	Ref.
Me (δ -Hexalactone)	Coconut Oil	60
	Beer	61
	Roasted Hazelnuts	62
Et (δ -Heptalactone)	Black Tea	63
	Strawberries	64
<i>n</i> -C ₃ H ₇ (δ -Octanalactone)	Cheddar Cheese	65
	Apricots	66
	Roasted Hazelnuts	62
	Coconut Oil	60,67
	Pineapple	68
	Passion Fruit	69
	Butter Oil	70
	Strawberries	64
	Jamaica Rum	71
<i>n</i> -C ₅ H ₁₁ (δ -Decalactone)	Milk	72,73
	Animal Fats	74,75
	Peaches	76,77
	Apricots	66
	Cheddar Cheese	65
	Coconut Oil	60,67
	Rum	71
	Black Tea	63
	Raspberries	78
	Butter	70

/cont.

TABLE 2 (cont)

R	Source	Ref.
$n\text{-C}_6\text{H}_{13}$ (δ -Undecalactone)	Whisky Pork Fat	79 75
$n\text{-C}_7\text{H}_{15}$ (δ -Dodecanalactone)	Milk Butter Fat Animal Fat Peaches Coconut Oil Jamaica Rum	72,80 70,81 74,75 77 60 71
$n\text{-C}_9\text{H}_{19}$ (δ -Tetradecalactone)	Animal Fats Coconut oil	74,75 60
(42) 	Burley Tobacco	82
(43) 		
(44) 		

The chirality of these lactones is not restricted to L-only forms⁸³ and racemisation does not occur to give the opposite form.

It has been reported⁸⁵ that δ -undecalactone in fruits acts as an insect pheromone. If it is an insect attractant then its presence in the fruit is surprising as it would be more beneficial to the plant for it to be present at the flower fertilisation stage (though there is no evidence that this is not the case). If it is a repellent its presence is more understandable as it would tend to protect the fruit from an egg-laying insect.

While the concentration of these lactones in foods is low compared to other constituents (in Jamaica Rum⁷¹ δ -decalactone occurs at 0.025 ppm; most other components occur at >1 ppm) most workers suggest that they make a significant contribution to the flavour: other work on flavour thresholds⁸³ would seem to refute this (Table 3).

TABLE 3

δ -Lactone	Threshold/ppm a	Flavour
Hexalactone	b	Sweet
Octalactone	0.57	Coconut, goaty
Nonalactone	b	Creamy, milky, buttery
Decalactone	0.16	Creamy, sweet, coconut, peach, milk
Undecalactone	b	Creamy, fatty, peach
Dodecalactone	0.1 - 1.0	Pear, plum, peach
Tetradecalactone	9.8	b

a. Level detectable in aqueous solution

b. Not given

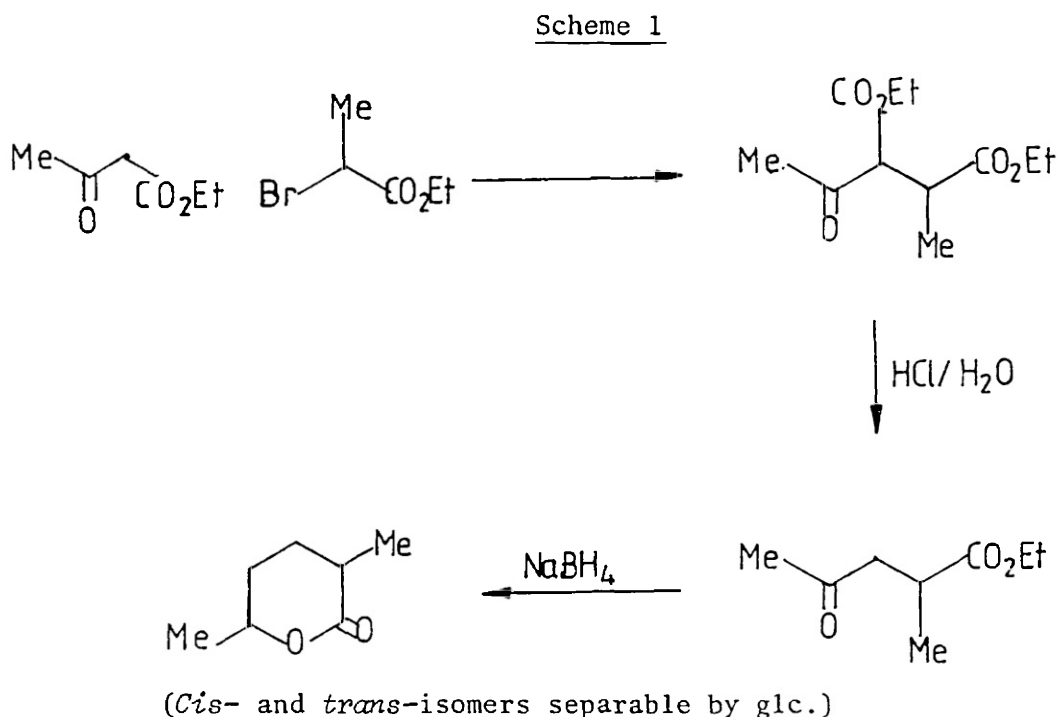
The effect of the presence of δ -lactones is very noticeable in milk where δ -decalactone has been shown to be responsible for the 'off-flavour' in dried milk which has been heated or stored for a long

time.⁷³ δ -Decalactone does not occur naturally in milk but can be produced by heating. Inclusion of a double bond in the lactone ring at C-2 seems to impart a slight peppermint or camphor flavour to the lactone.⁸³

2. Synthesis of Lactones

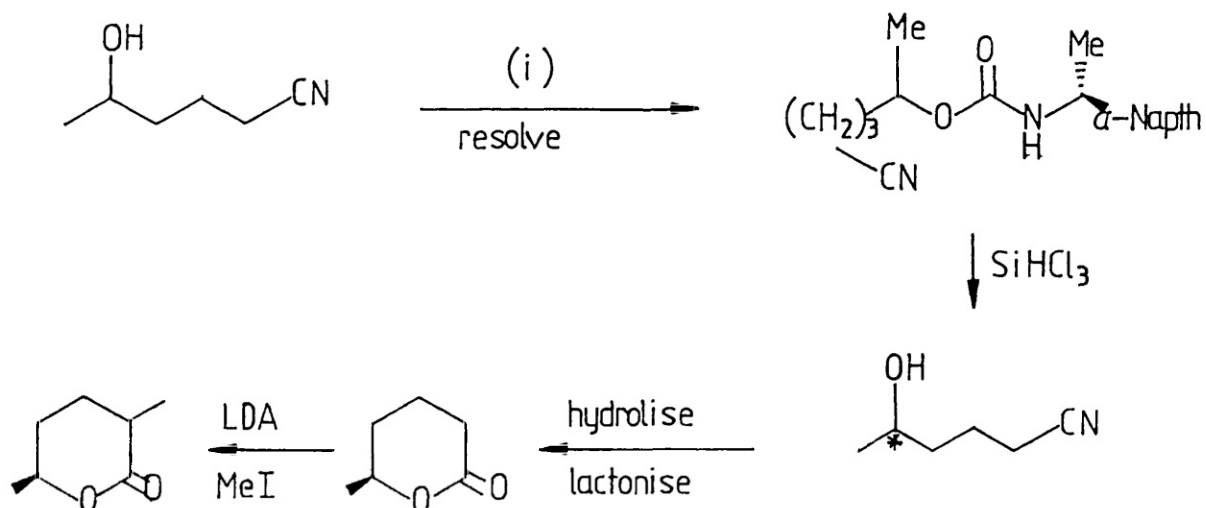
2.1 Carpenter Bee Pheromone

The first synthesis, (which was not reported as such) by Pyysalo⁸⁶ (Scheme 1) is racemic and no yields are given.



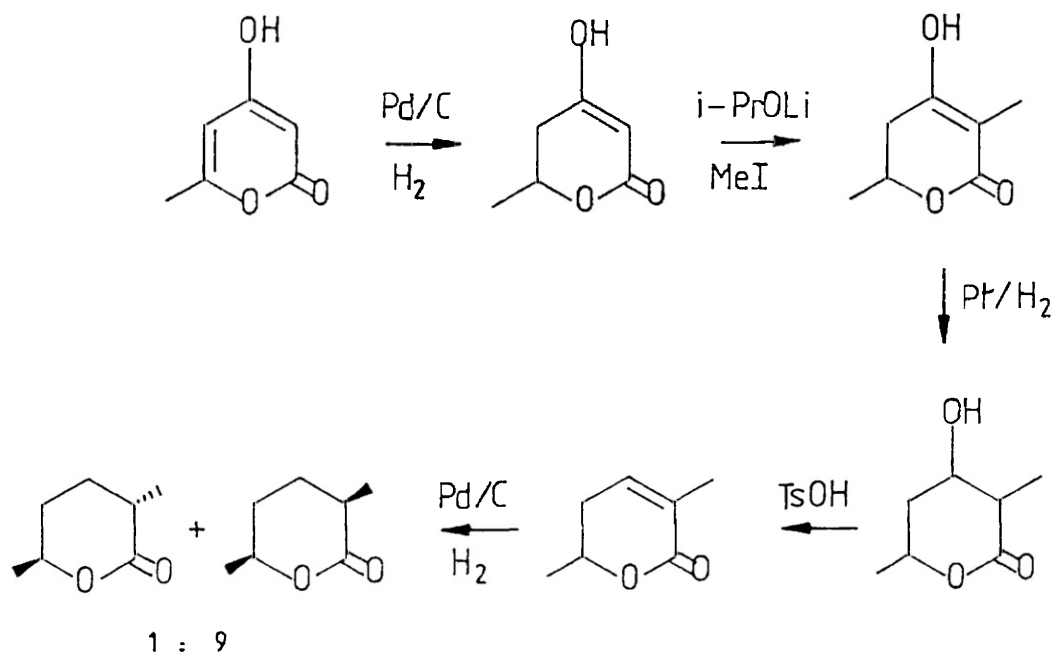
Pirkle and Adams^{87,88} produced a synthesis of chiral material (Scheme 2) involving a resolution by HPLC, which can produce all four stereoisomers, but no yields are given. A racemic synthesis from triacetic acid (an industrially available starting material) has been achieved by Bacardit⁸⁹ (Scheme 3). No yields are given. An asymmetric synthesis has been reported by Hannessian⁹⁰ but this report is confused, showing the pheromone with the wrong stereochemistry at C-2, and the *trans*- rather than the *cis*- form being synthesised.

Scheme 2



(i) R-(-)-1-(1-naphthyl) ethyl isocyanate

Scheme 3

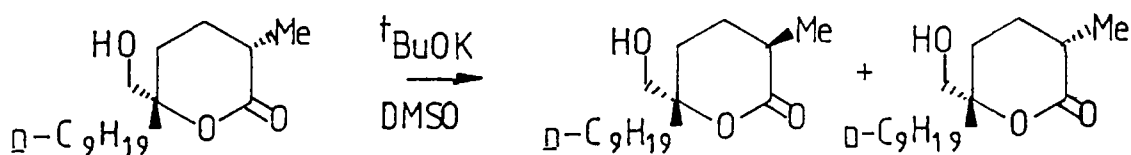


2.2 Malyngolide

There have been five syntheses, all published within two years. Sakito⁹¹ uses an asymmetric auxiliary, (S)-2-(α -cyanomethyl)pyrrolidine to effect an asymmetric synthesis in ten steps. More interesting however is

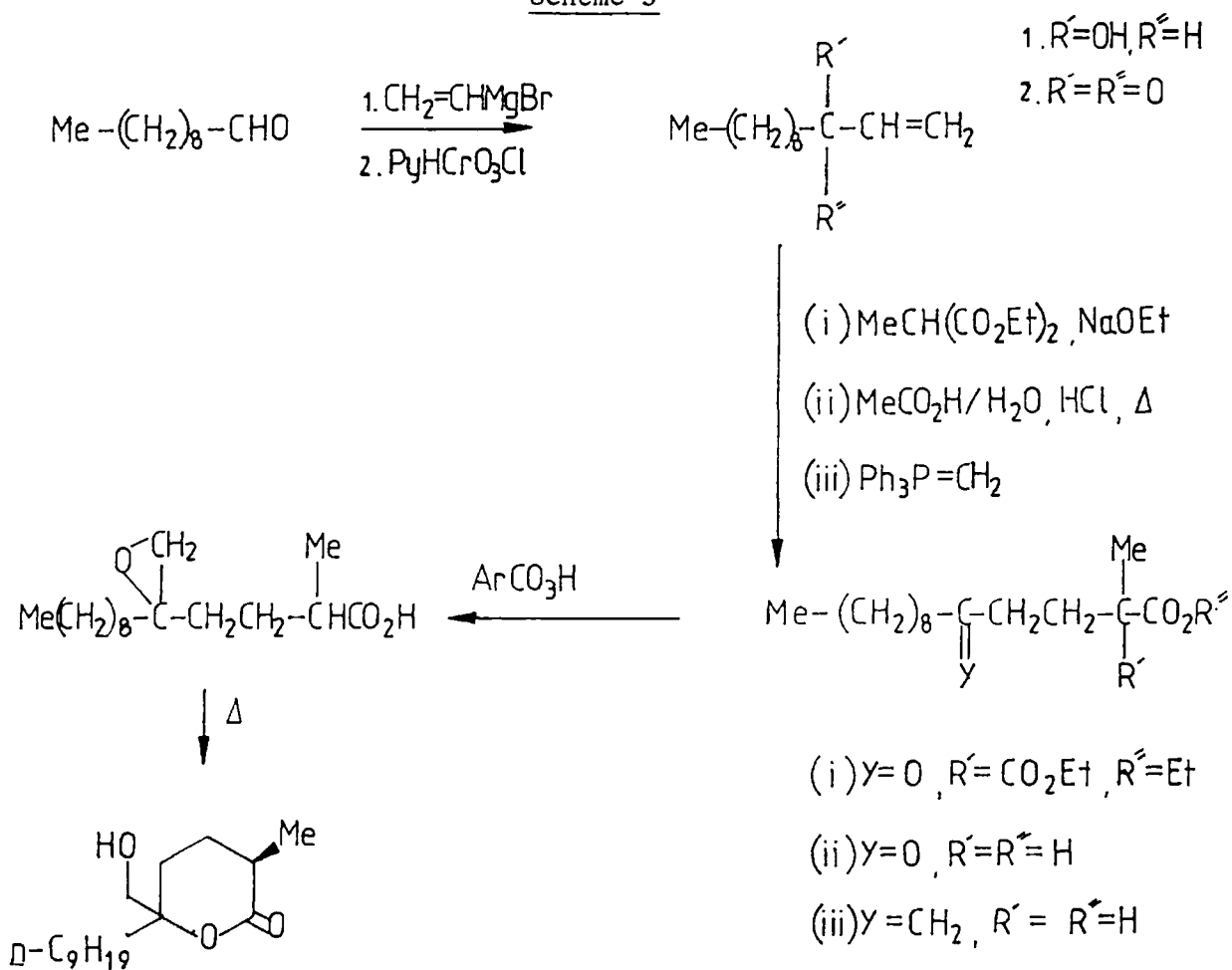
Sakito's finding that the unrequired epimer can be partially converted into the required one (Scheme 4).

Scheme 4

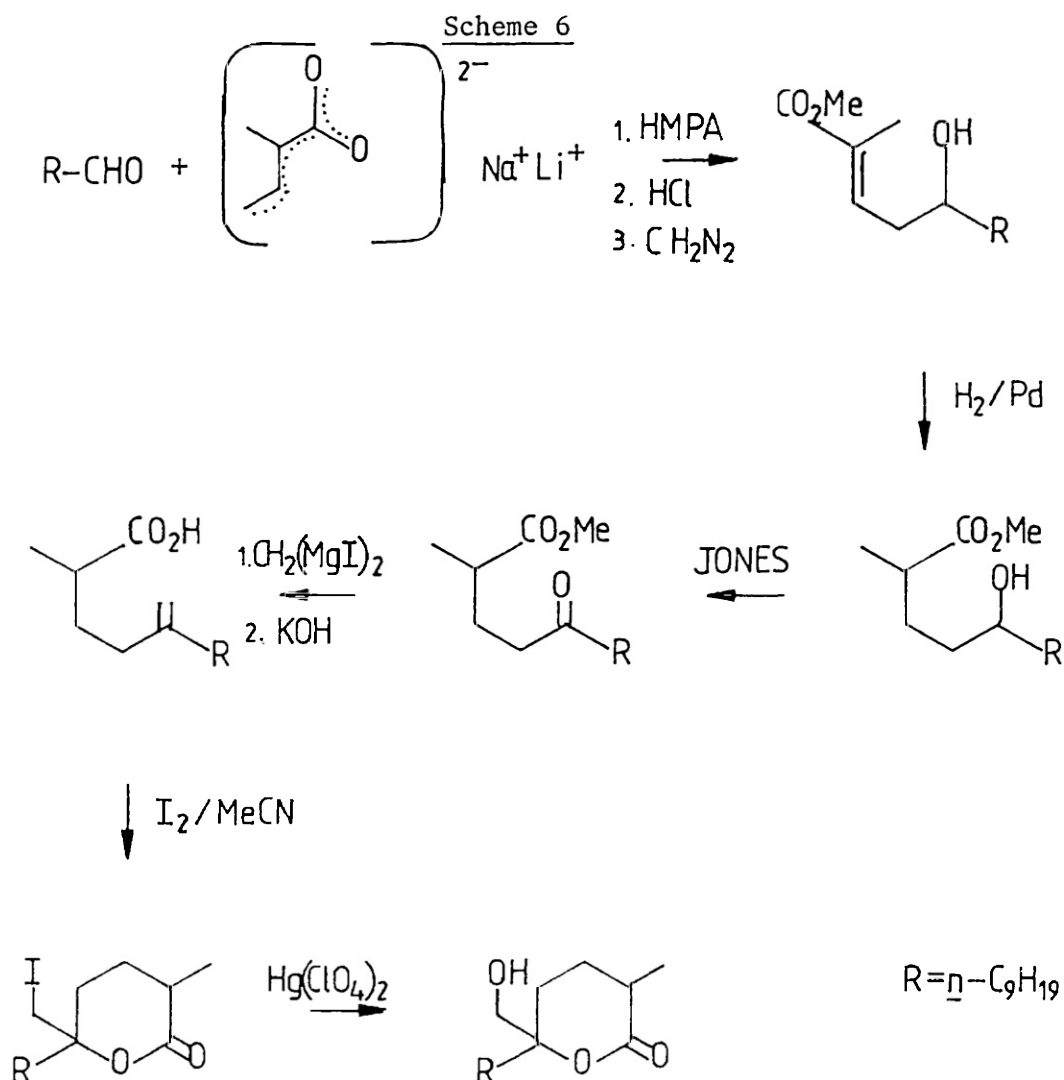


Babler's⁹² synthesis is racemic (Scheme 5) but has the advantage that it is adaptable to the preparation of other similarly functionalized δ -lactones.

Scheme 5

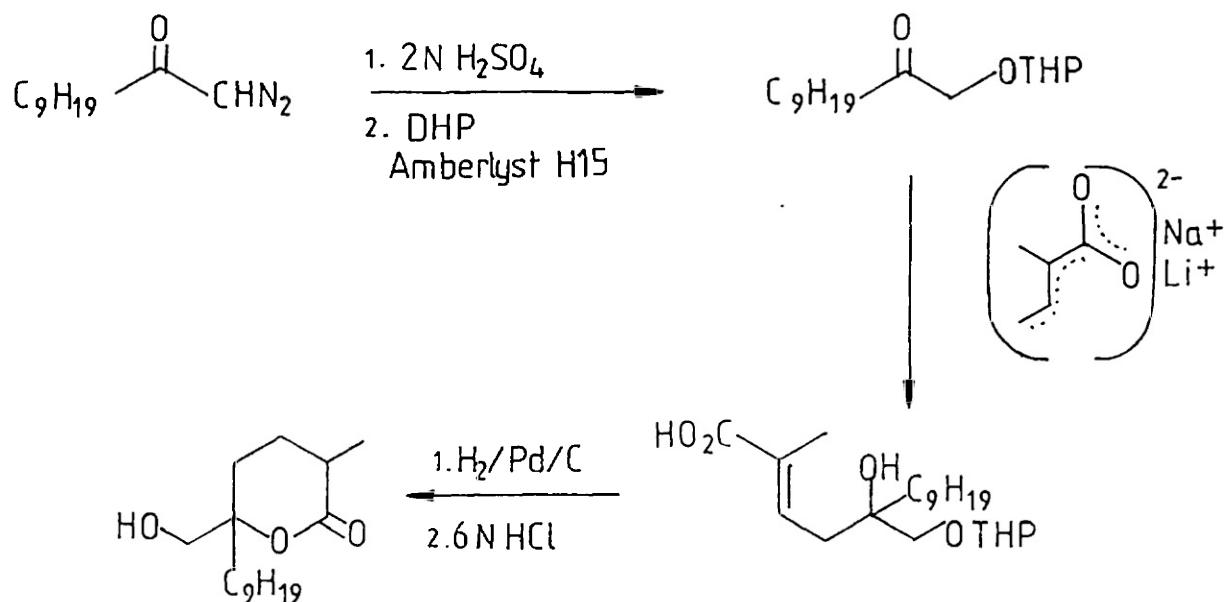


Cardillo⁹³ reports two syntheses both using a dianion. His first route (Scheme 6) involves standard chemistry, the lactone ring being closed by iodolactonisation, to give a mixture of isomers in 35% overall yield.

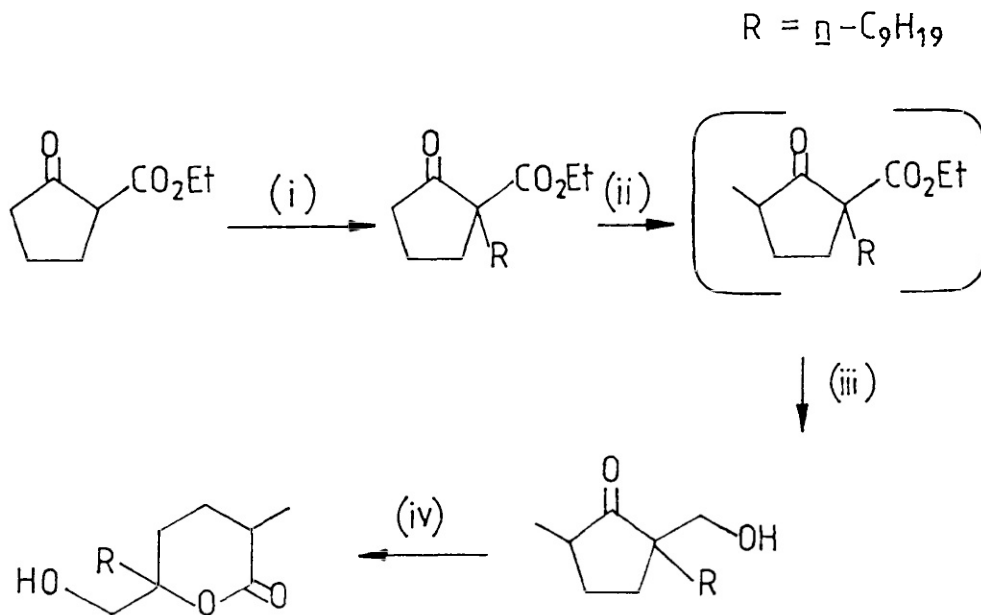


The second route uses a tetrahydropyran protecting group throughout and closes the ring with 6N HCl (Scheme 7) in 45% overall yield. Matsuo's synthesis⁹⁴ is also racemic but very short - only four steps from 2-ethoxycarbonyl cyclopentanone (Scheme 8). Finally Torii⁹⁵ uses electro-oxidation as the first step (Scheme 9) which opens up the cyclopentanone ring. The functional groups are then modified before ring closure *via* iodolactonisation. This gives a short synthesis

Scheme 7



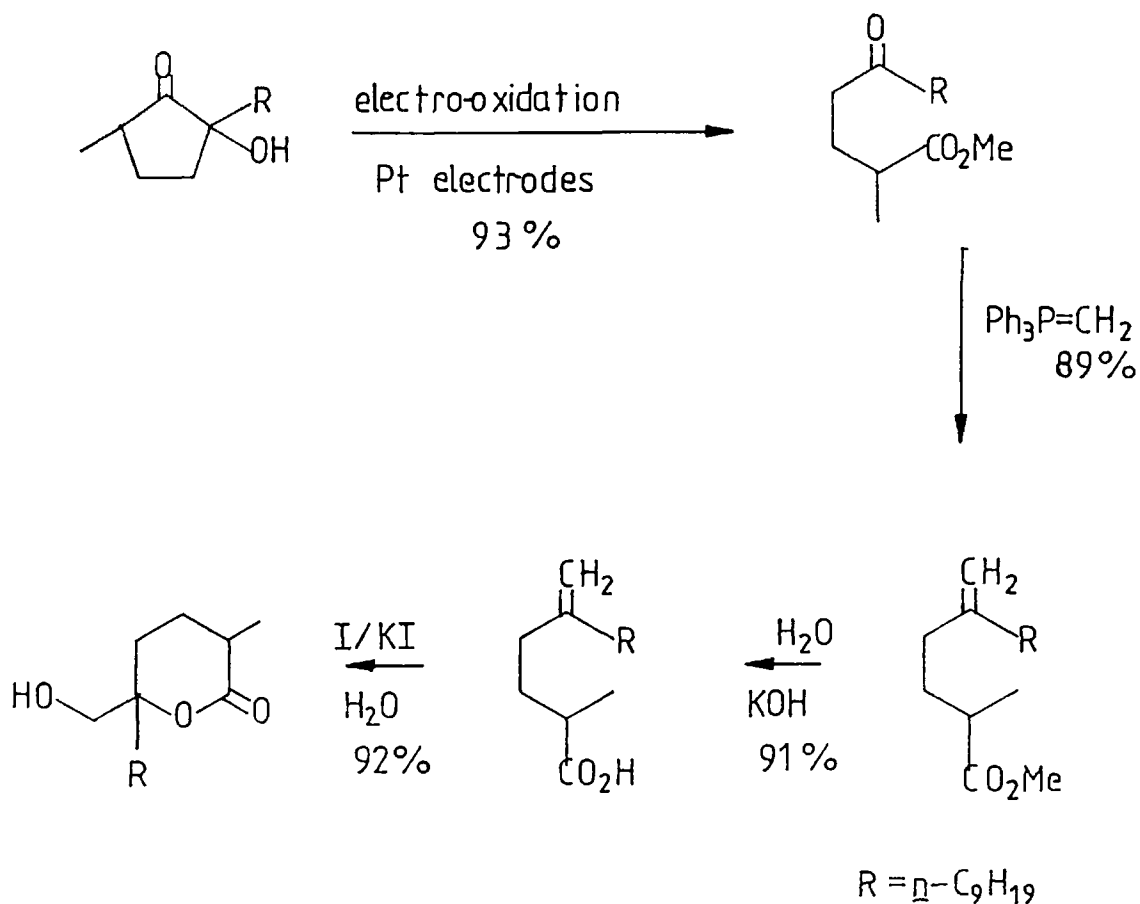
Scheme 8



(i) NaH , RBr . (ii) LDA , MeI , HMPA . (iii) LAH , LDA . (iv) MCPBA .

which would be feasible on a large scale, but otherwise is not so elegant as that of Matsuo.

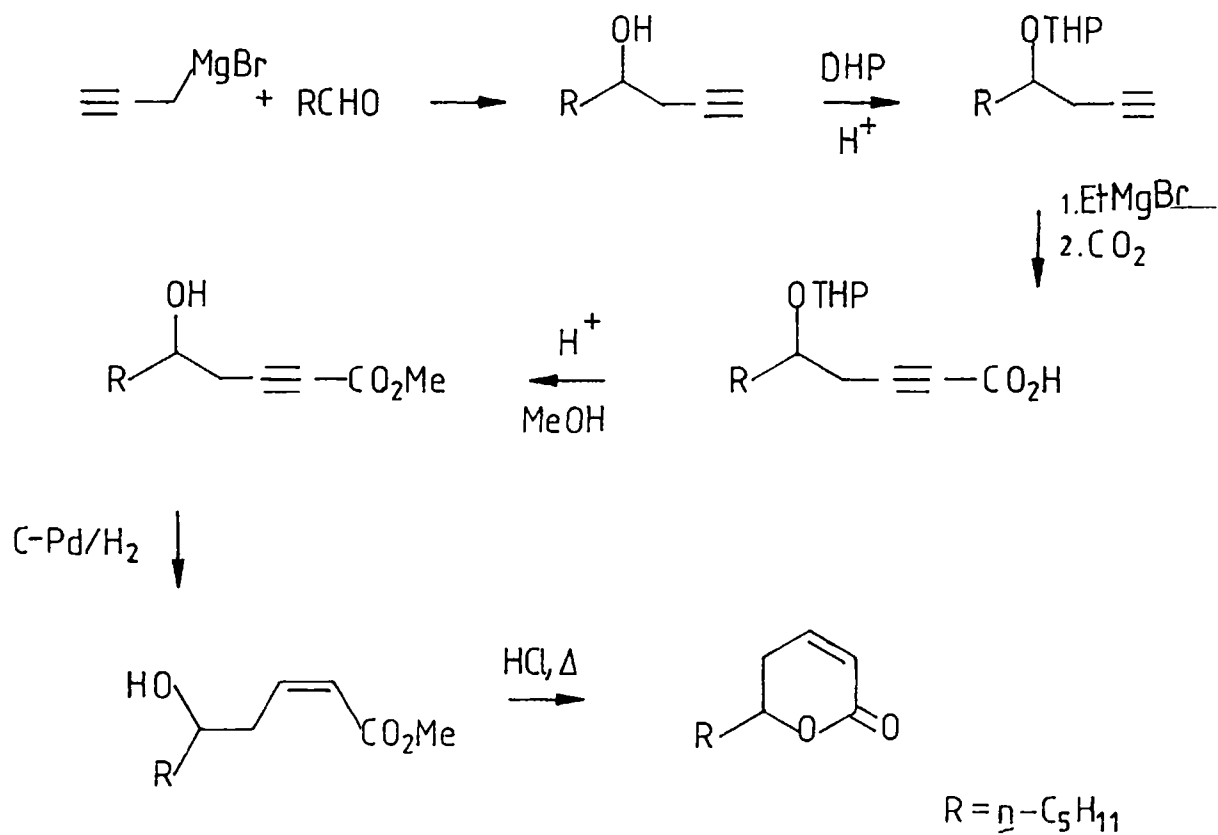
Scheme 9



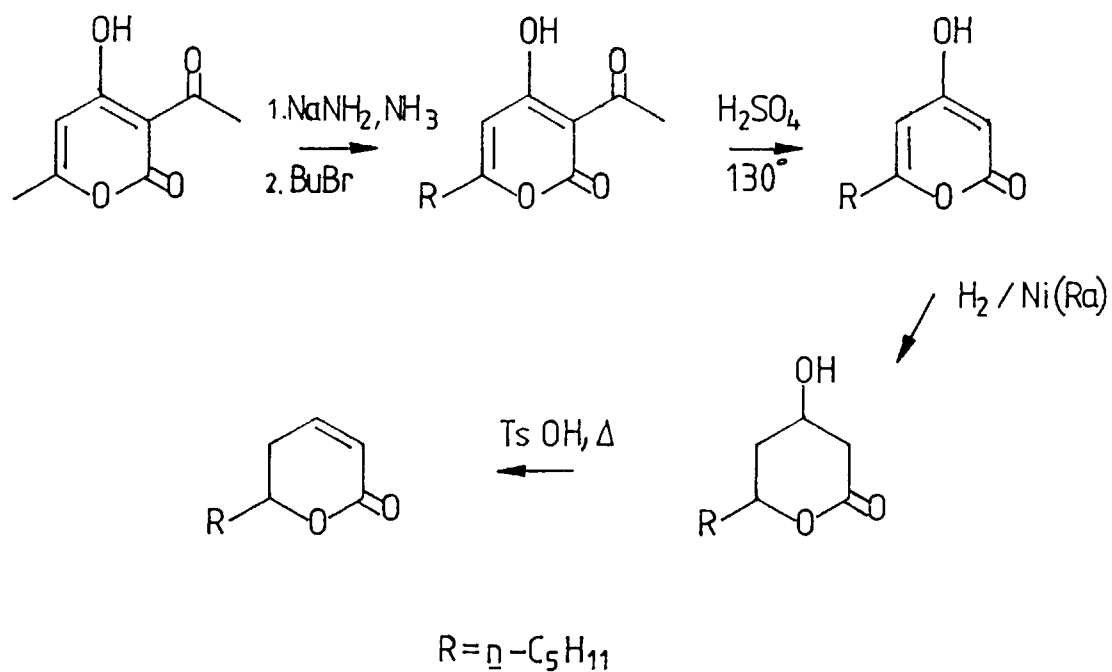
2.3 Massoia Lactone

The first synthesis was by Crombie⁹⁶ but not reported as such until later.⁹⁷ It is racemic and involves standard chemistry. No yields are given (Scheme 10). Bacardit^{98,99} has used a method very similar to his synthesis of the carpenter bee pheromone, starting from dehydroacetic acid (again industrially available) (Scheme 11). Jurczack¹⁰⁰ has produced a very short synthesis using a Diels-Alder reaction to build the 6-membered ring in the first step (Scheme 12).

Scheme 10



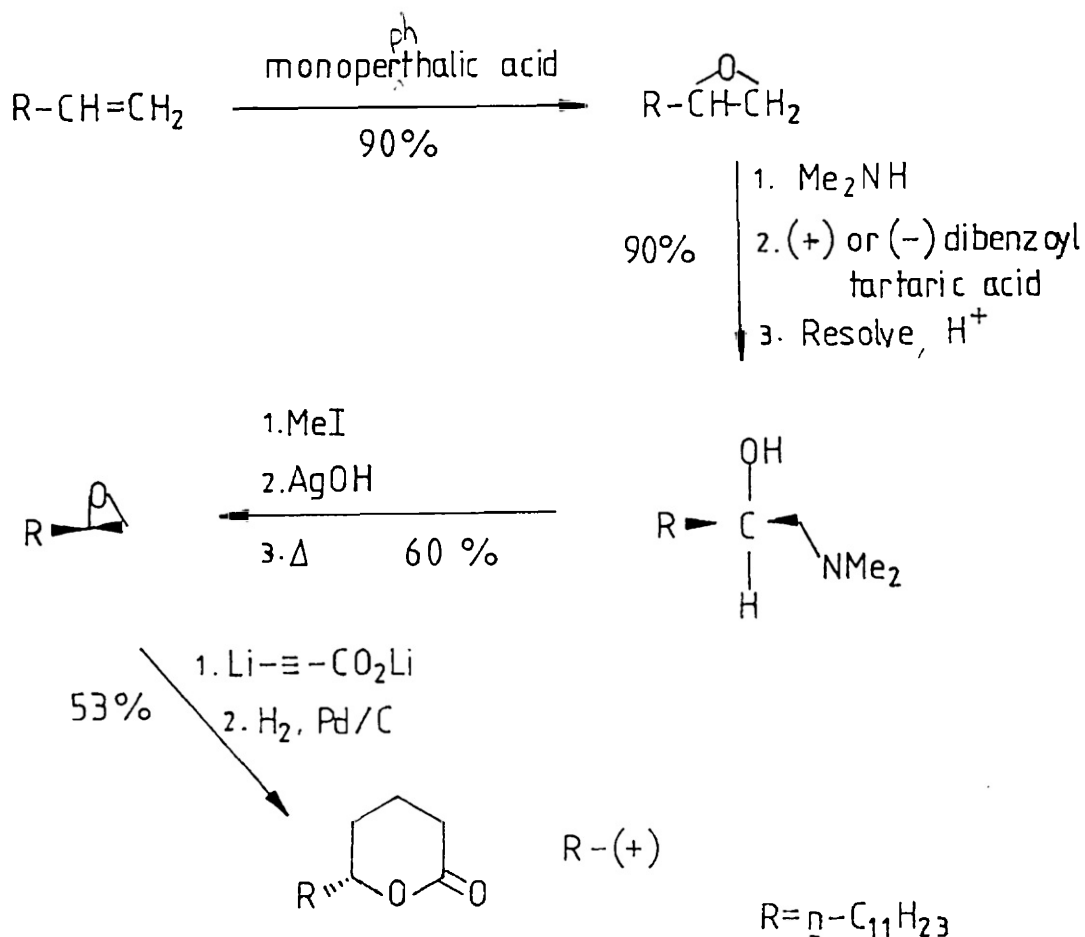
Scheme 11



The use of the alkyne side chain was necessary as the alkane cyanoalcohol (as in Scheme 2) could not be resolved by conventional chromatography. The alkyne gives a more rigid chain which then allows resolution.

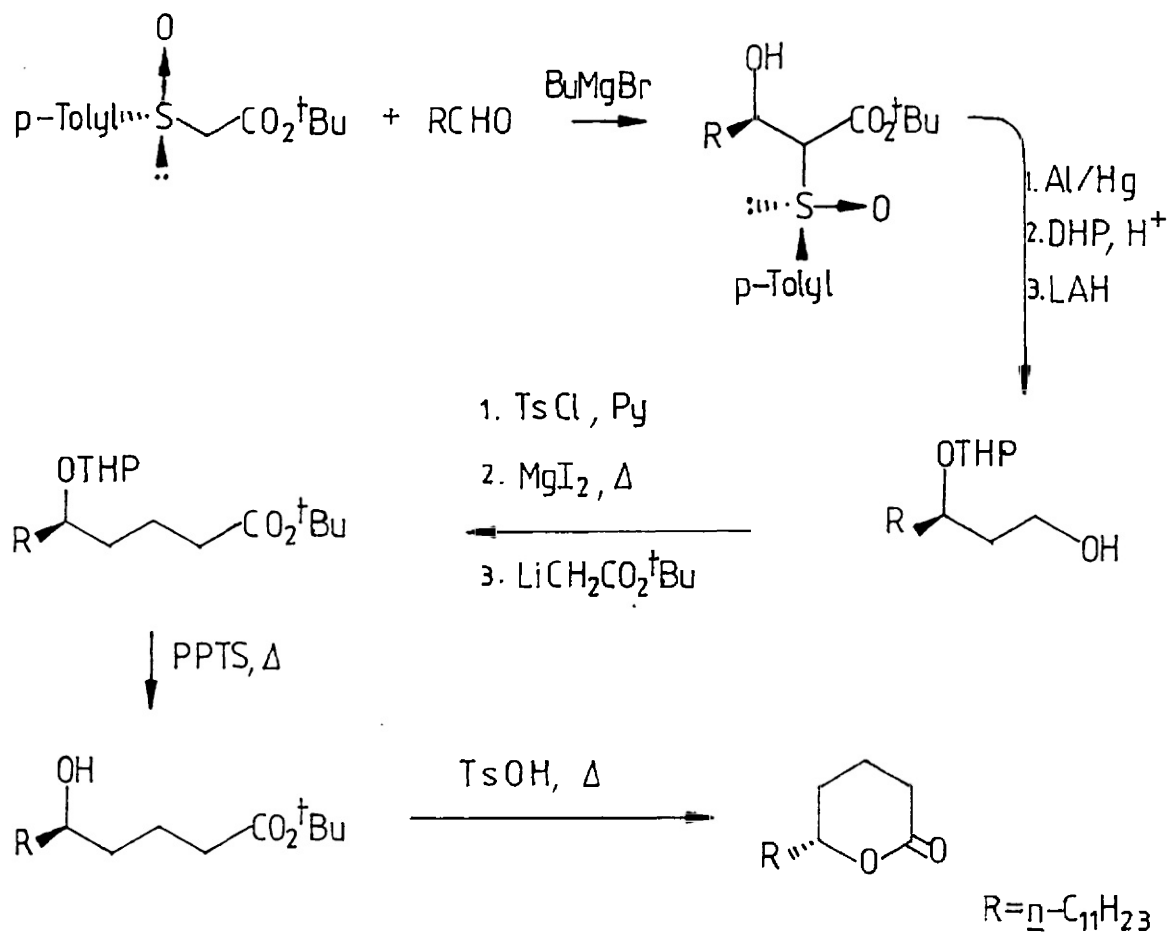
Coke and Richon¹⁰¹ also make use of resolution, of β -amino alcohols to give an asymmetric synthesis of both isomers, (Scheme 14).

Scheme 14

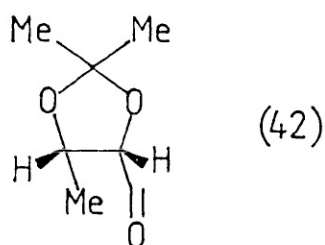


Solladié¹⁰² uses a chiral sulfoxide with dodecaldehyde to give a separable diastereomeric mixture (Scheme 15).

Scheme 15



The most recent synthesis by Servi¹⁰³ (which claims to be the first synthesis of pure R- and S-isomers!) starts from a chiral synthon (42) derived from microbiological action of fermenting baker's yeast on cinamaldehyde and acetaldehyde. The synthesis may produce

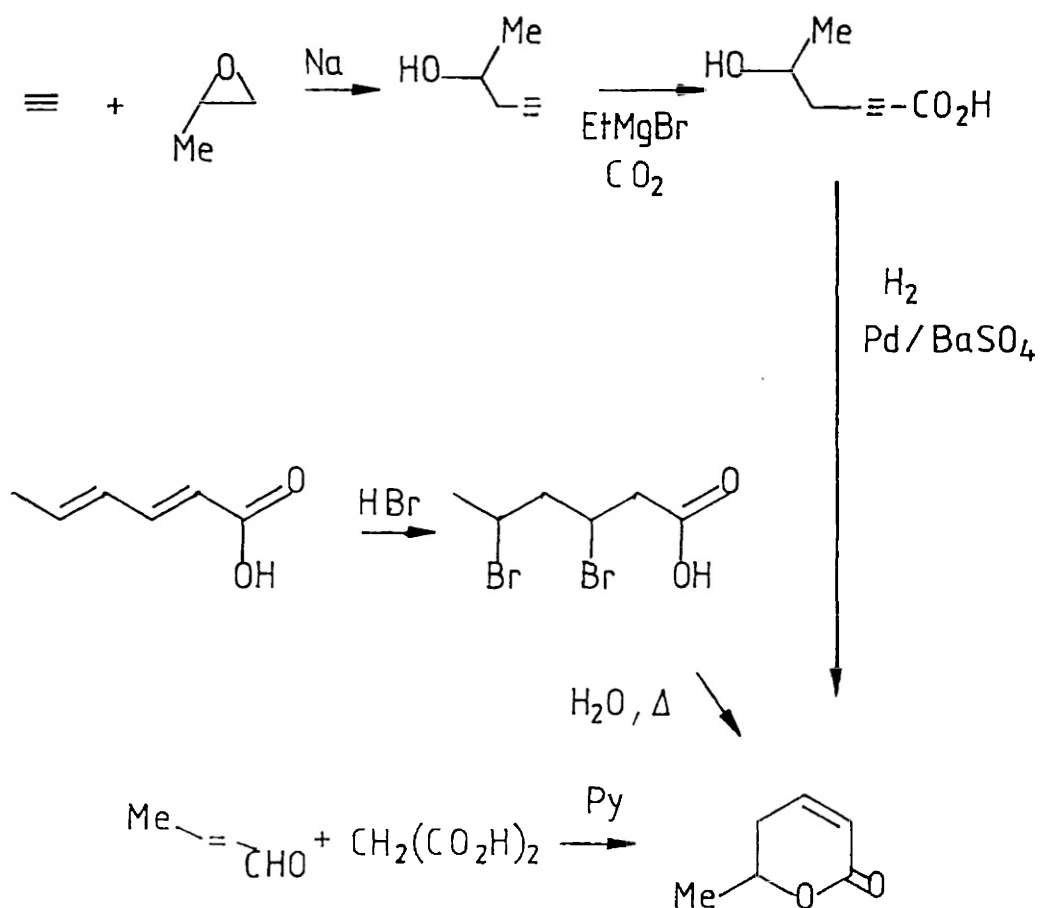


pure isomers (as do those of Coke and Pirkle which Servi ignores) but is long and involves much protection, deprotection and reprotection. It is much less elegant than all of the others and the yields are lower too.

2.5 Parasorbic Acid

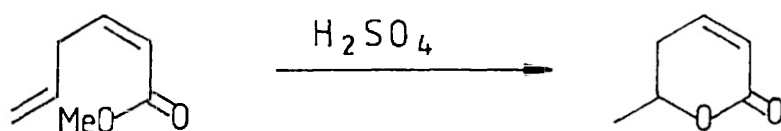
There are three relatively old syntheses¹⁰⁴ (Scheme 16), all racemic, and giving low yields.

Scheme 16



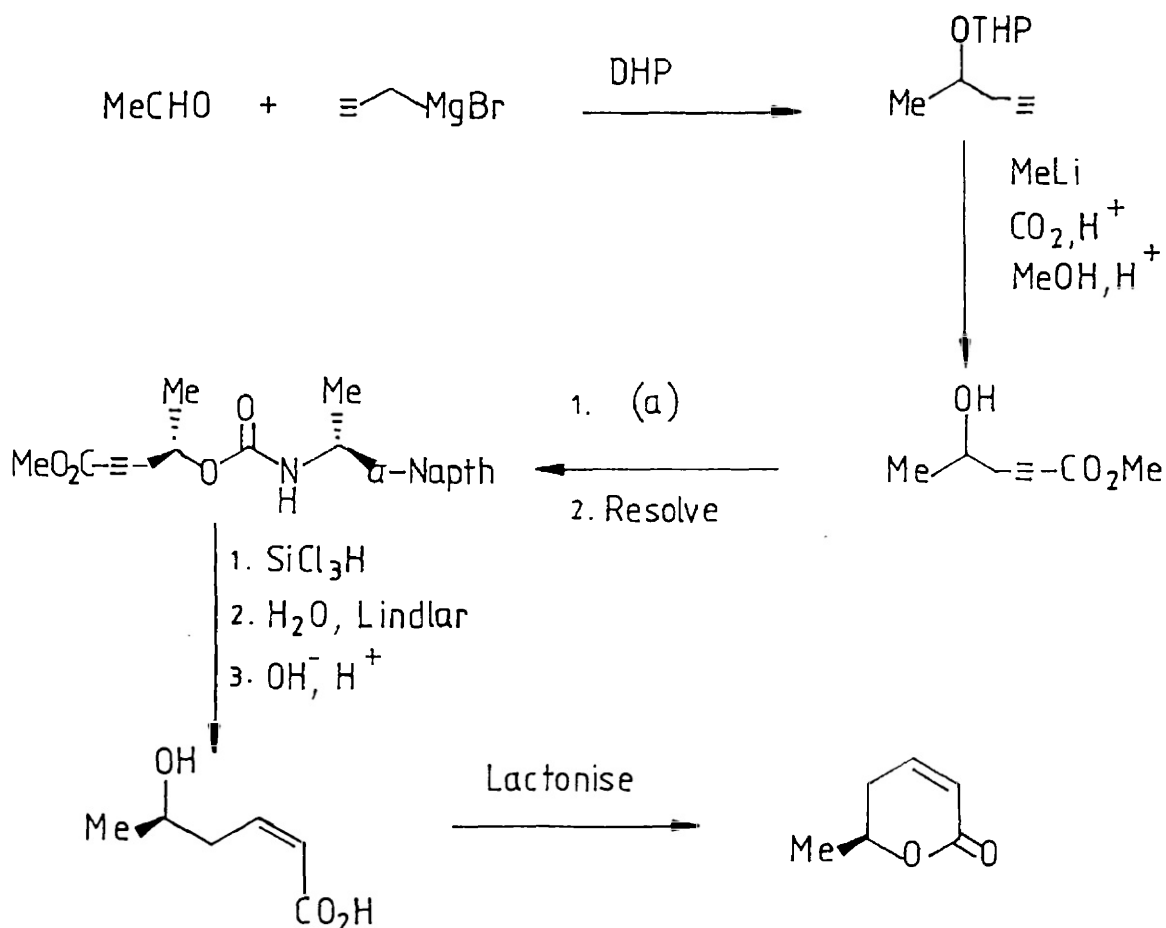
Another more recent¹⁰⁵ synthesis of this type involves treatment of a *cis*-unsaturated ester with 60-90% sulphuric acid (Scheme 17), with a yield of 84%.

Scheme 17



Pirkle and Adams¹⁰⁶ use another variation of their carpenter bee pheromone synthesis to give pure R- and S-isomers (Scheme 18). It does seem, however, a long and tortuous route for a very simple product which can be easily obtained enantiomerically pure from berries of the Rowan Tree.

Scheme 18



(a) R-1-(1-naphthyl)ethyl isocyanate

Conclusion

There are a great many δ -lactones in nature which may be useful in pest control, medicine and the food industry. Racemic synthesis is relatively easy, but the product is unlikely to be useful as the unnatural isomer often acts as an inhibitor of the natural one. More recent asymmetric syntheses are often long-winded and require resolution or an optically active starting material. More and more biologically active δ -lactones are being discovered in algae and fungi, and as these can easily be cultured and produce stereochemically pure products, this would appear to be a feasible source of supply for the future. However the preparation of more (or less) active synthetic variants will always demand the skill and ingenuity of the synthetic organic chemist.

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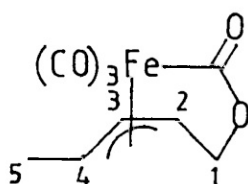
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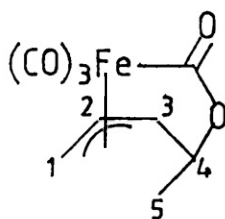
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Tricarbonyliron lactone complexes are white or yellow crystalline solids which are reasonably stable in air at room temperature, but are best stores for long periods at -23°C . Decomposition is accelerated by solvation, especially in chlorinated solvents, to give various organic products⁵ and elemental iron. The iron is bonded to the organic moiety by an iron-carbon sigma bond, and an iron-allyl bond. In the infrared spectrum, the diagnostic bands occur around 2000 cm^{-1} (C-O stretching in the carbonyl ligand) and typically at 1685 cm^{-1} (C-O stretching in the Fe-acyl carbonyl). ^1H Nmr spectra can be difficult to obtain, due to production of trace amounts of elemental iron which tends to broaden the peaks. The protons on the allyl unit and α - to the oxygen occur as multiplets in the range $\delta 2.04 - 6.04$ depending on other substituents, and their chemical shifts are very solvent dependant. The complexes are named according to the longest carbon chain, the O-CO-Fe unit is designated as 'formyloxy' and the allyl unit as 'enyl', following the Chemical Society recommendations. For example

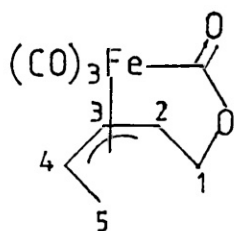


π -allyl-2,3,4- η^3 -(1-formyloxy-pent-3-en-2-ylato)tricarbonyliron

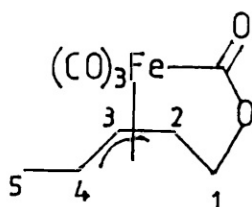


π -allyl-1,2,3- η^3 -(4-formyloxy-pent-2-en-3-ylato)tricarbonyliron

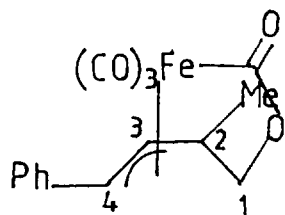
When a substituent on the allyl unit, or α - to the oxygen atom occurs, this can have two possible orientations. A substituent directed away from the $\text{Fe}(\text{CO})_3$ moiety is designated as the *exo*-form, and when directed towards the $\text{Fe}(\text{CO})_3$ group, as the *endo*-form. If no designation is given, then *exo*- is to be assumed. For example



4-*endo*- π -allyl-2,3,4- η^3 -(1-formyloxy-pent-3-en-2-ylato)tricarbonyliron



(4-*exo*-)- π -allyl-2,3,4- η^3 -(1-formyloxy-pent-3-en-2-ylato)tricarbonyliron



π -allyl-2,3,4- η^3 -(1-formyloxy-
(2-methyl)-4-phenylbut-3-en-2-ylato)
tricarboxyliron

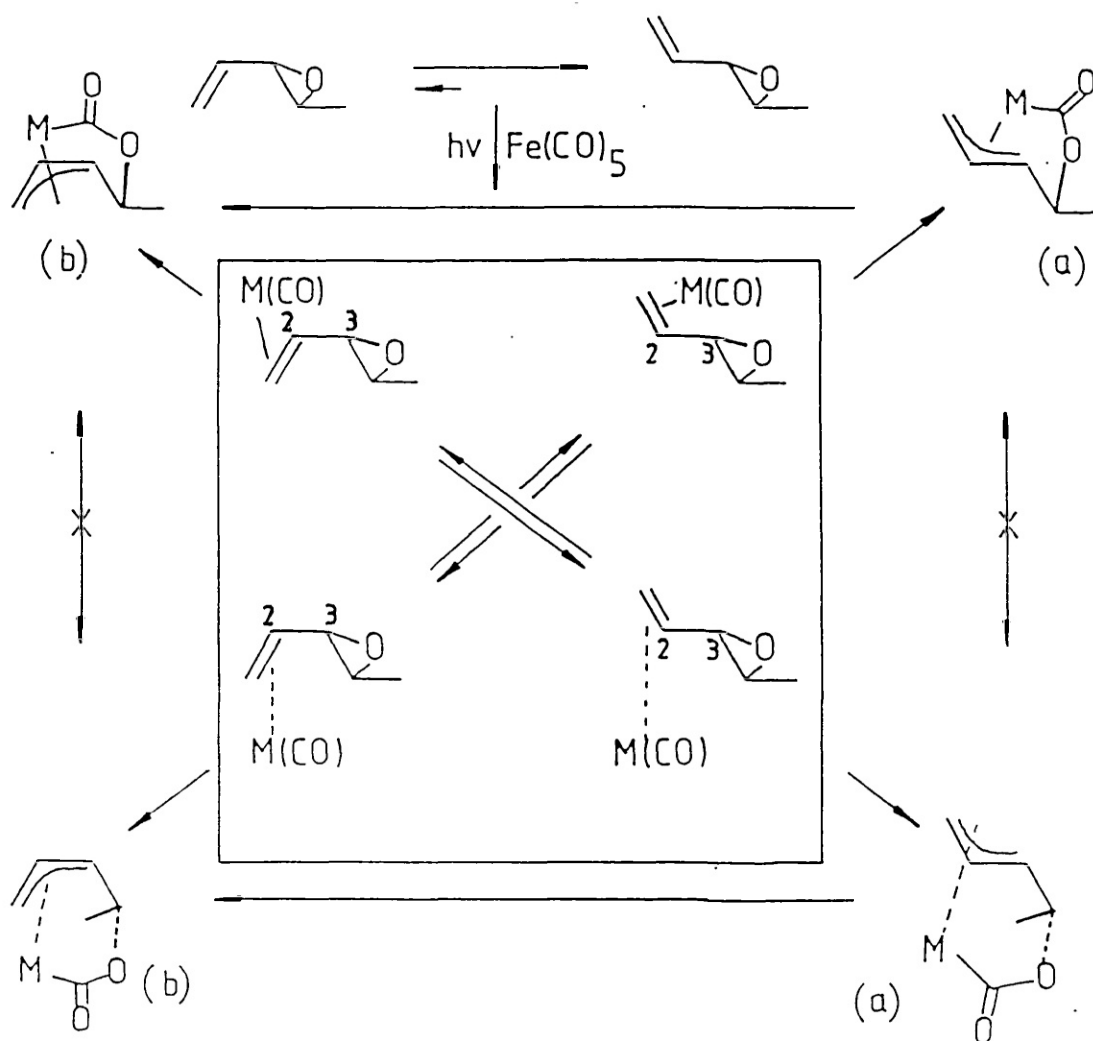
The structures are generally referred to as tricarboxyliron lactone complexes, but also simply as lactone complexes. Preparation of the lactone complexes is achieved by photolysis of an allyl epoxide in the presence of pentacarbonyl iron under argon. Other methods have been reported,⁶ but many of these require heating, which often causes substantial decomposition during reaction, consequently they are not routinely employed.

Aumann³ has proposed a mechanism for the formation of the π -allyl-tricarboxyliron lactone complexes involving photolytically promoted loss of a carbonyl ligand from the iron to give the co-ordinatively unsaturated and reactive species $\text{Fe}(\text{CO})_4$. (Species such as $\text{Fe}(\text{CO})_3$ and $\text{Fe}(\text{CO})_2$ may also be formed) (Scheme 2). Attack of the alkene follows to give an iron-tetracarbonyl-alkene complex (box) in which rotation around the C_2 - C_3 bond can lead to different isomeric forms. Attack on a carbon monoxide ligand by the epoxide oxygen then occurs giving a tricarboxyliron lactone complex.

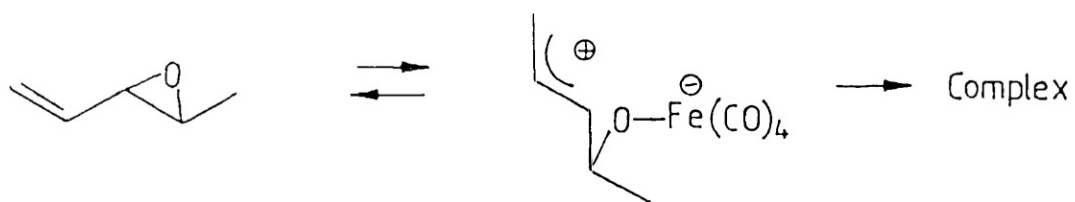
Formation of any of the thermally labile '*trans*'-tricarboxyliron complexes (a) would be followed by isomerisation to the '*cis*'-tricarboxyliron complexes (b), even at low temperatures.

An alternative mechanism involves primary attack on the coordinatively unsaturated $\text{Fe}(\text{CO})_4$ species of the oxiran ring of the allyl epoxide (Scheme 3).

Scheme 2



Scheme 3

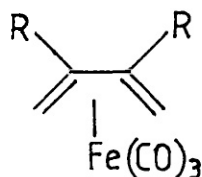


However, this reaction pathway is energetically less favourable since the immediate allyl cation cannot be stabilised by the metal.

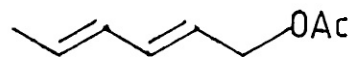
2.2 Sources of Reactive Iron: The Ultrasound Reaction.

The use of pentacarbonyliron as the source of a reactive iron moiety is not an ideal choice as it is a highly toxic and volatile (b.p. 103°C) liquid. Photolysis using pentacarbonyliron requires high dilution conditions (typically 3.5 mmol of allyl epoxide in 350 ml of benzene), a wavelength filter system, and usually an internal cooling system. Preparation of complexes in quantities in excess of one gram therefore is not feasible. Consequently a more flexible and convenient method was urgently needed.

Suslick⁷ recently reported that the effect of ultrasound on pentacarbonyliron, (neat or in various solvents) causes disassociation to give $\text{Fe}(\text{CO})_4$, followed by ligand substitution if phosphines are present. Attempted preparation of a tricarbonyliron lactone complex using a similar procedure however gave none of the required product. On the other hand, sonolysis of a suspension of nonacarbonyl diiron ($\text{Fe}_2(\text{CO})_9$) (a much more convenient source of iron carbonyl) did lead to complex formation, accompanied by some dodecacarbonyl triiron ($\text{Fe}_3(\text{CO})_{12}$) formation. (Sonolysis of a suspension of nonacarbonyl diiron alone gave pentacarbonyl iron, finely divided iron and carbon monoxide. Sonolysis of dodecacarbonyl triiron, with or without an allyl epoxide present, gave no reaction.) These results contradict Suslick's later suggestion⁸ that sonolysis of all three iron carbonyls gives the same reactive species. The formation of the coordinatively unsaturated reactive species $\text{Fe}(\text{CO})_4$ is also open to question, as, if this is the case, the formation of known diene complexes of the type (2) would be expected in the presence of dienes. When isoprene,



(2)



(44)

2,3-dimethylbutadiene, or the acetoxy diene (44) are sonolysed in the presence of nonacarbonyl diiron however, no diene complex formation is observed.

The chemical effects of high intensity ultrasound arise from the phenomenon of cavitation - the formation of microscopic cavities in a liquid and their subsequent collapse. When ultrasonic waves are propagated through a liquid, a temporary reduction in pressure during the rarefaction part of the cycle causes a break in the continuity of the liquid - a cavity. This is filled with vapour from the surrounding liquid, either gases dissolved in the liquid or the vapour of the liquid itself. The compression part of the wave cycle causes the collapse of the cavity and this is accompanied by hydraulic shock,⁹ which can be heard as a noise resembling high pitched 'white noise'. The energy released by this collapse causes intense but transient local heating and pressures, which have been calculated¹⁰ to be as high as 10,000°C and 10,000 atm. These conditions can give rise to high energy species in solution. Although cavitation can occur in degassed solvents, solvents containing dissolved gases or impurities give rise to cavitation more easily, as cavitation nuclei are more available.¹¹ Interfaces of different acoustic impedance (e.g. solvent-glass or solvent-impurity interfaces) will tend to promote cavitation.¹²

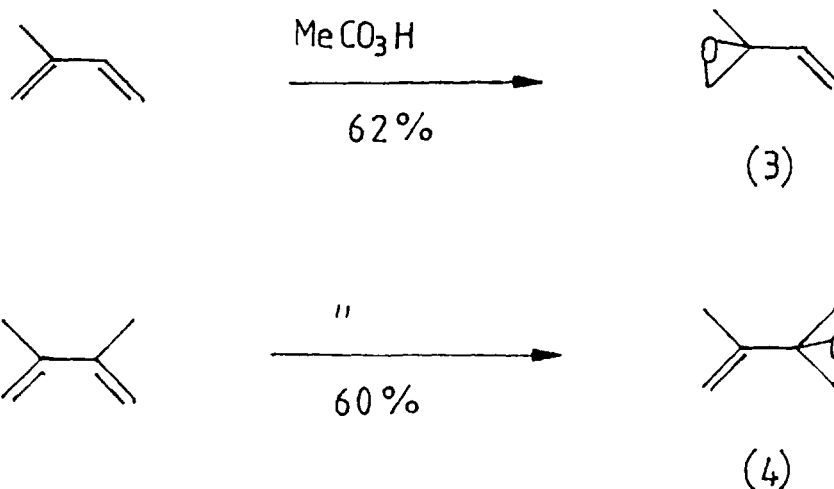
Until more recently the use of ultrasound in organic chemistry was restricted to increasing rates of reaction¹³ (particularly heterogeneous reactions), and oxidation by OH radicals in aqueous systems.⁹

One report even states that organic solvents will not support cavitation!¹⁴

In order to develop the use of sonochemistry as a standard method for the preparation of tricarbonyliron lactone complexes, various allyl epoxides were synthesised, and subsequently converted into lactone complexes.

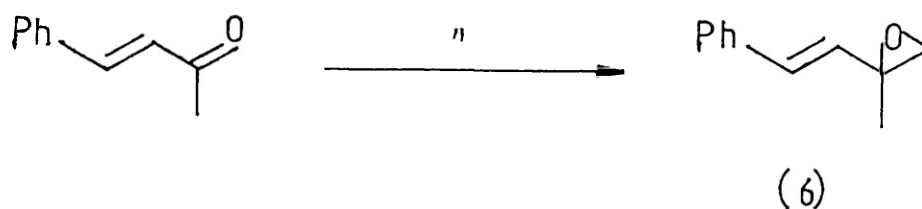
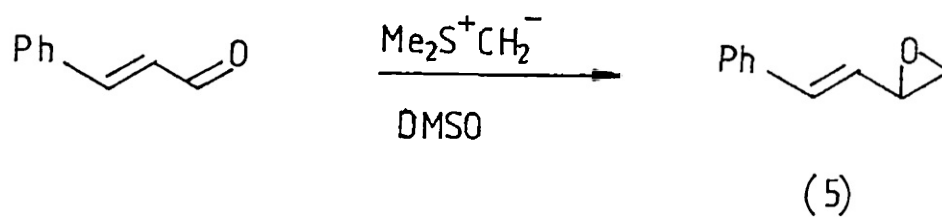
2.3 Preparation of Epoxides

As has been shown in section 2.1, the direct precursors of the iron carbonyl lactone complexes are allyl epoxides; these were prepared by two main methods. The simplest of these is the regio-selective epoxidation of dienes using a peracid in the presence of a sodium carbonate buffer. For example, the epoxides (3) and (4) are produced by epoxidation of isoprene and dimethylbutadiene respectively.

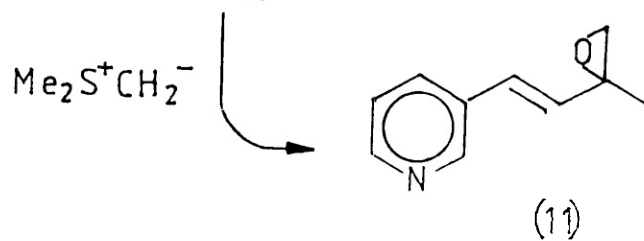
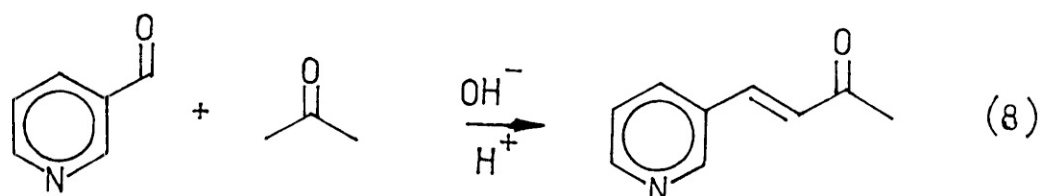
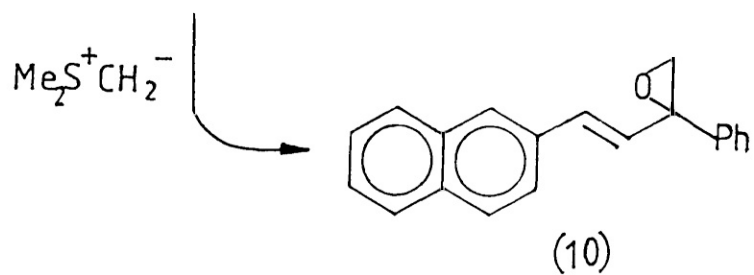
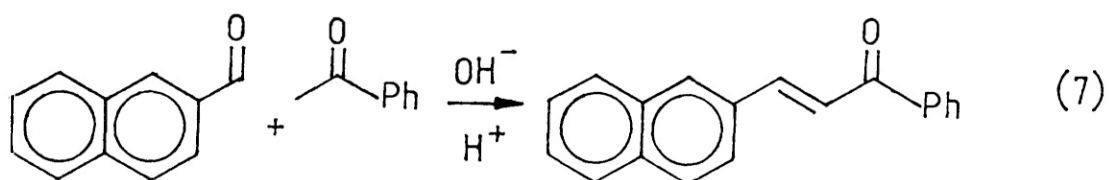


The second method involves the treatment of α,β unsaturated aldehydes or ketones with dimethylsulphonium methylide.¹⁵ Thus cinnamaldehyde and benzalacetone afford the epoxides (5) and (6) respectively. This method is complementary to the method using a peracid as it is possible

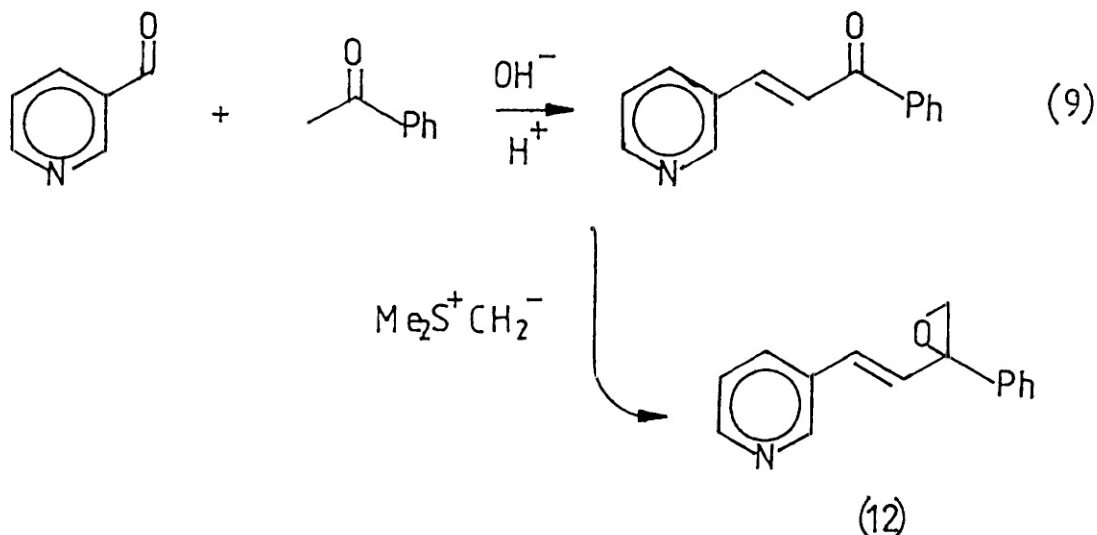
for the allyl epoxide produced to have a tri- or tetra-substituted double bond.



Scheme 4



Scheme 4 (continued)



As these epoxides tended to polymerise, they were best used immediately (often in crude form), or they could be stored at -23°C for several weeks. Satisfactory i.r. spectra could not be obtained for many of them as they tended to decompose in the i.r. beam.

Other allyl epoxides, (10) to (12) could be similarly prepared. These were obtained from the corresponding enones, (7) to (9) which in turn were prepared by mixed condensation reactions (Scheme 4).

2.4 Preparation of Complexes

The ability of a solvent to support cavitation is dependant on the strength of the liquid, which is directly related to its vapour pressure. The use of different solvents was, therefore, investigated. A standard ultrasound cleaning bath containing water was used. Into this was placed the reaction flask, about one third full, with a suba-seal in the neck. (This allows a slight build up of pressure due to the released carbon monoxide, which when using a low-strength organic solvent will aid cavitation⁹ by promoting collapse of cavities.)

In an ultrasound bath there are areas of high and low activity throughout the liquid,¹¹ so that, shape of flask, position of the flask in the water, and how full it is, can all make a difference to the yield. The results of all these factors on the yield are shown in Table 1 and Table 2. Yields were determined after filtering the mixture through Celite, concentrating, and purification by flash chromatography.

Table 1

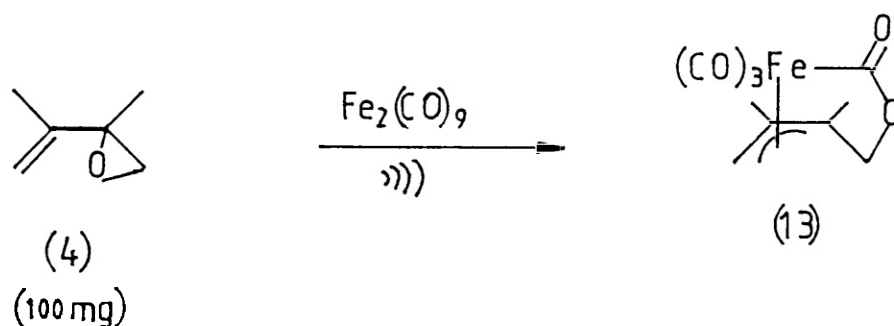
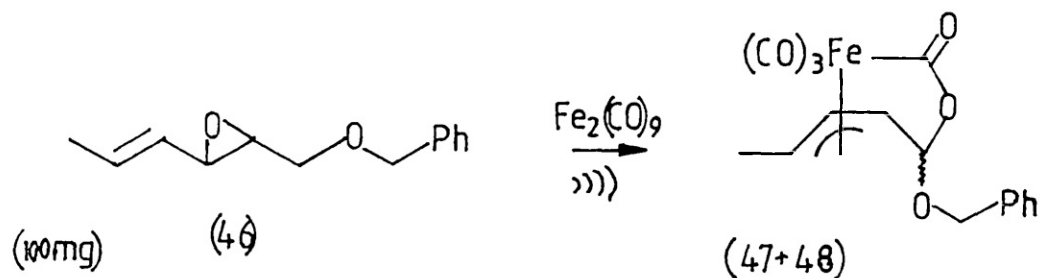


Table 2



Solvent	Vol./ml	eq. Fe_2CO_9	Time/h	% yield
Ether	25	1.5	0.3	11
"	"	"	2	21
"	"	"	3.5	16
"	"	"	5	42
Benzene	"	"	5	71
"	"	"	18	79
"	"	1.0	18	42

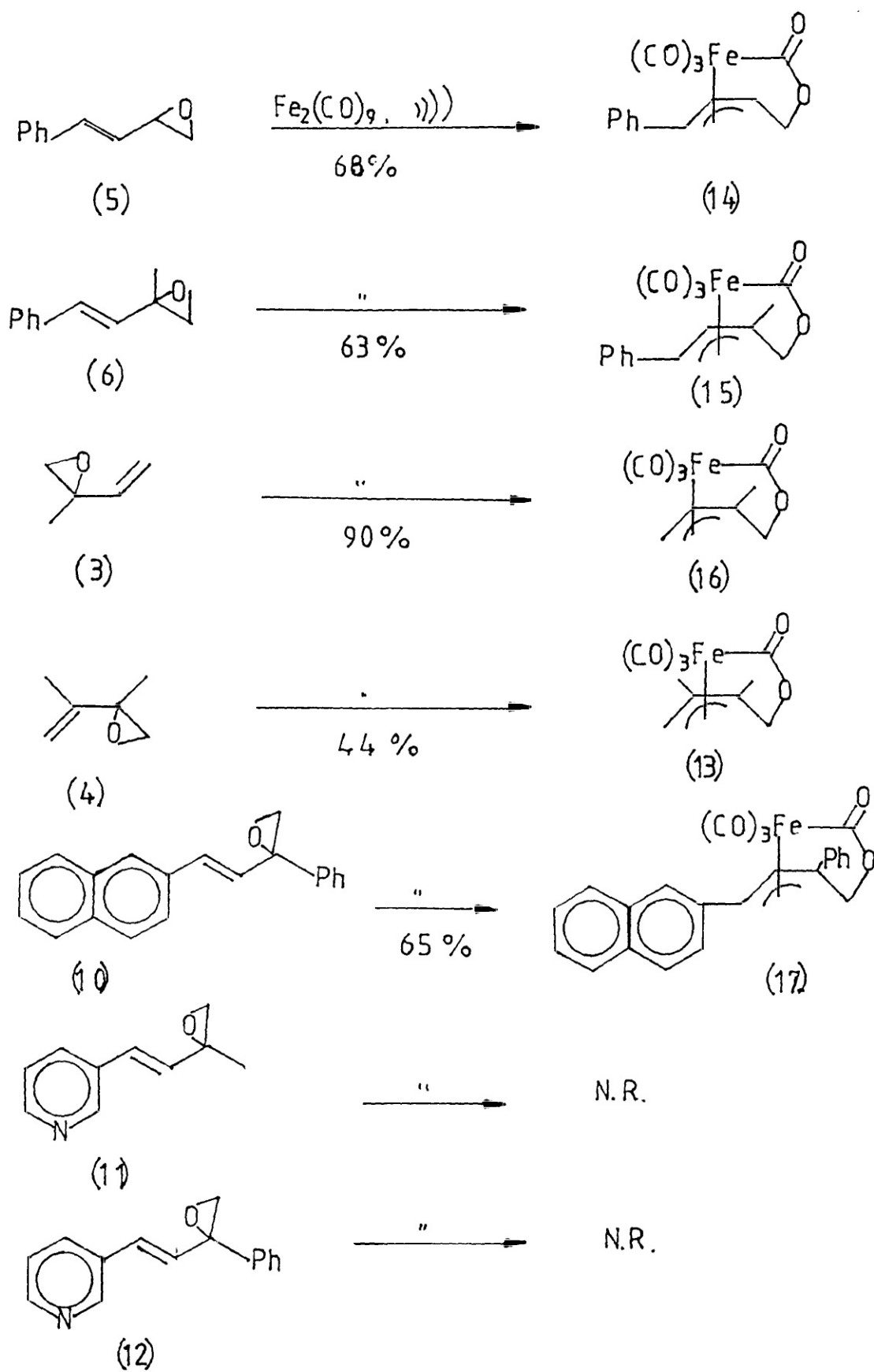
The ideal conditions for this reaction can therefore be stated as follows:-

1. Benzene solvent (preferably not degassed, distilled or dried).
2. Reaction time of 1-5 hours.
3. Use of a dilute solution.
4. 1.5 eq. of nonacarbonyl diiron.
5. Use of a round bottomed flask, about one third full, placed just in the ultrasound bath, to give maximum agitation.
6. Inert atmosphere not required (a carbon monoxide atmosphere caused a slower, less clean reaction with lower yield).
7. Suba-sealed reaction flask.

These reactions can be scaled up to 2-3g without noticeable effects upon yield. In the case of epoxide (4), the low yields were found to be due to the volatility of the epoxide under the reaction conditions. If the epoxide was used in a five fold excess the yield could be increased to 90% with respect to nonacarbonyl diiron. Using the sonolysis method, a series of iron carbonyl lactone complexes were subsequently prepared from the various allyl epoxides previously prepared, (Scheme 5). Attempts to prepare complexes containing a pyridine ring however failed. The reason for this failure is explained in Section 4.3. Cotton¹⁶ has reported that nonacarbonyl diiron reacts with tetrahydrofuran under carbon monoxide to give an $\text{Fe}(\text{CO})_4\cdot\text{THF}$ species. We found that iron complexes could be prepared, using nonacarbonyl diiron in tetrahydrofuran with the allyl epoxides, in yields similar to those obtained using the ultrasound method. A simple substitution reaction, of the THF ligand by the alkene of the allyl epoxide, would seem the most likely mechanism for complex formation. However, as Cotton points out, when carbon monoxide pressure is not maintained the situation is much more complex. Iron complexes were prepared with or without a carbon monoxide atmosphere, and surprisingly the reaction is quicker and cleaner without. The carbon monoxide ligands are labile and will exchange with those in a carbon monoxide atmosphere.¹⁶ Clearly more work is required to fully understand the mechanism of complex formation in tetrahydrofuran.

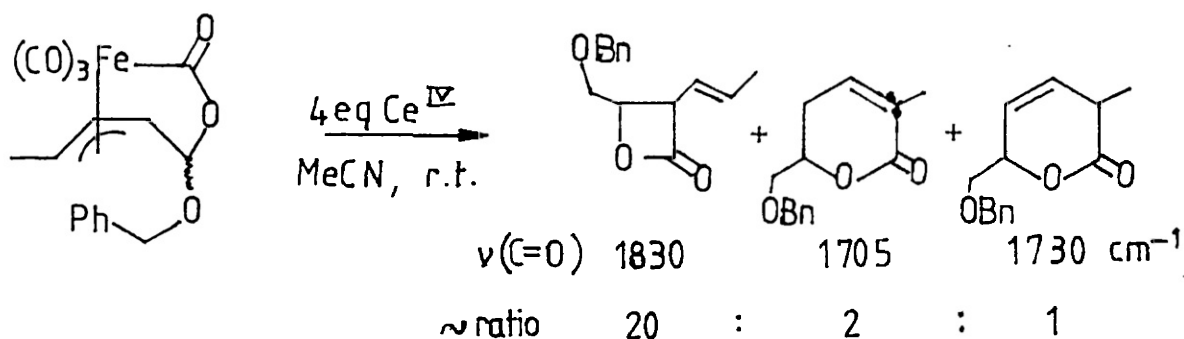
Both methods for preparation of complexes are complementary and are now used routinely. Complex preparation from volatile and aliphatic epoxides proceeds best in tetrahydrofuran while aromatic epoxides give best results using ultrasound. Only in one case (malyngolide synthesis, see Section 3.4) was there any major difference between the methods.

Scheme 5



2.5 Preparation of Lactones

Oxidation of tricarbonyliron lactone complexes using ceric ammonium nitrate in a protic solvent has been shown^{1,2} to give predominantly β -lactones when carried out below 0°C. However, oxidation at room temperature, and change of solvent did give some δ -lactone formation as seen by the carbonyl stretch in the i.r.

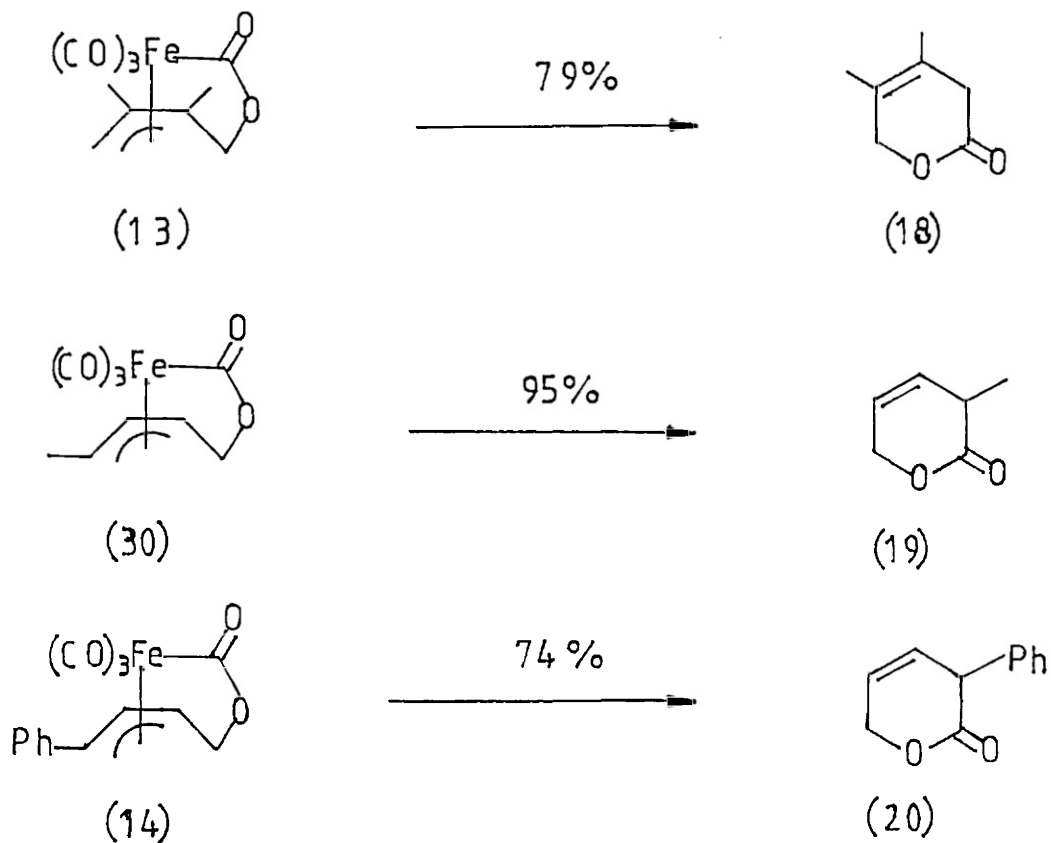


β -Lactone formation still predominated and further increase in temperature or change in solvent did not produce the δ -lactones exclusively.

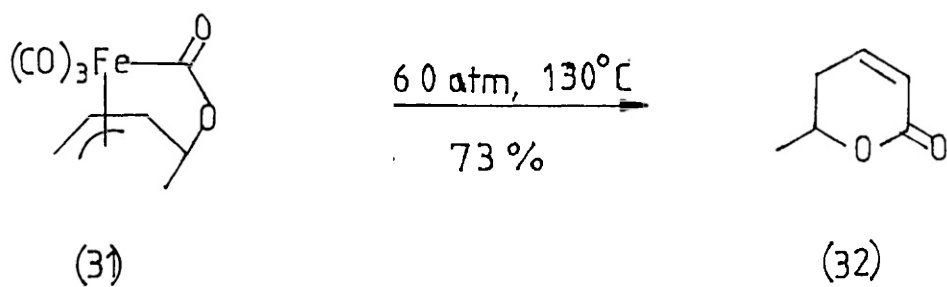
Aumann³ reports that carbonylation of tricarbonyliron lactone complexes under 200 atm of carbon monoxide at 75°C gives a mixture of α,β -, β,γ -, and γ,β -unsaturated lactones. Other reports¹⁷ suggest that use of 60 atm of carbon monoxide at 130°C gives mainly α,β -unsaturated lactones, but in lower yields.

As many new complexes were readily available *via* the ultrasound method, their further reaction under high pressures of carbon monoxide was investigated. At 150 atm of carbon monoxide and 75°C the reaction was poor; much starting material remained. Increasing the reaction time had little effect, while increasing the temperature to 130°C tended to produce mixtures of products and yields of around 30%. However, using 300 atm of carbon monoxide at 90°C, β,γ -unsaturated lactones were exclusively produced in high yields. Thus complexes (13), (14) and (30) were smoothly converted into their respective lactones (Scheme 6).

Scheme 6

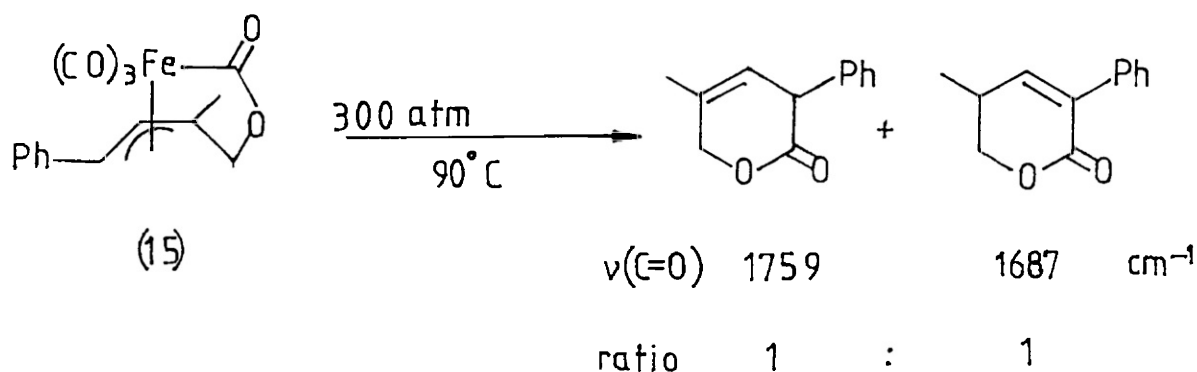


The effect of a lower pressure and higher temperature carbonylation of complex (31) resulted in exclusive formation of the α,β -unsaturated lactone (32).



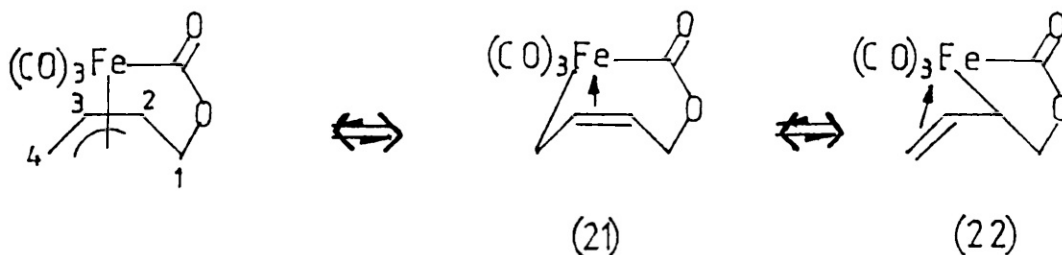
In one case, the higher pressure method gave a mixture of α,β - and β,γ -unsaturated lactones, as identified from the carbonyl stretch in the ir, and from the nmr spectrum (Scheme 7).

Scheme 7



The mechanism for these reactions must explain the selective production of the lactone products. As it is known¹⁸ that pentacarbonyl iron promotes isomerisation of double bonds at high temperatures it would seem reasonable to expect that during the carbonylation the β,γ -unsaturated lactones are produced, but that at higher temperatures isomerisation to the α,β -unsaturated lactones occurs.

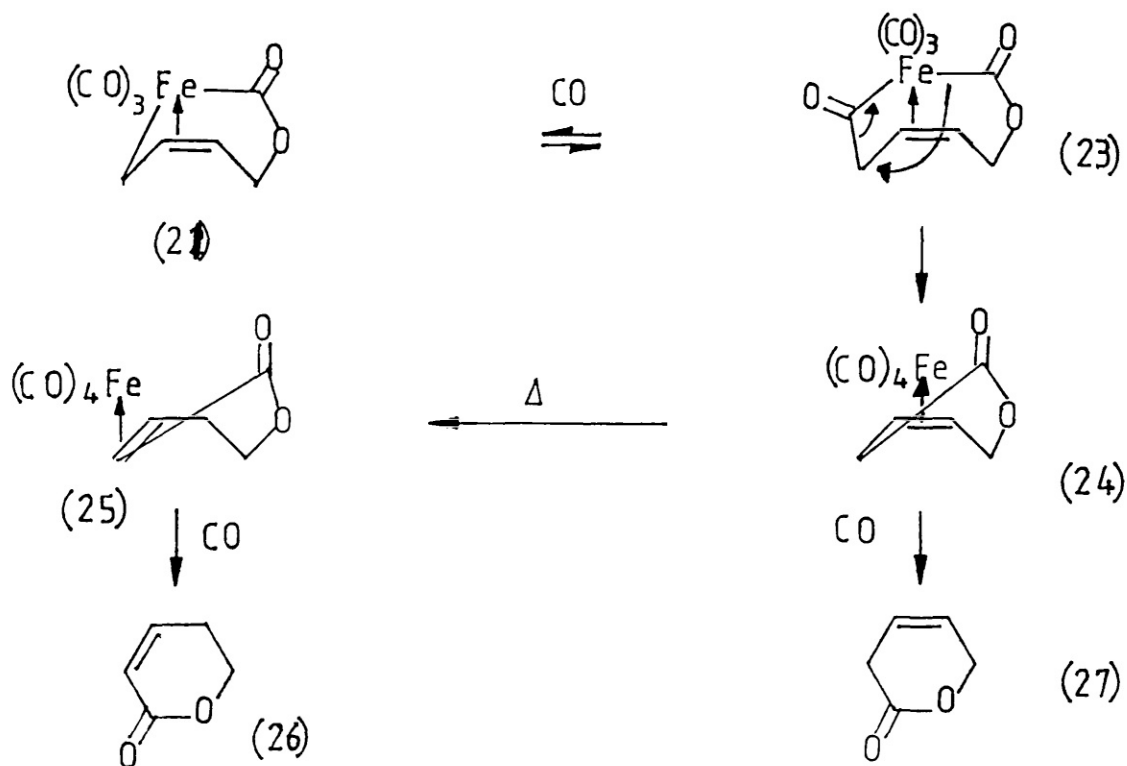
The structure depicting a π -allyl-iron bond in a complex is an idealised structure, and is in fact more realistically represented by resonance forms (21) and (22), depending on the substituents on C-2 and C-3.



X-ray structures of various complexes^{4,19} show the terminal carbon of the allyl unit (C-4) to possess a great deal of sp^3 character, suggesting that resonance form (21) is predominant.

Under a high pressure of carbon monoxide, the first step of the proposed mechanism (Scheme 8) involves carbonyl insertion into the

Scheme 8



iron-carbon bond to give species (23). Migration of the acetyl carbonyl to the terminal carbon atom would then give the alkene-iron-tetracarbonyl complex (24). (The Fe-CO₂ bond would be weaker than the Fe-CO bond, and therefore easier to break.) At this stage, the higher temperature conditions would allow isomerisation of the β,γ -lactone (24) to the α,β -lactone (25) (still as an alkene-iron-tetracarbonyl complex). Under the high pressure of carbon monoxide, both these intermediate complexes can now break down to give lactones (26) and (27).

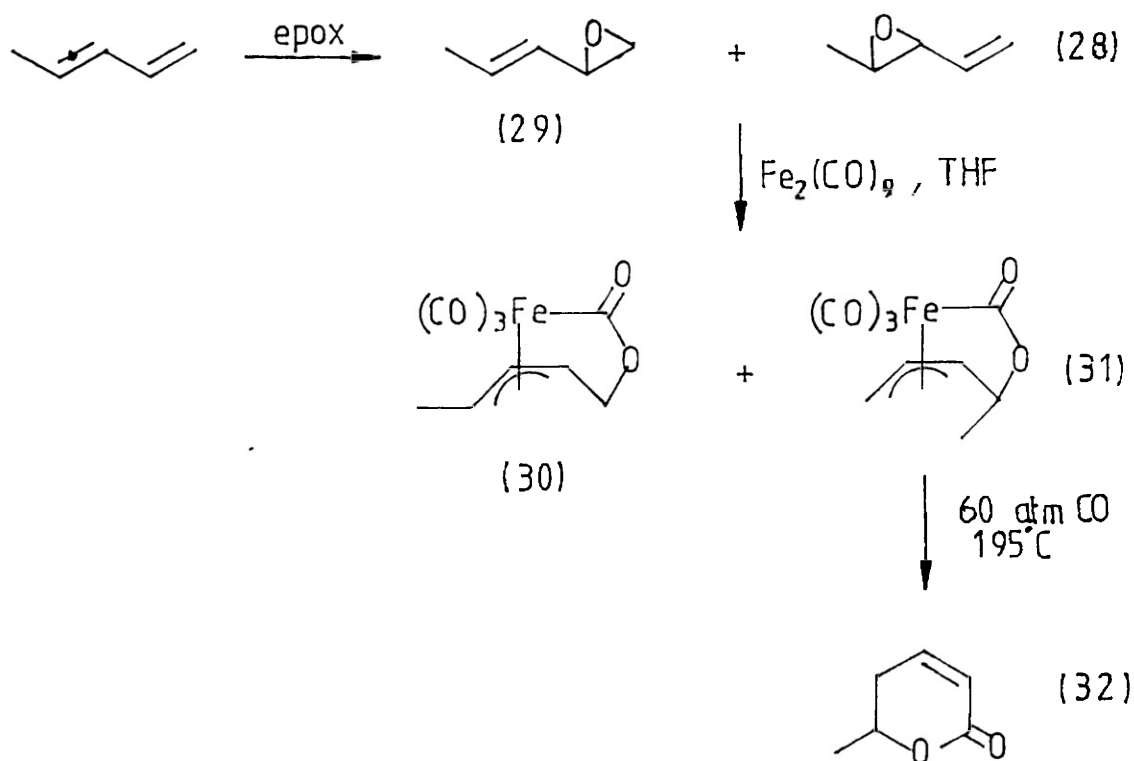
3. NATURAL PRODUCT SYNTHESIS

Having developed a simple and high yielding method for preparation of tricarbonyliron lactone complexes and simple δ -lactones, their application to the synthesis of various δ -lactone natural products was investigated.

3.1 Synthesis of Parascorbic Acid

Epoxidation of *trans*-pentadiene using a variety of peracids gave inseparable mixtures of epoxides (28) and (29). However, conversion of this mixture to the iron complexes (30) and (31) then permitted separation. Carbonylation of the 2-*endo*-complex (31) using the high temperature and lower pressure conditions gave the natural product parascorbic acid (32) in 73% yield (Scheme 9).

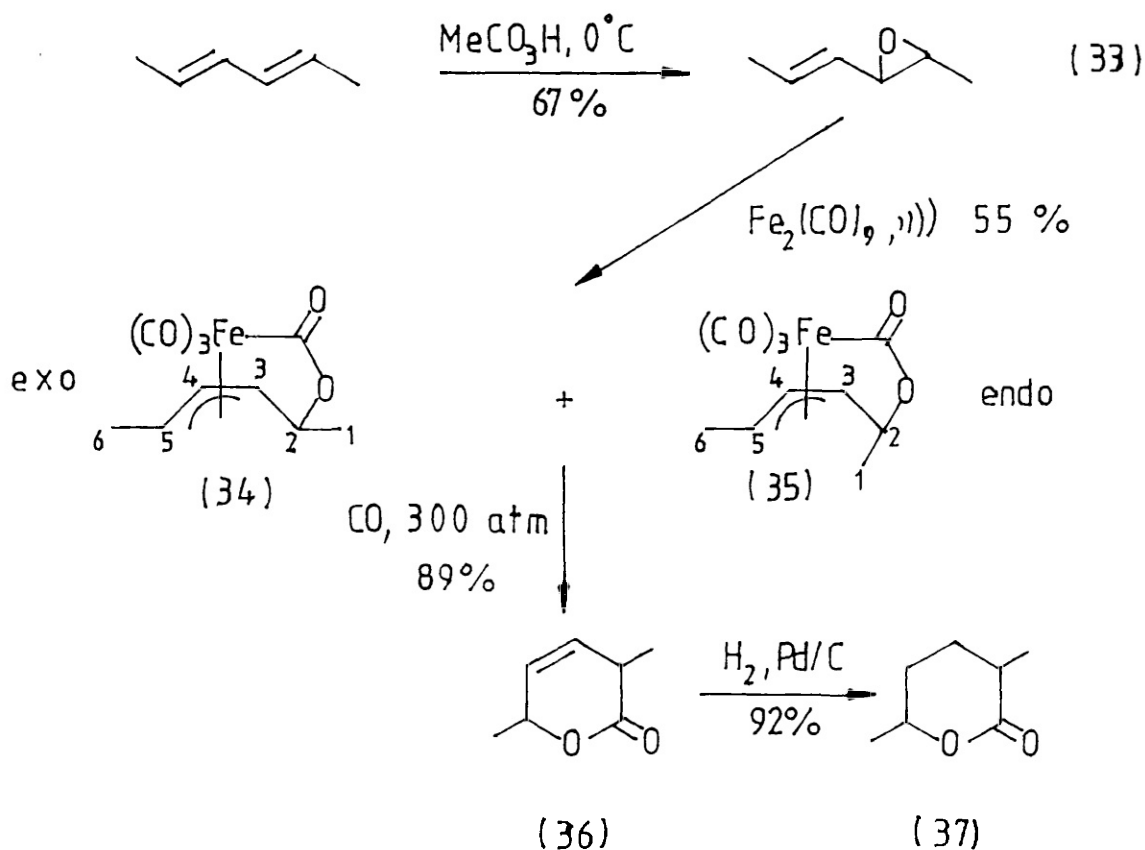
Scheme 9



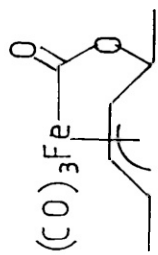
3.2 Synthesis of the Sex Pheromone of the Carpenter Bee

Epoxidation of *trans-trans*-hexadiene using peracetic acid gave the epoxide (33) in 67% yield, which upon reaction with nonacarbonyl diiron under ultrasound conditions afforded the complexes (34) and (35) in 55% yield, in a ratio of 4:1, (Scheme 10). Alternatively, photolysis of the epoxide in the presence of pentacarbonyl iron gave predominantly the 2-*endo* complex (35) in 50% yield.

Scheme 10



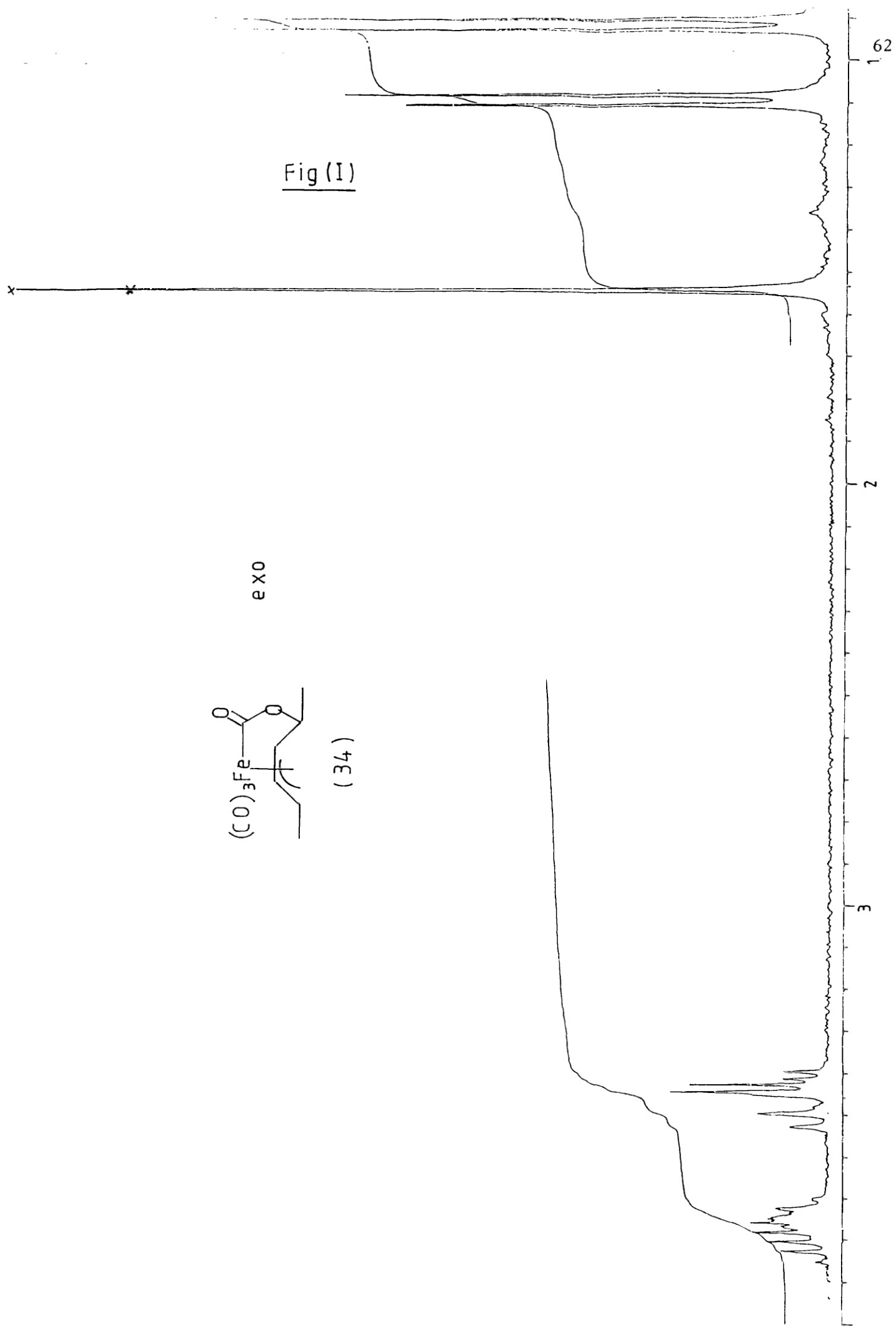
The complexes were separated by flash chromatography, and were assigned as the 2-*exo*- (34) and the 2-*endo* (35) isomers on the basis of their nmr spectra, Fig. (I) and (II). The shielding effect of the iron causes protons and methyl groups which are *endo*- to the iron to be shifted upfield. Thus the 2-*endo* methyl group in complex (35) is shifted upfield to $\delta 0.92$, compared to the 2-*exo* methyl signal at $\delta 0.98$.

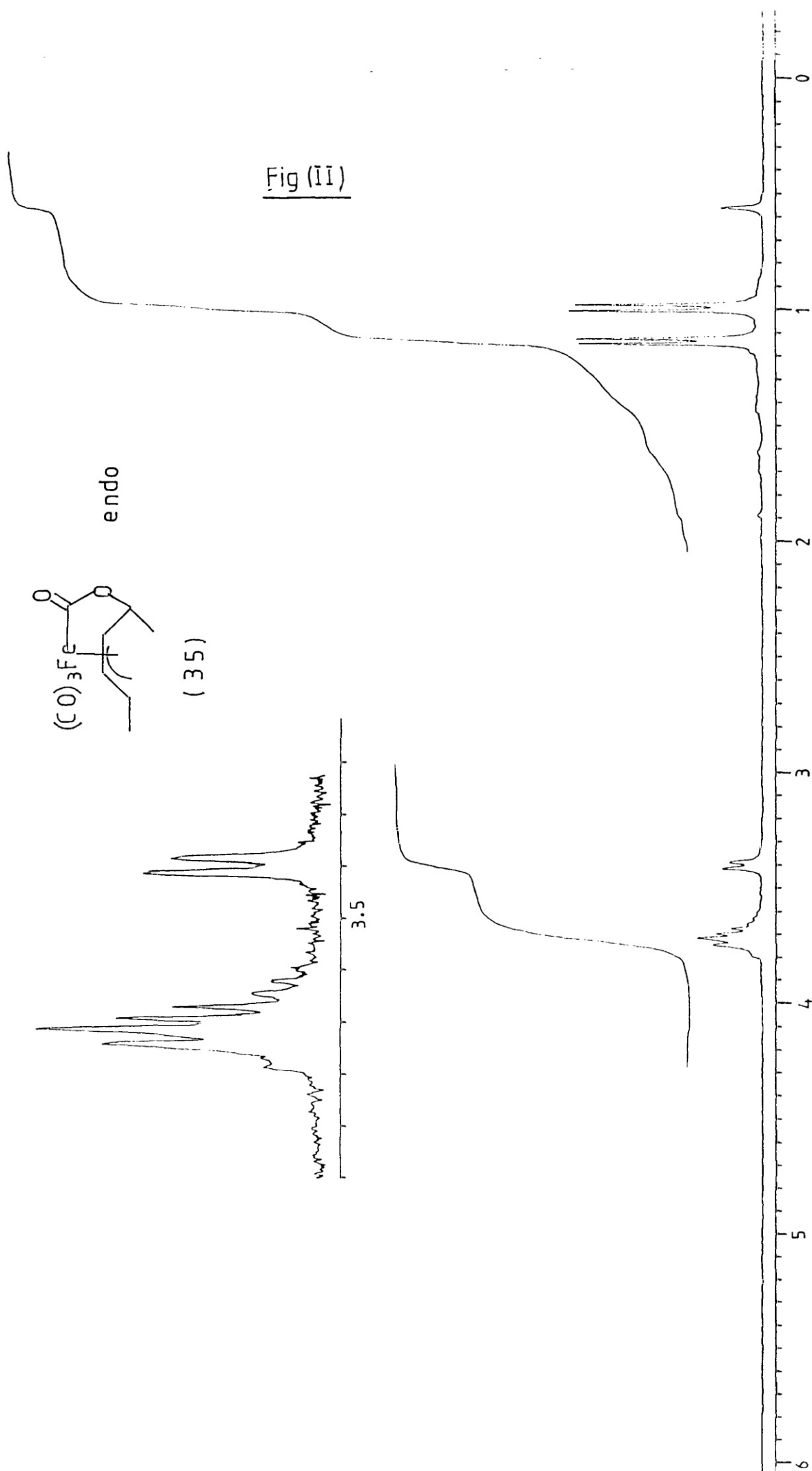


(34)

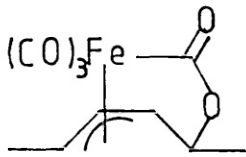
exo

Fig (I)





Fig(III)



(34)

exo

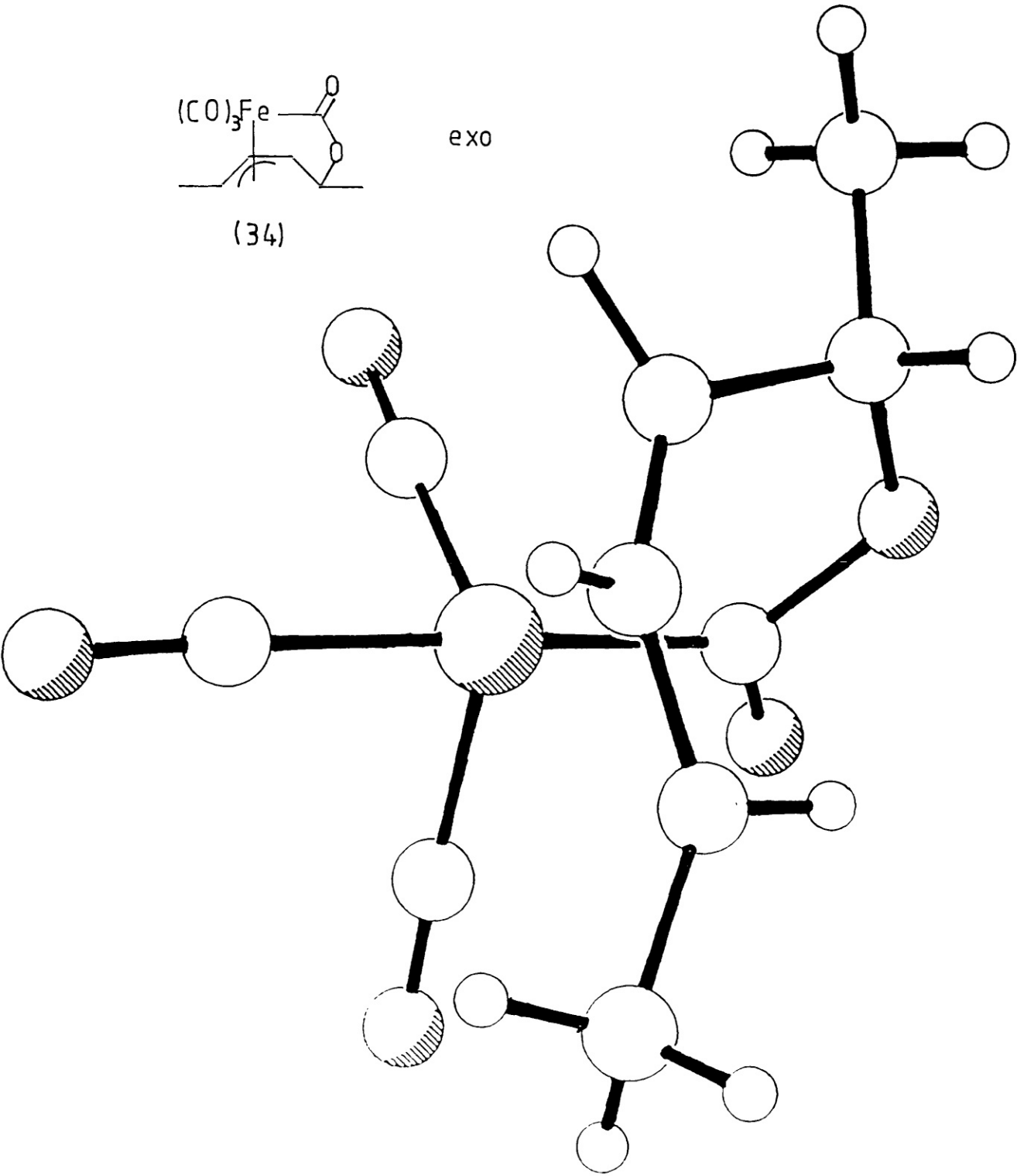
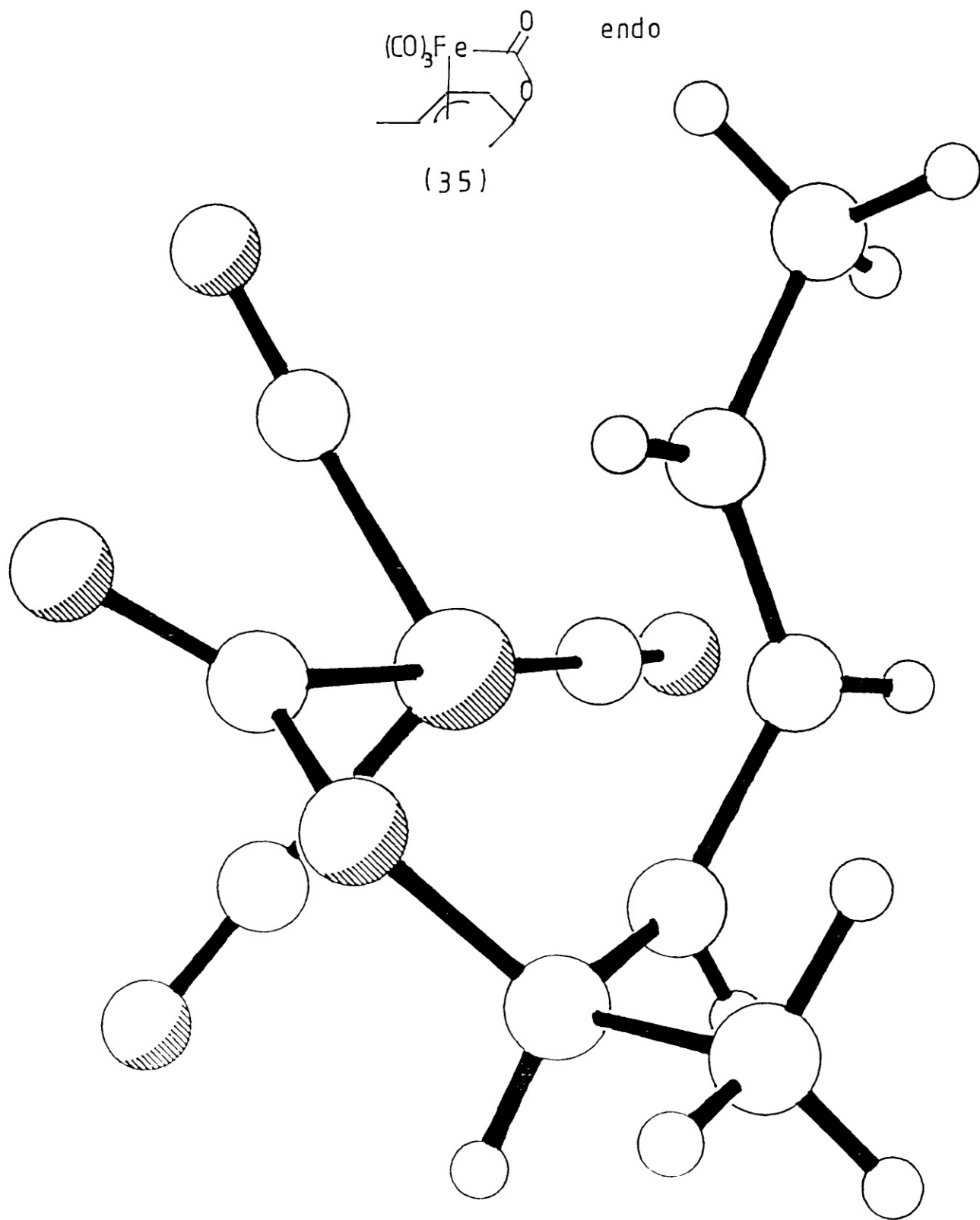


Fig (IV)



in complex (34). (Aumann³ similarly assigns the higher field signal to the *endo*-methyl group, but Moriaty²⁰ does not.)

In the 2-*exo*-complex (34), the protons on C-2 and C-~~3~~⁵ are both *endo*- to the iron, and are therefore assigned as the higher field multiplet at $\delta 3.46$. The protons on C-3 and C-4 can then be assigned as the multiplet at $\delta 3.78$.

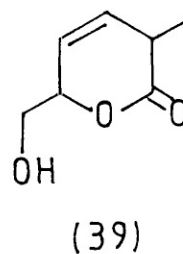
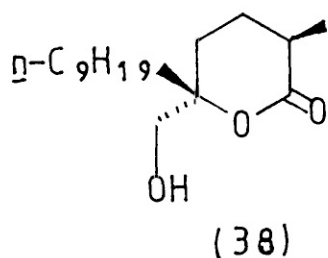
In the 2-*endo*-complex (35) only the proton on C-5 is *endo* to the iron and it occurs at $\delta 3.40$, while the *exo*-proton on C-2 occurs along with protons on C-3 and C-4, as a multiplet at $\delta 3.70$.

The 2-*exo*- and 2-*endo* structures were confirmed by the X-ray studies, Fig. (III) and (IV), which also shows that in the 2-*exo*-complex (34) the 6-carbon chain lies in a plane, while that of the 2-*endo*-complex (35) is puckered, the 2-*endo*-methyl sitting well below the plane (on the opposite side to the iron). High pressure carbonylation (300 atm, 90°C) gave a high yield of the pungent unsaturated lactone (36), and hydrogenation using a palladium on charcoal catalyst gave the pheromone (37) as a 1:1 mixture of *cis*- and *trans*- isomers (determined by glc²¹) in 30% overall yield.

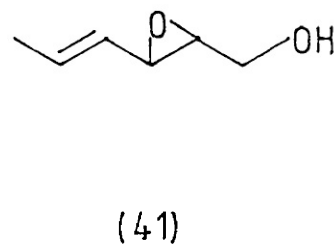
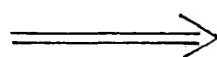
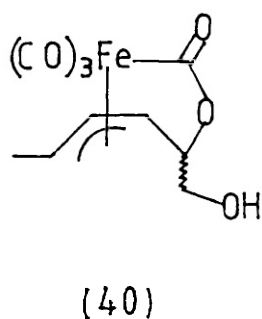
Carbonylation of the individual complexes, followed by hydrogenation, gave the same ratio of products, indicating that *endo* $\rightleftharpoons$ *exo* isomerisation occurs freely under the carbonylation reaction conditions.

3.3 Model Synthesis for the Natural Product Malyngolide

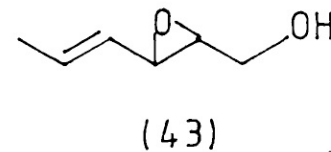
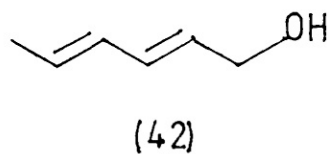
The antibiotic malyngolide (38) is an example of a more complex naturally occurring δ -lactone. Before attempting its synthesis a route towards a simpler model compound (39) was developed.



The model compound should be derived by carbonylation of the complex (40) which in turn results from the allyl epoxide (41).



Careful reduction of sorbic acid at 0°C with lithium aluminium hydride gave the alkenol (42). Enantioselective epoxidation *via* the Sharpless²² method to produce chiral epoxides, using (+) or (-) diethyl tartrate to induce chirality, gave none of the required product (43).



$J_{4,5}$ 15.6 Hz

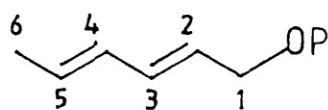
Recent reports²³ indicate that a fully saturated centre α - to the epoxide (δ - to the -OH group) is required for the reaction to proceed.

Epoxidation using *t*-butylhydroperoxide²⁴ with a vanadylacetoacetate ($\text{VO}(\text{acac})_2$) catalyst^{24,25} was therefore employed.

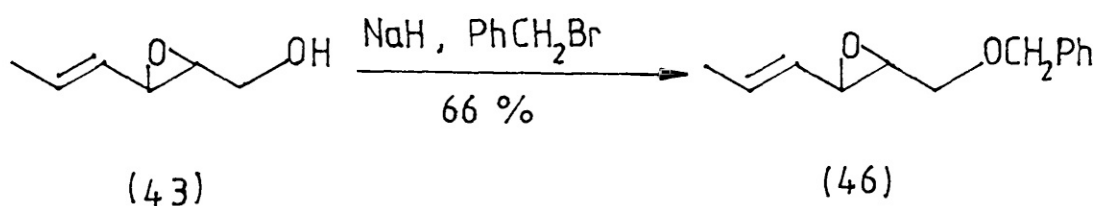
Action of *t*-butylhydroperoxide with the vanadyl catalyst in dichloromethane or benzene at 0°C or room temperature on the alcohol (42) gave an incomplete reaction, while heating tended to cause decomposition with no increase in the yield. It was noticed that the reaction proceeded quickly for the first few minutes and then appeared to stop completely. Addition of more catalyst or *t*-butylhydroperoxide had no effect.

Other workers²⁶ suggest that the byproduct of this reaction, *t*-butyl alcohol, quickly deactivates the catalyst, which would prevent any further reaction. The problem was solved by carrying out the reaction in benzene under reflux, when reaction occurred in five minutes, which was a sufficiently short time to prevent decomposition. On a large scale removal of the *t*-butylhydroperoxide and *t*-butyl alcohol caused some problems. Consequently the reaction was carried out in batches of up to 3g, when purification was possible by chromatography.

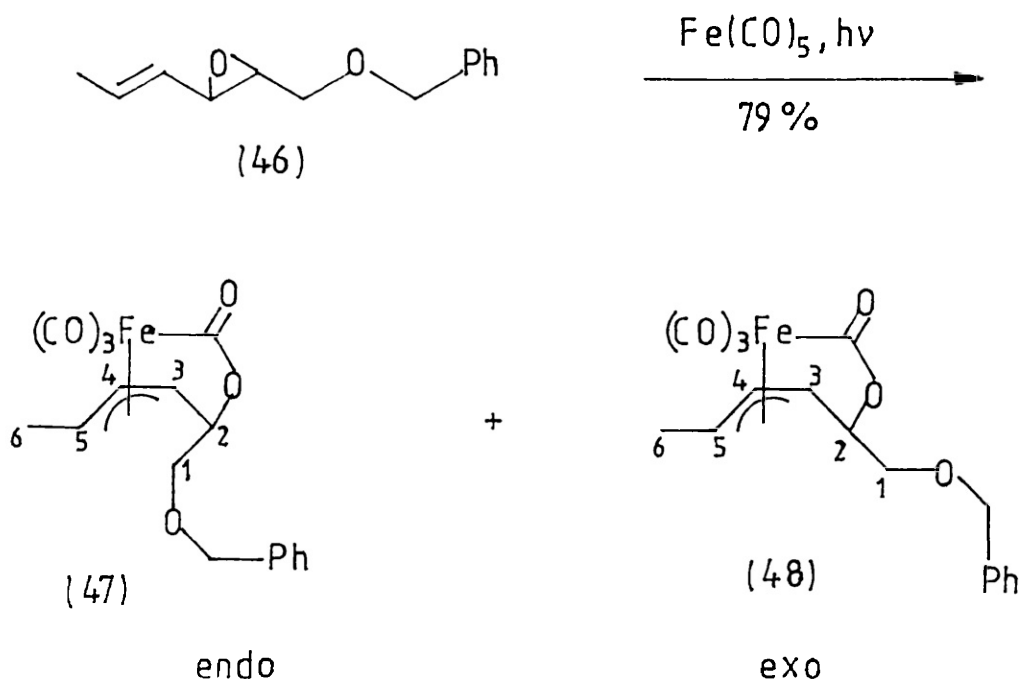
Unfortunately reaction of the epoxyalcohol (43) with pentacarbonyl iron gave no complex formation. (The methods using nonacarbonyl diiron had not been developed at this time). This was thought to be due to reaction between the -OH group and pentacarbonyl iron. The -OH group therefore had to be protected prior to the iron carbonyl reaction. The acetate (44) and benzyl ether (45) of the alcohol (42) were easily prepared, but regiospecific epoxidation of these was not possible.

(44) $P = -\text{COMe}$ (45) $P = -\text{CH}_2\text{Ph}$

m-Chloroperbenzoic acid and peracetic acid both gave mixtures of the 2,3- and 4,5-epoxides while the *t*-butylhydroperoxide/vanadyl acetate-acetate system gave no product. The -OH group was therefore protected as a benzyl ether after epoxidation, to give the allyl epoxide (46).

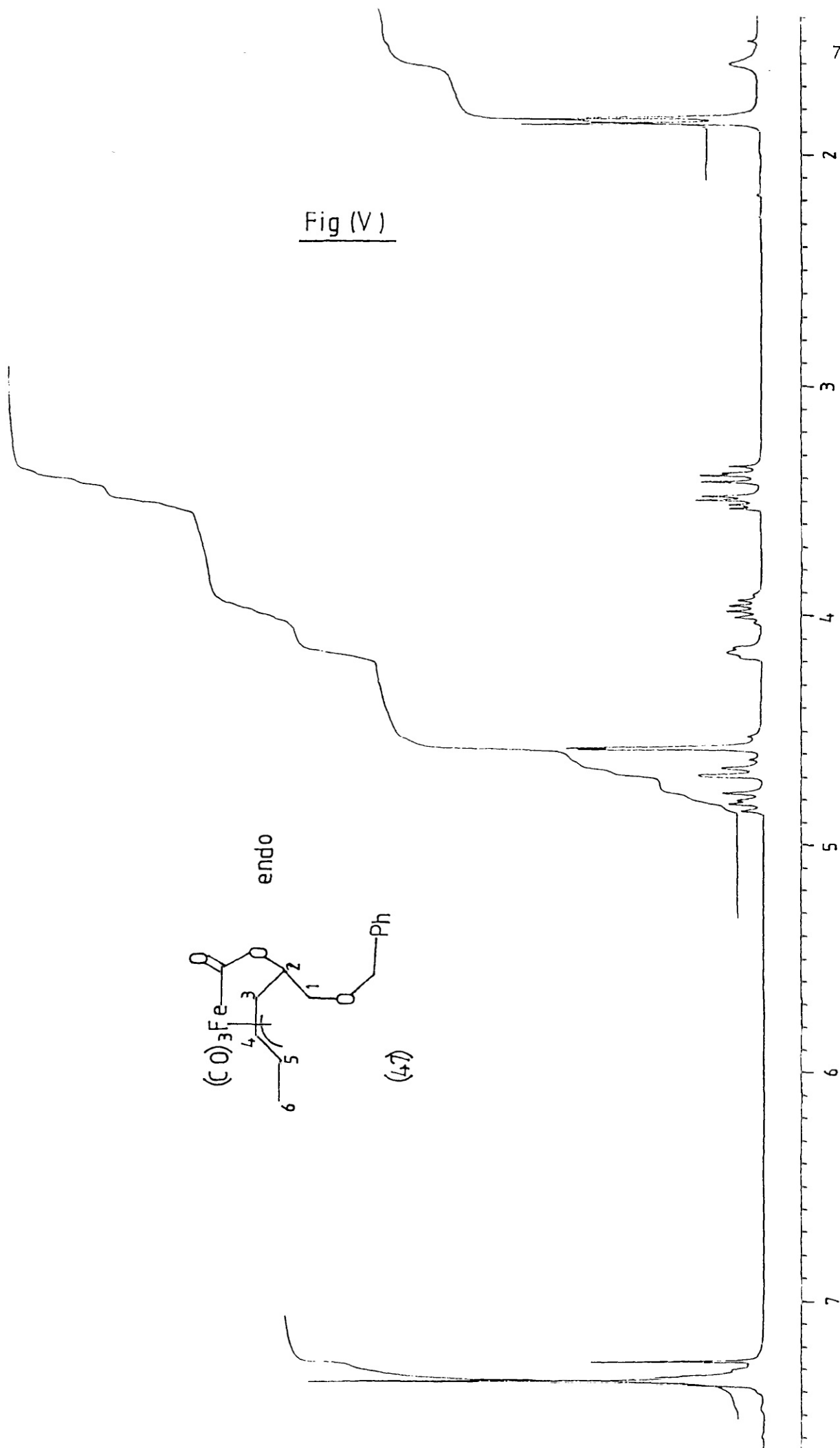


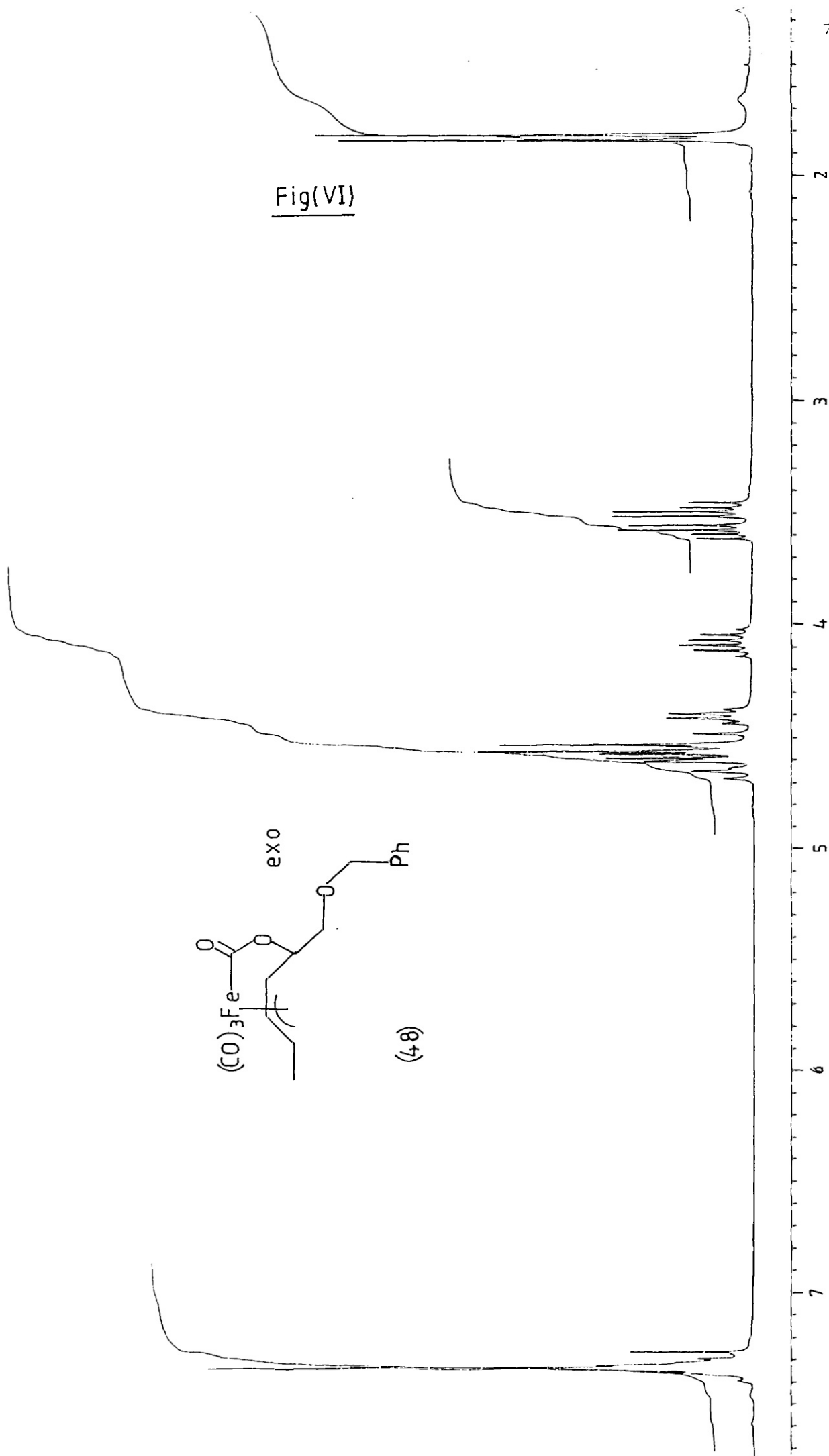
Photolysis of the protected epoxide (46) with pentacarbonyl iron in benzene afforded the iron complex as a mixture of two isomers, in 79% yield which were assigned as the 5-*endo* (47) and the 5-*exo* (48) isomers.



Several separations of the mixture by flash chromatography (using a silica substrate ratio of 50:1) yielded a small amount (2 mg) of each separate isomer, which was used to study the 250 MHz ^1H nmr spectrum, Figs. (V) and (VI). In both the *exo*- and the *endo*-complexes, the methyl group on C-5 occurred as a doublet at δ 1.83, $J_{5,\text{Me}}$ 6.1 Hz. Irradiation of this signal caused the 6-line signal at δ 4.07 (*exo*-isomer) at δ 3.96 (*endo*-isomer) to collapse to a doublet, indicating that it is an overlapping double quartet due to the proton on C-5 (*exo*- δ 4.07, $J_{5,\text{Me}}$ 6.1 Hz and $J_{4,5}$ 6.1 Hz, *endo*- δ 3.96 $J_{5,\text{Me}}$ 6.1 Hz and $J_{4,5}$ 6.1 Hz).

In the *exo*-complex Fig. (VI), the protons on C-1 occur as an AB quartet (J_{AB} 10.1 Hz) which is further split by the proton on C-2 ($J_{1,2}$ 5.8 Hz) to give a double AB quartet around δ 3.54. Irradiation of this signal causes the double doublet at δ 4.4 to collapse to





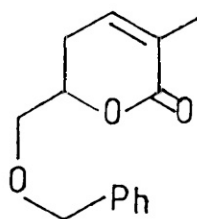
NB Solvent impurity at δ 4.5 - 4.6

a doublet ($J_{2,3}$ 10.8 Hz) indicating that this signal is due to the proton on C-2.

In the *endo*-complex Fig. (V), however, the closer proximity of the $-CH_2$ group to the iron, and the resulting shielding effect of the iron, causes the resonance of the $-CH_2$ group to move upfield. The inequality of the two protons is also enhanced; the gem splitting constant is similar to the *exo*-complex (J_{AB} 9.5 Hz) but the $J_{1,2}$ splitting constant is 7.1 Hz for the proton at δ 3.37, and 4.05 Hz for the proton at δ 3.50. (Compared with 5.8 Hz for both protons in the *exo*-complex.) This inequality can also be seen in the signal for the proton on C-2, which occurs as a broad multiplet at δ 4.15.

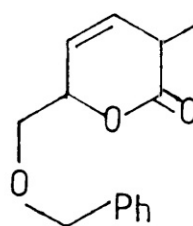
In both complexes the remaining protons (3-H, 4-H and 1- OCH_2) occur as a multiplet between δ 4.35 and δ 4.85, while the phenyl protons occur as a singlet at δ 7.34.

At this time, carbonylation reactions could only be carried out at 150 atm of carbon monoxide. At 90°C under these conditions, a mixture of the complexes (47) and (48) gave a mixture of lactones (49) and (50). Increasing the reaction time had no effect, but increasing the temperature to 130°C selectively gave the 3,4-dehydro-lactone (50) in 30% yield. Later carbonylation at 300 atm carbon monoxide at 90°C gave the lactone (50) exclusively in 60% yield.



(49)

$\nu(C=O)$ 1710 cm^{-1}



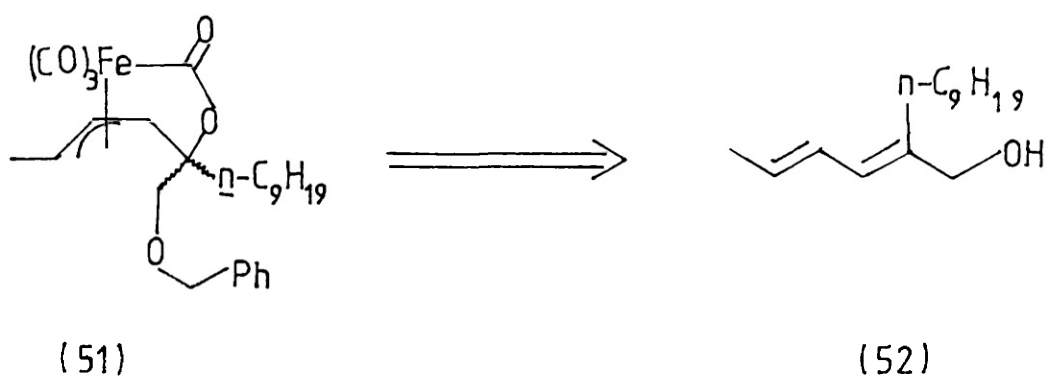
(50)

$\nu(C=O)$ 1725 cm^{-1}

The procedures developed for this model compound synthesis could now be applied to malyngolide.

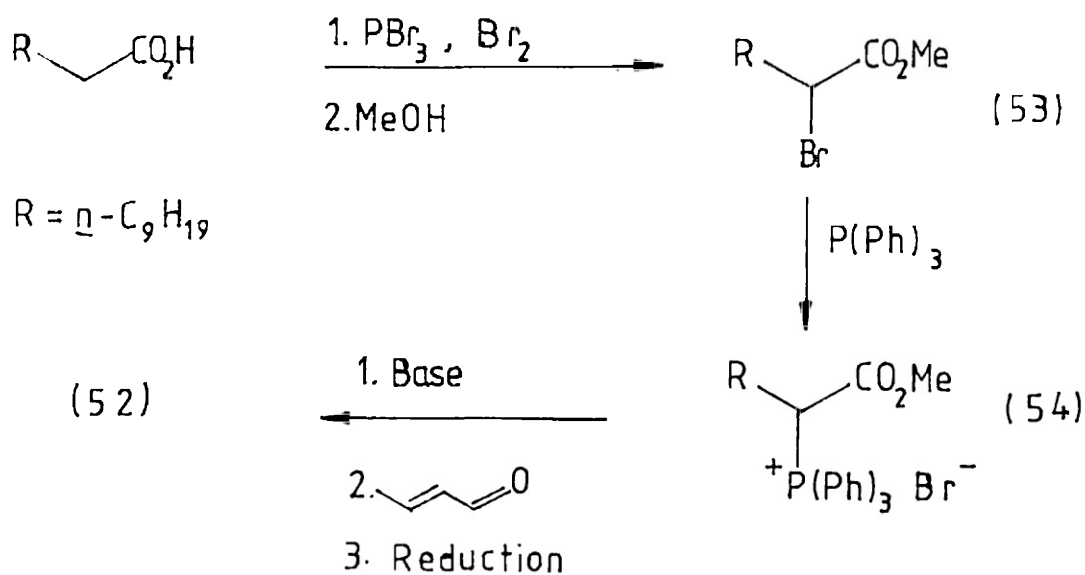
3.4 Synthesis of Malyngolide

The target tricarbonyliron lactone complex for the synthesis of malyngolide is therefore compound (51), which could be prepared after epoxidation and protection of the dienol (52).



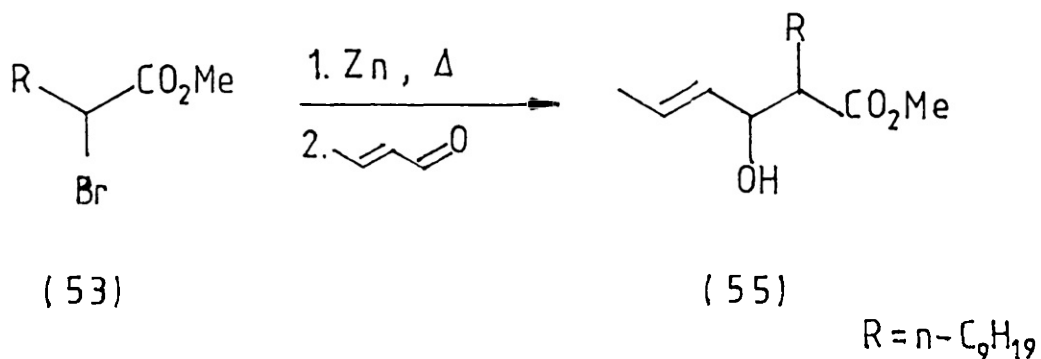
The original intention was to prepare this dienol *via* the Wittig reaction of an ylid derived from undecanoic acid (Scheme 11).

Scheme 11



The α -bromoester (53) was easily prepared in good yield. However, reaction with triphenyl phosphine, even at 150°C in a sealed tube, gave none of the required salt (54). An alternative route using the Reformatsky reaction was therefore studied (Scheme 12).

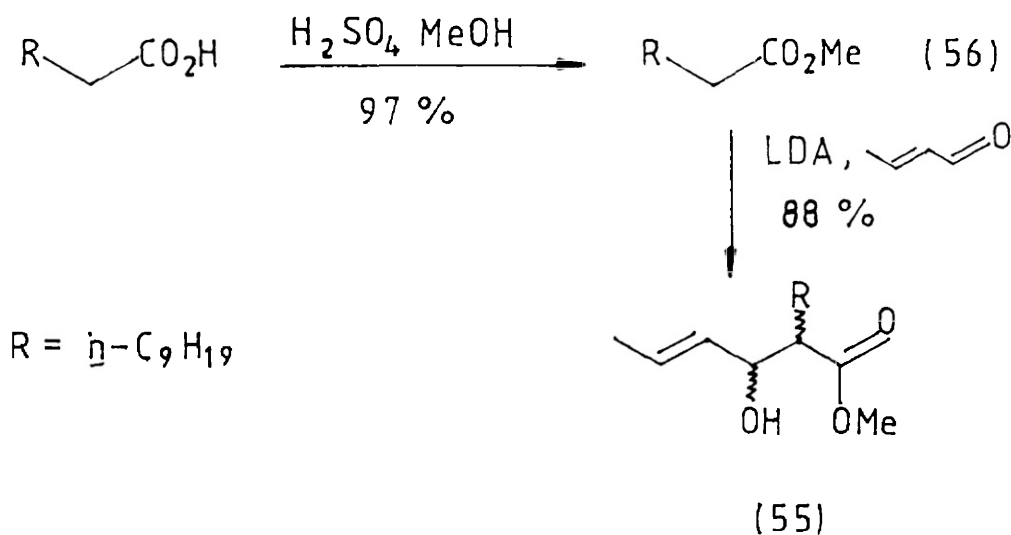
Scheme 12



This reaction always gave mixtures of products in poor yields, despite using iodine or copper catalysts, or Burgess's salt²⁷ to cause elimination, followed by reduction to give the required diene (52).

Eventually it was found that a condensation reaction of methyl undecanoate (56) with crotonaldehyde using lithium diisopropylamine could be used to prepare the required compound as a mixture of diastereomers (55) in 88% yield (Scheme 13).

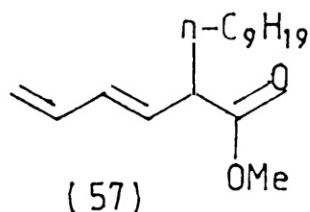
Scheme 13



The alcohol (55) proved to be very resistant to dehydration, probably because access of a base to the proton α - to the ester is sterically hindered by the long aliphatic chain. (This steric hinderance could also account for the problems encountered in preparation of the phosphonium salt previously discussed, and of the zinc reagent in the Reformatski reaction.) The action of organic bases, phosphoryl chloride and pyridine, and vacuum pyrolysis gave no reaction; concentrated sulphuric acid, Burgess's salt,²⁷ or N,N'-dicyclohexylcarbodiimide gave mixtures of products and starting materials.

Acetylation and mesylation of the -OH group could be achieved without difficulty, but elimination using triethylamine, 1,8-diazobicyclo[5.4.0]undec-7-ene or 1,5-diazobicyclo[4.3.0]non-5-ene was not possible. Heating the acetate with tetrakis(triphenylphosphine) palladium²⁸ gave no reaction. It seemed that removal of the proton was the problem, rather than loss of the leaving group.

Finally, when heating in toluene under reflux with ten equivalents of potassium hydrogen sulphate for 48h under Dean-Stark conditions, a diene was obtained which turned out to be the terminal diene (57). This conjugate elimination is further evidence of the steric hinderence of the α -proton.



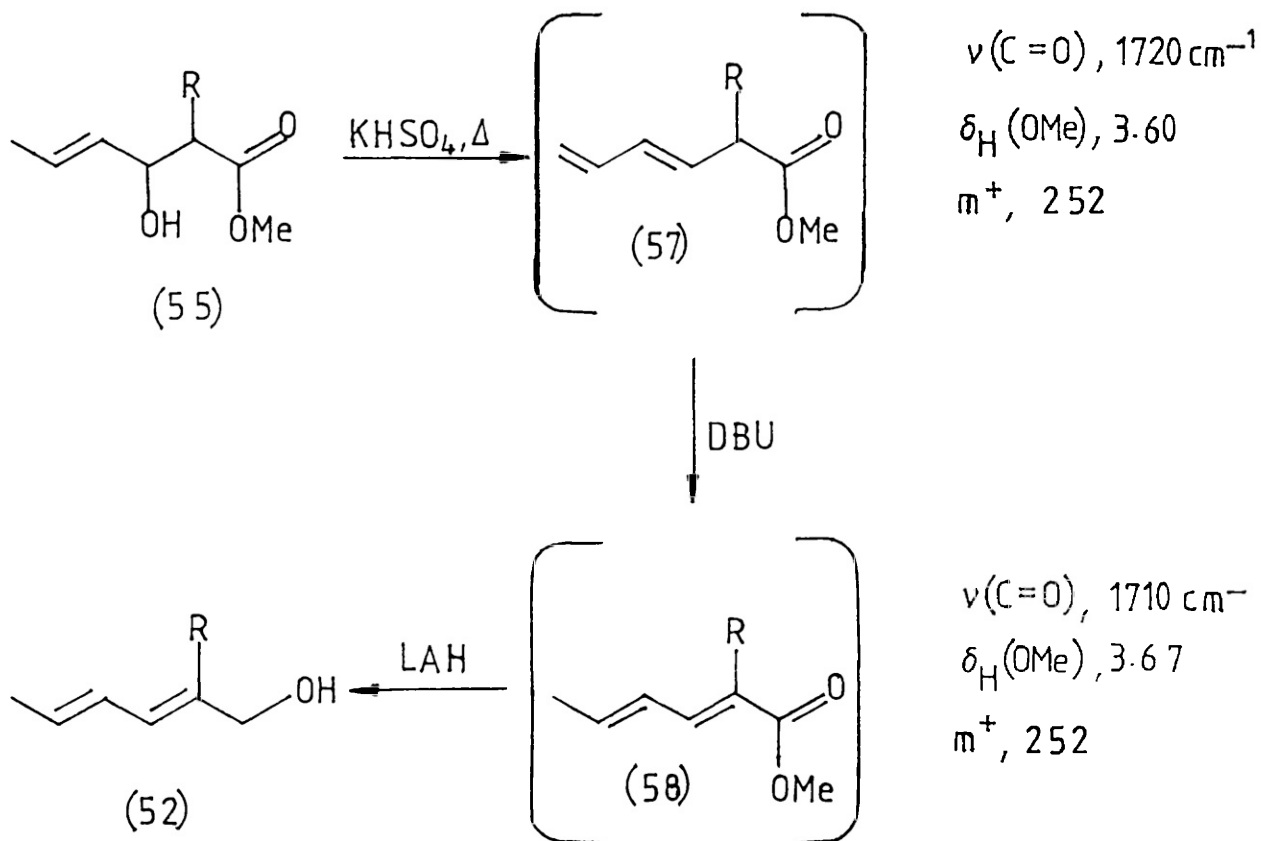
$$\begin{aligned} \nu(\text{C}=\text{O}) & 1720 \text{ cm}^{-1} \\ (\text{C}=\text{C}) & 1625, 1590 \text{ cm}^{-1} \end{aligned}$$

$$\delta_{\text{H}} \quad 4.8 - 6.5, 5\text{H}, \text{m}$$

Isomerisation of this diene to the fully conjugated isomer was attempted by reduction to the alcohol followed by oxidation to the aldehyde. The product tended to undergo self condensation and gave very poor yields of the conjugated aldehyde. Use of rhodium trichloride²⁹ in hot methanol directly on the diene ester (57) had no effect.

Attempts to cause isomerisation during dehydration (or direct dehydration to the required diene) were also studied. If 1,8-diazobicyclo[5.4.0]undec-7-ene was included in the mixture both conjugated (58) and unconjugated diene (57) were formed. Adding 1,8-diazobicyclo[5.4.0]undec-7-ene after the reaction at room temperature for 24h gave predominantly the required diene. (This could be followed by ^1H nmr of the crude reaction mixture, by monitoring the integral of the methoxy signal.) Work up however still gave a mixture of both dienes. This was prevented by reduction of the crude dehydration reaction mixture with lithium aluminium hydride at 0°C to give the long sought after dienol (52) in respectable yield (Scheme 14).

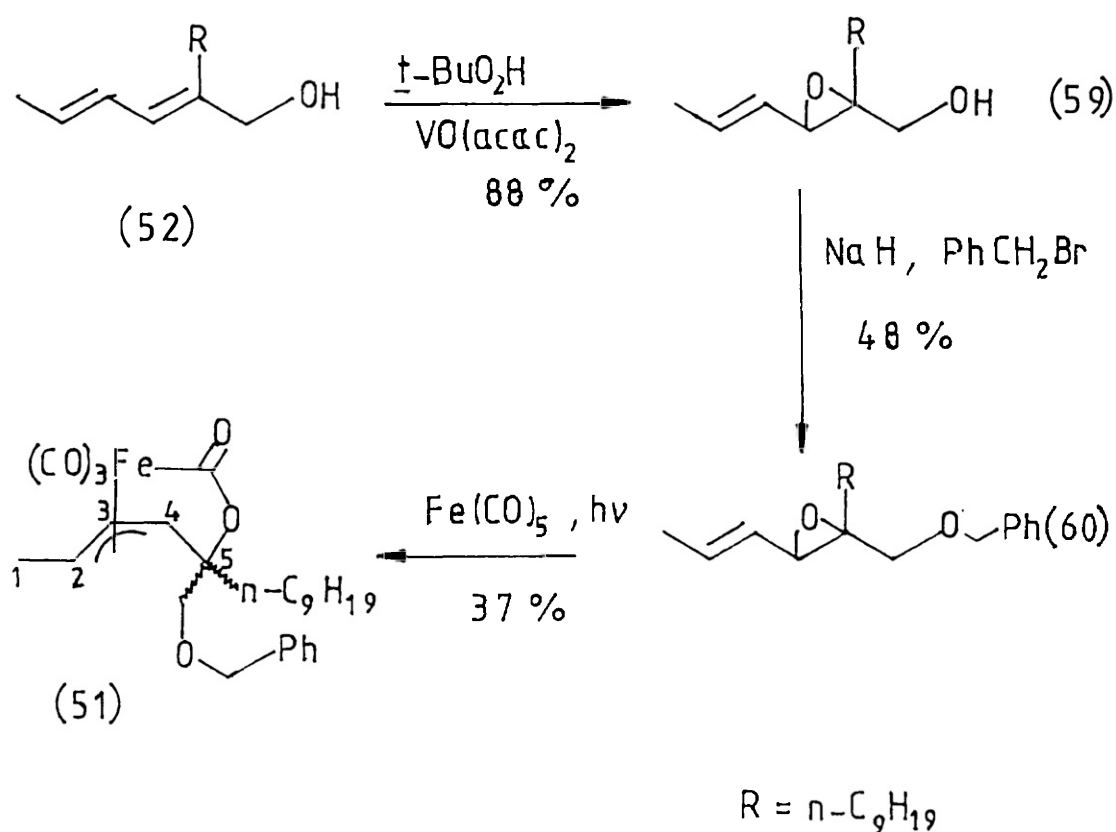
Scheme 14



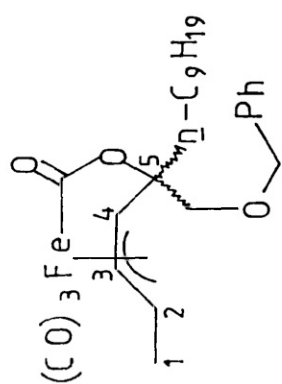
$\text{R} = n\text{-C}_9\text{H}_{19}$

71 % from (55)

The dienol (52) was epoxidised by the method developed in the model synthesis to afford the allyl epoxide (59) in 88% yield. Protection of the -OH group as a benzyl ether was not as easy as in the model synthesis, and under a variety of conditions could not be achieved in greater than 48% yield. Photolysis of the protected epoxide (60) in the presence of pentacarbonyl iron gave the complex (51) as a mixture of isomers at C-5, separable by chromatography.

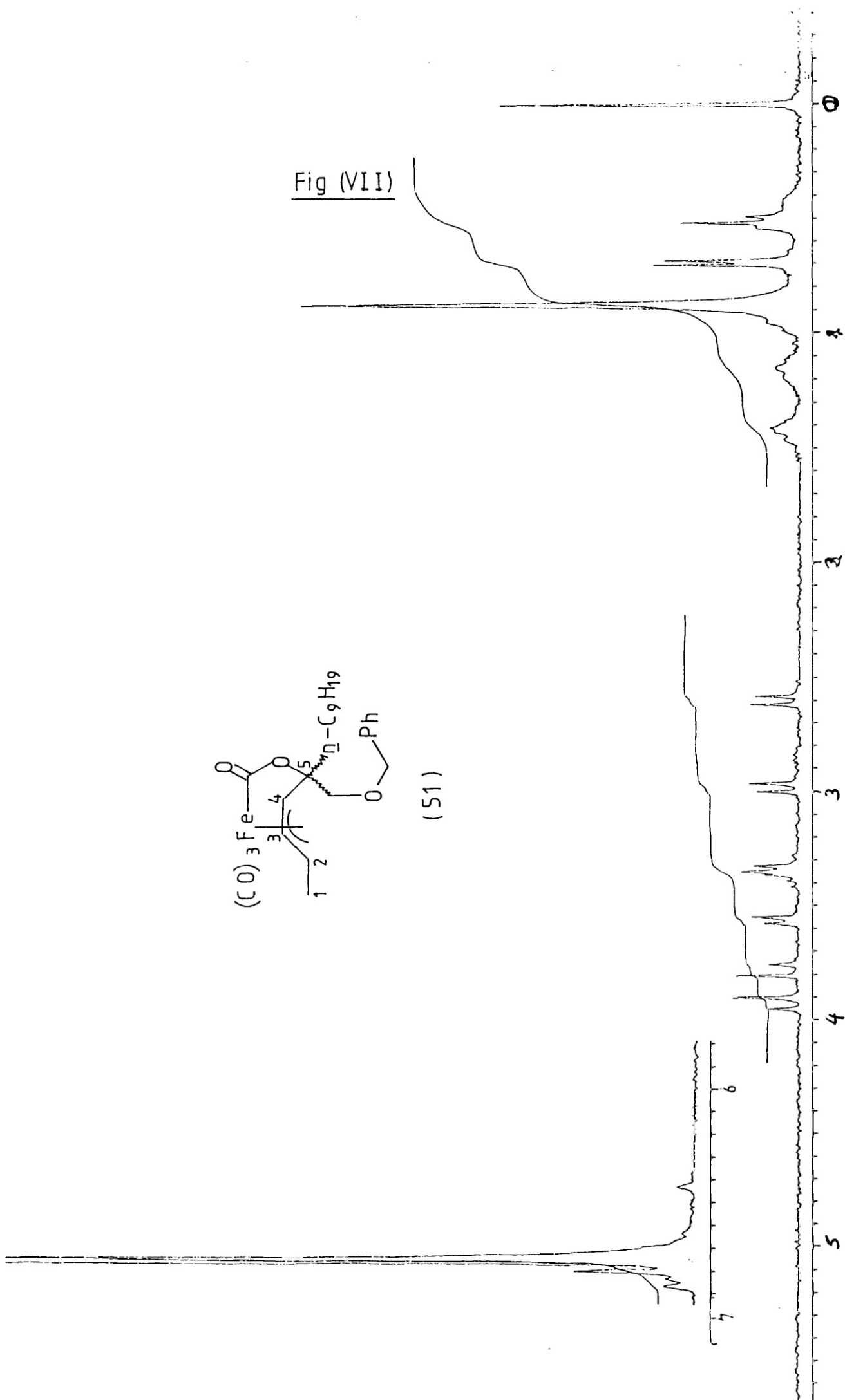


Only one isomer was stable enough in solution to allow a 250 MHz ^1H nmr spectrum to be obtained Fig. (VII). This is similar to that of the lactone complex prepared for the model synthesis. The 2-Me group occurs as a doublet at $\delta 0.70$ ($J_{2,\text{Me}}$ 5.0 Hz) and the aliphatic chain is at $\delta 0.8 - 1.6$, with the terminal methyl occurring as a triplet at $\delta 0.52$ ($J_{13-\text{Me}}$ 6.7 Hz). The $-\text{CH}_2\text{O}$ group on C-5 is seen as an AB quartet at

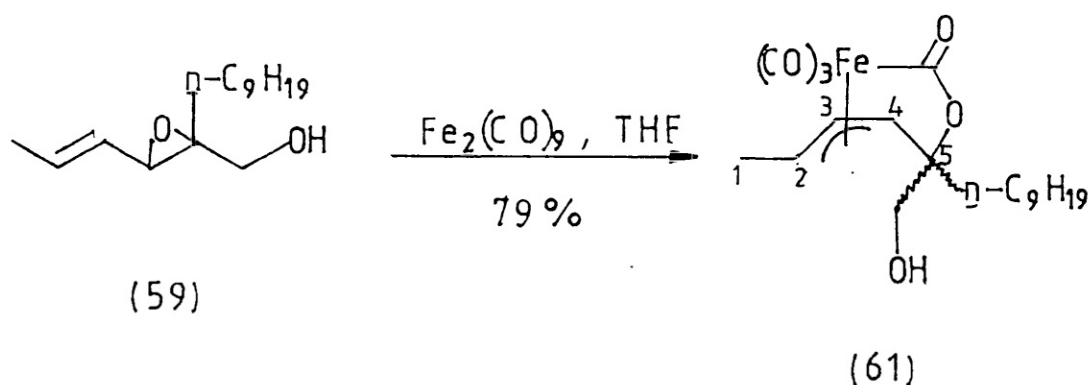


(51)

Fig (VII)



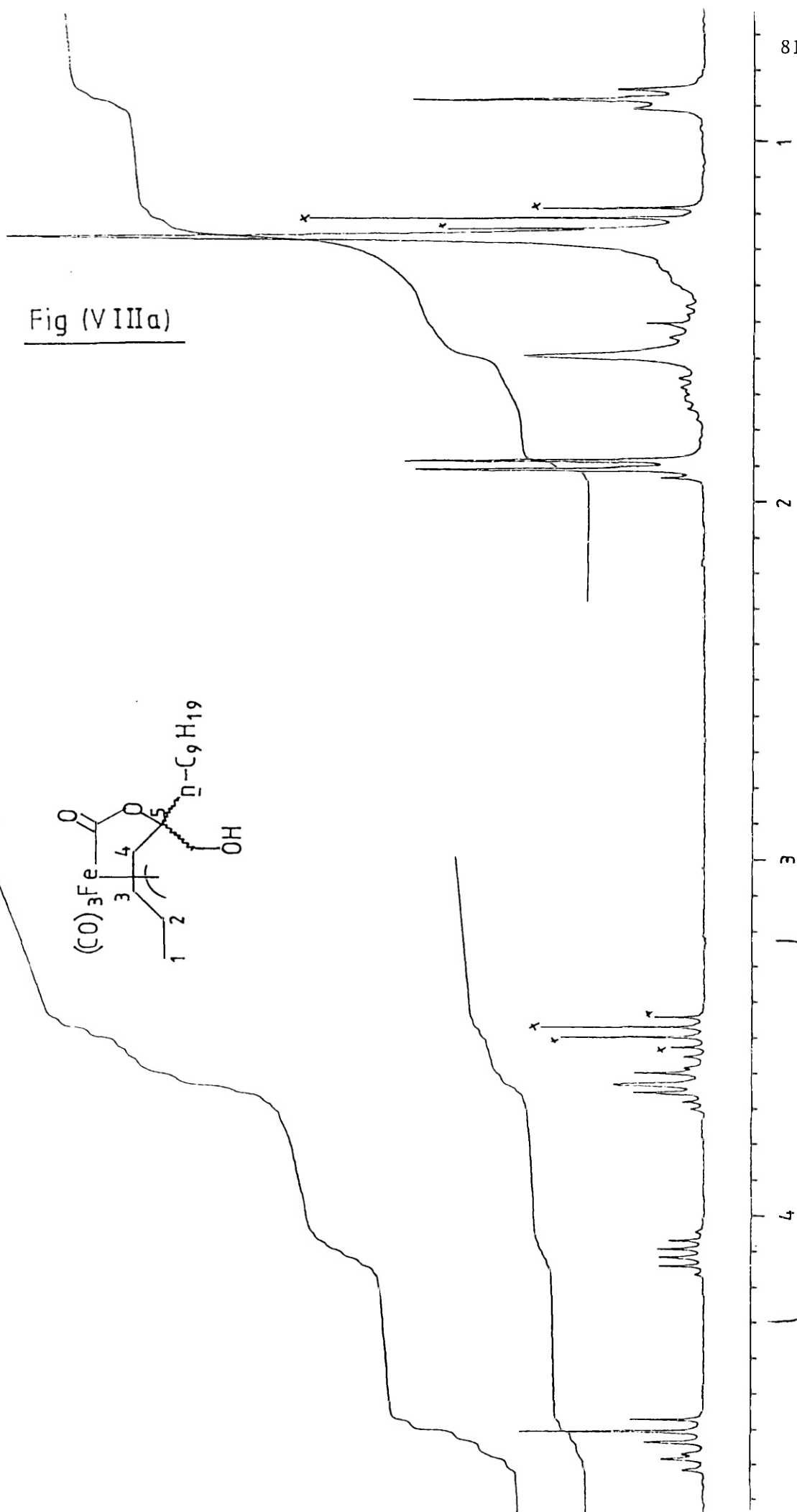
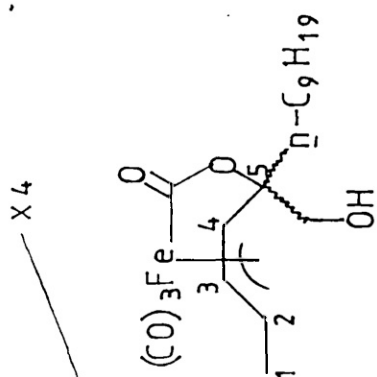
δ 2.60 and 2.99 (J_{AB} 9.2 Hz), but it is not possible to determine whether this group is *endo*- or *exo*- to the iron moiety. The CH_2 -Ph group also occurs as an AB quartet at δ 3.77 and 3.94 (J_{AB} 11.7 Hz) and the phenyl protons are at δ 6.75, (along with some benzene- d_5 contamination). Integration shows the peaks at δ 3.35 and 3.56 to be 2 protons and one proton respectively, and hence they are assigned as 2-H and 4-H at δ 3.35, and the proton on C-3 as the doublet at δ 3.56 ($J_{3,4}$ 6.7 Hz). By this time, however, the preparative methods using nonacarbonyl diiron had been developed. While the unprotected allyl epoxide (59) gave no complex under photolysis or ultrasound conditions, reaction with nonacarbonyl diiron in tetrahydrofuran gave the hydroxy complex (61) as a mixture of isomers at C-5 in good yield.



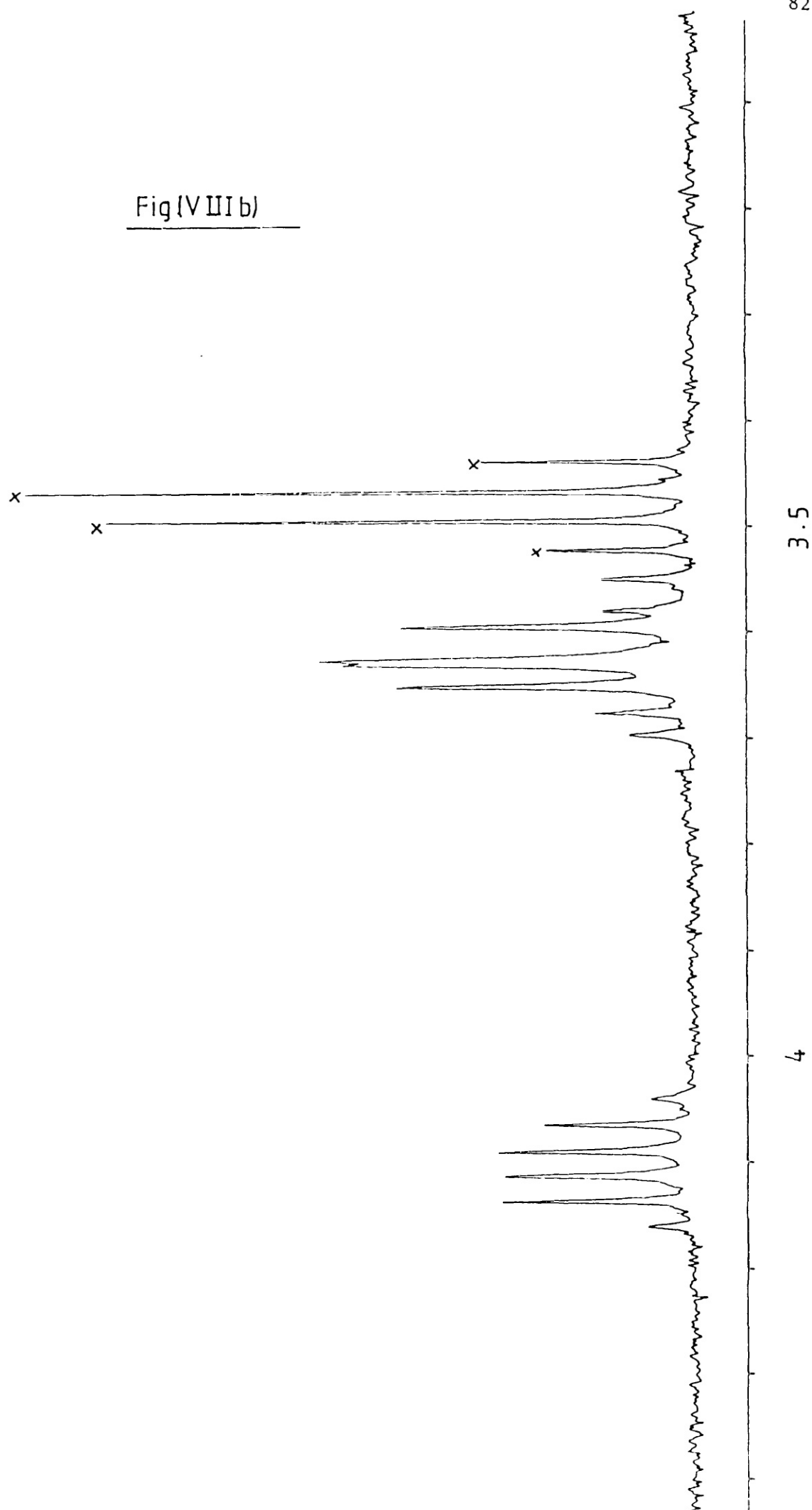
The ^1H nmr spectrum of the mixture of *endo*- and *exo*- isomers, Fig. (VIIIa,b) shows the aliphatic chain as a multiplet between δ 1.15 and δ 1.80, with the terminal carbon as a triplet ($J_{3,Me}$ 7.6 Hz) at δ 0.87. (N.B. Contamination of the deuteriochloroform solvent with ethanol accounts for the triplet at δ 1.20, the quartet at δ 3.48, and part of the broad singlet at δ 1.56.) The methyl group on C-2 occurs as a doublet ($J_{2,Me}$ 6.4 Hz) at δ 1.87.

The proton on C-3 at the centre of the allyl unit occurs at lowest field, δ 4.67 as a double doublet ($J_{2,3}$ 11.9 Hz and $J_{3,4}$ 7.6 Hz)

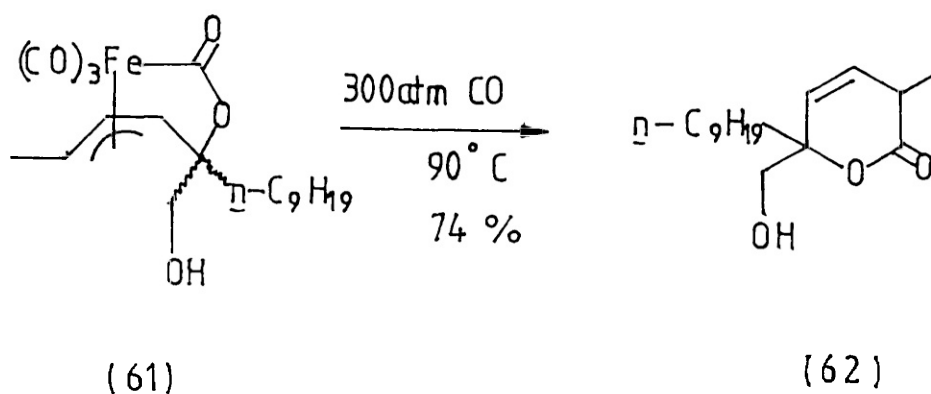
Fig (VIIIa)



expanded in Fig (VIII b)

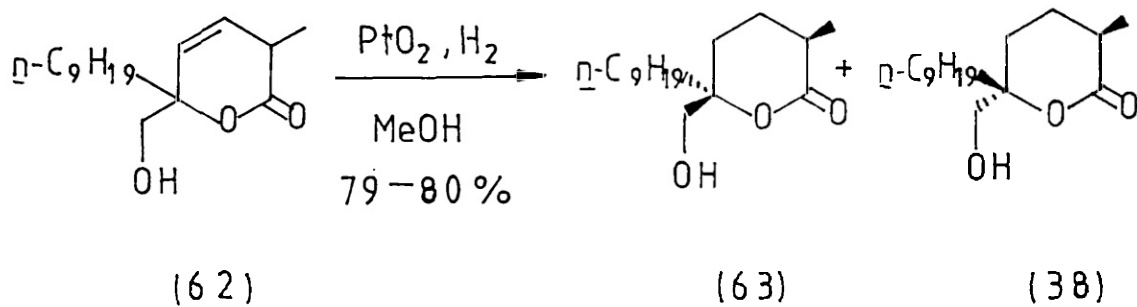


and superimposed on this is the proton on C-4 as a doublet δ 4.58 ($J_{3,4}$ 7.6 Hz). The double quartet at δ 4.10 is the proton on C-2, split by the methyl group (J_{2-Me} 6.4 Hz), and the proton on C-3 ($J_{2,3}$ 11.9 Hz). The $-CH_2$ group on C-5 can be seen as two AB quartets, the *exo*- CH_2 group occurring at lower field (δ 3.64 and 3.68, J_{AB} 5.0 Hz) and the *endo*- CH_2 group at higher field (δ 3.56, and 3.61, J_{AB} 7.5 Hz). The $-OH$ signal occurs at δ 1.56. High pressure carbonylation of the complex (61) gave the unsaturated lactone (62) as a separable mixture of *cis*- and *trans*- isomers.



Attempted hydrogenation of lactone (62) using a palladium on carbon catalyst in ethyl acetate or methanol under atmospheric pressure of hydrogen yielded none of the required product. Higher pressures of hydrogen, or the use of excess catalyst caused hydrogenolysis of the lactone ring. Similar results were obtained using a rhodium on alumina catalyst; in ethyl acetate no reaction occurred, whereas in methanol the lactone ring was opened. Diimide (prepared *in situ* from triisopropylbenzene sulphonylhydrazide or potassium azodicarboxylic acid precursors) also failed to hydrogenate the double bond.

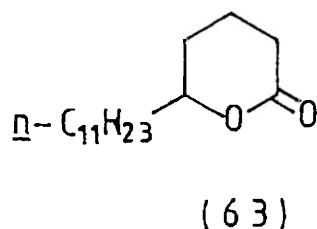
Finally platinum oxide in methanol was found to effect the required reaction. The least polar isomer of lactone (62) (Isomer 1) afforded the *trans*-unsaturated lactone (63) in 80% yield, and the most polar isomer (Isomer 2) afforded *cis*-malyngolide (38) in 79% yield.



Sakito³⁰ has shown that the *trans*-isomer can be isomerised to a mixture of 9:1 of the *cis:trans* isomers (see page 25).

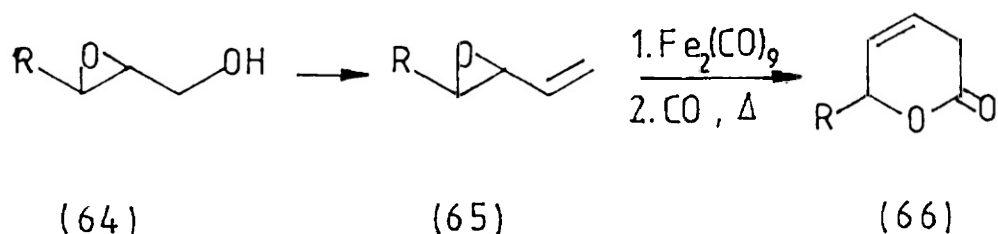
3.5 Attempted Synthesis of the Sex Pheromone of the Oriental Hornet (*Vespa Orientalis*)

Synthesis of chiral molecules is an important goal of synthetic chemists. Consequently an enantioselective synthesis of the pheromone (63) was envisaged.



As the absolute stereochemistry of the natural product is unknown, both isomers would have to be synthesised. A chiral epoxy alcohol (64), which can be prepared by the method of Sharpless²² could be converted into an enantiomerically pure epoxyalkene (65). Reaction with nona-carbonyl diiron followed by carbonylation would yield a chiral lactone (66) (Scheme 15).

Scheme 15

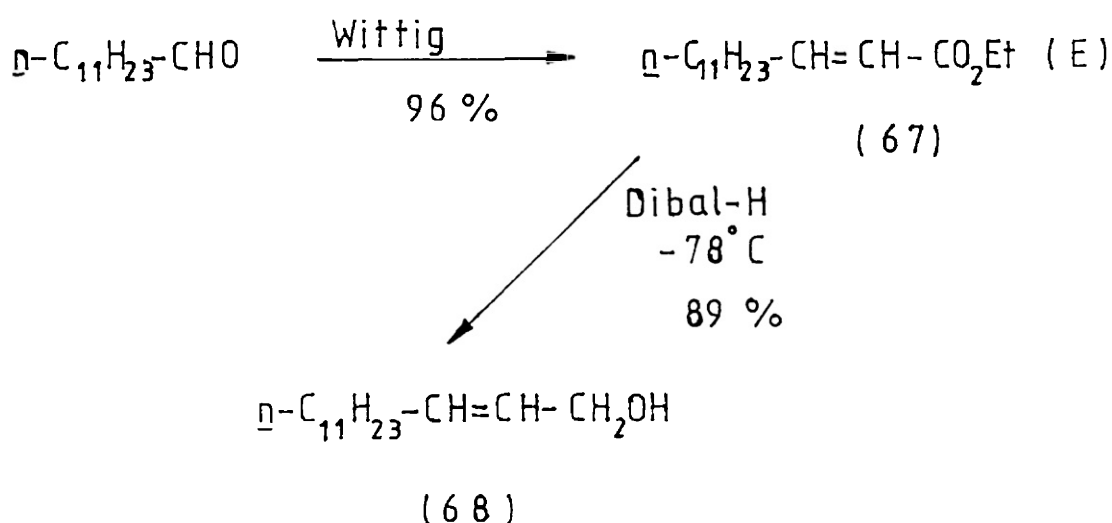


The epoxyalkene (65) therefore becomes the prime synthetic target.

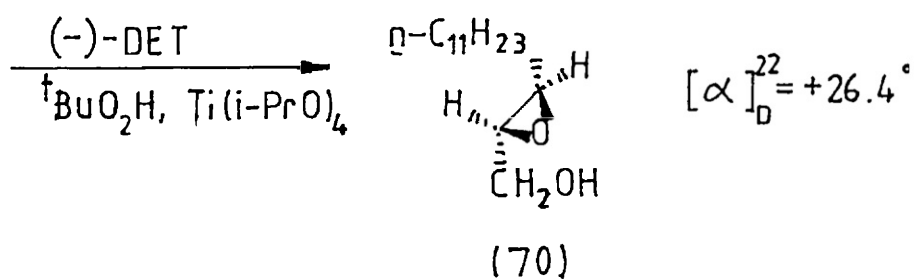
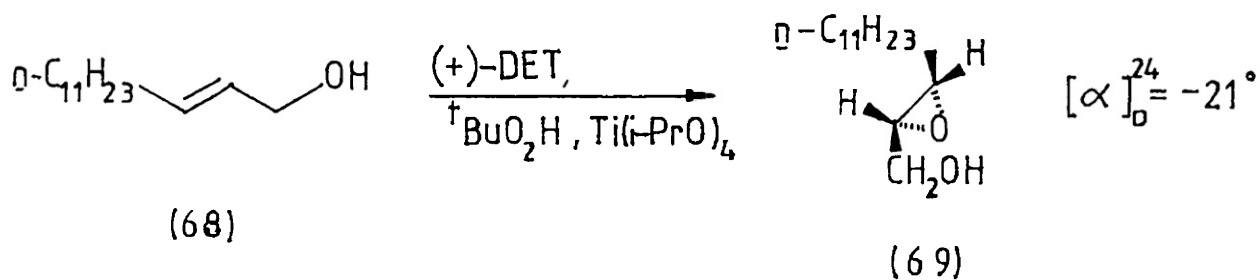
Olefination of dodecanaldehyde with the (carbethoxymethylene)-triphenylphosphine reagent gave the unsaturated ester (67) in 96% yield. A splitting constant of 16 Hz for the olefinic protons confirms the *trans*-stereochemistry of the double bond. Reduction with lithium

aluminium hydride gave the fully saturated alcohol although sodium bis(2-methoxyethoxy) aluminium hydride and diisobutylaluminium hydride both gave mixtures of the saturated and unsaturated alcohols. When using diisobutylaluminium hydride lowering the reaction temperature prevented formation of the saturated product, but also inhibited complete reaction. This could be overcome by using four equivalents at -78°C , to give the *trans*-allyl alcohol (68) in 89% yield (Scheme 16).

Scheme 16

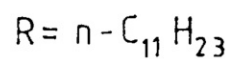
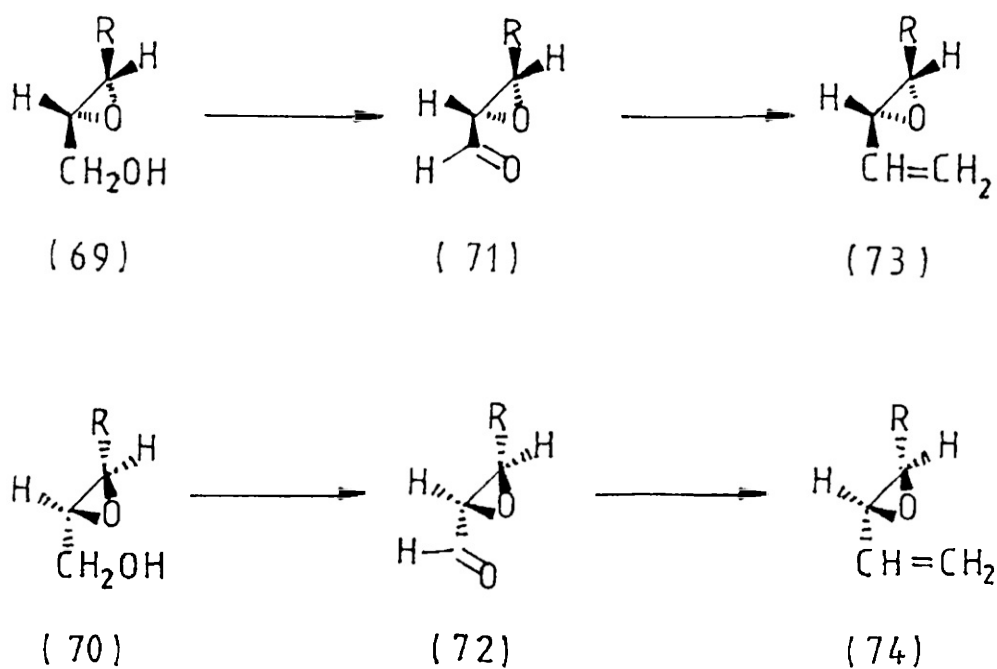


Sharpless epoxidation²² to give the chiral epoxide proved to be very slow despite using a large excess of *t*-butylhydroperoxide. The reaction was therefore carried out at -17°C for 1-4 days; higher temperatures tended to give addition products of the alcohol and diethyl tartrate. The (S),(S)- and (R),(R)-epoxyalcohols (69) and (70) were thus prepared using (+)- and (-)-diethyl tartrate respectively, in 88 and 82% yield.



In order to convert the epoxyalcohols to the required epoxyalkenes (73) and (74), oxidation to the aldehydes (71) and (72) followed by olefination was necessary (Scheme 17).

Scheme 17

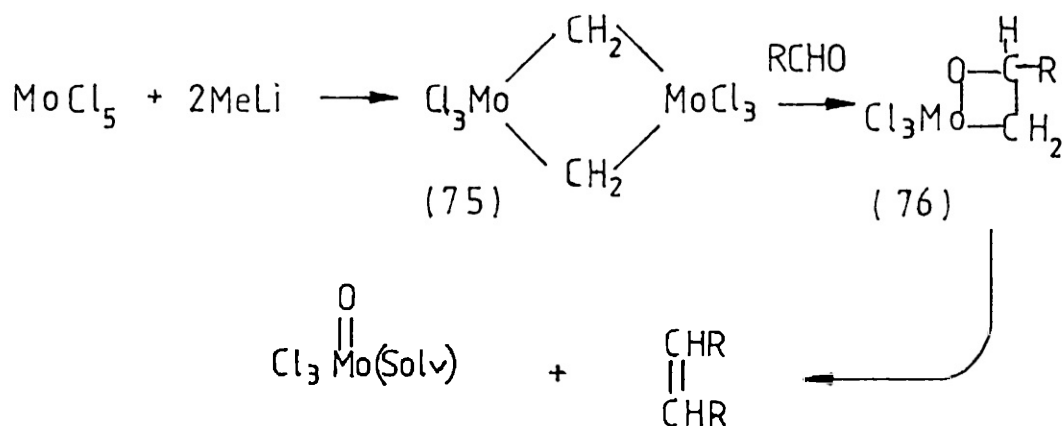


Swern oxidation³¹ of the alcohols to the aldehydes gave low yields, even when carried out with varying amounts of reagent (2 - 3.5 eq) and over a range of temperatures (-50° to -10°C). Using the pyridine/sulphur trioxide complex as an oxidant no reaction occurred.

The use of pyridinium dichromate³² gave one product, but the reaction was very slow (up to four days) and the product began to decompose before complete reaction.³³ Heating the reaction reduced the time required to 14h, but significant amounts of starting material still remained. Addition of 2g per mmol of powdered 3Å molecular sieves³⁴ permitted complete reaction in less than an hour, to give the aldehydes (71) and (72) in 70% and 64% yield respectively. Pyridinium chlorochromate³⁵ under the same conditions gave a 53% yield.

Olefination of the epoxyaldehydes to give the required allyl epoxides (73) and (74) proved to be a major problem. The epoxide is sensitive to both acidic and basic conditions so this rules out methods such as the Peterson olefination.³⁶ Methods using metallic reagents were investigated. Molybdenum pentachloride and methyl lithium react to give the dimer (75)³⁷ which reacts with aldehydes to give the metallo-cycle (76) which then collapses to give an alkene. (Scheme 18).

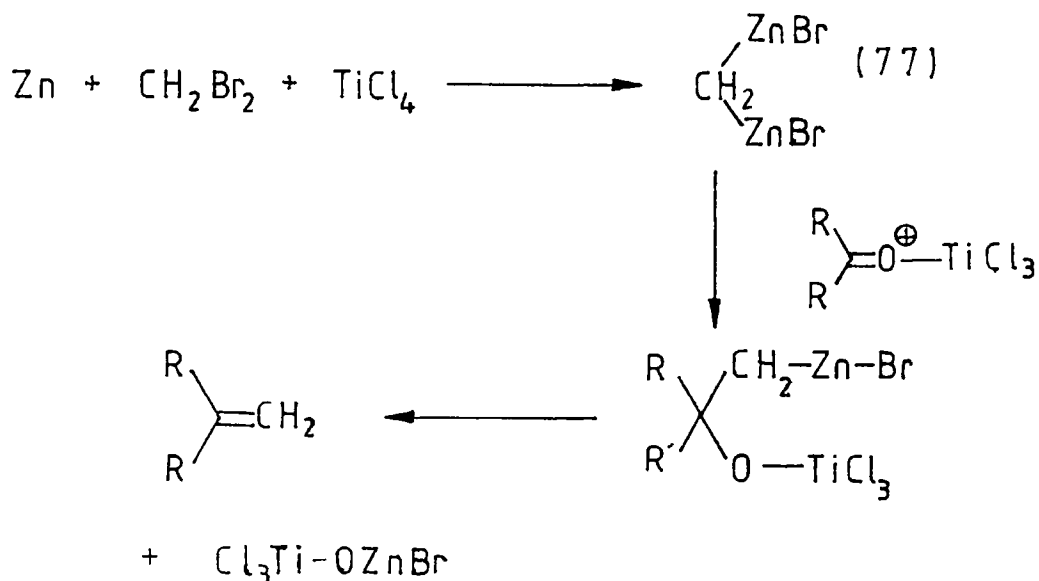
Scheme 18



The reagent (75) when used with the epoxyaldehyde (71) caused total loss of the epoxide moiety.

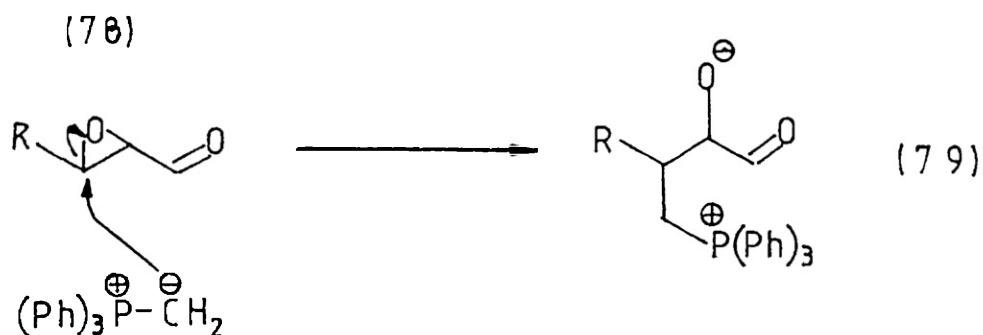
The reagent derived from zinc, dibromomethane and titanium tetrachloride,³⁸ which is thought to form the gem-dimetallic species (77) reacts with carbonyls (activated by the Lewis acid) like a Grignard reagent, to give alkenes (Scheme 19).

Scheme 19

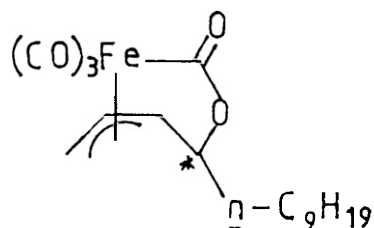


When this reagent was used with epoxyaldehyde (71), total loss of the epoxide occurred, and no identifiable products could be extracted from the reaction mixture.

The Wittig reagent (78) did react very slowly with epoxyaldehyde (71) to give an olefinic product. Examination of the i.r. spectrum showed the carbonyl group to be intact, and the ¹H n.m.r. spectrum showed loss of epoxide protons. The Wittig reagent had reacted with the epoxide rather than with the aldehyde³⁹ (which would be deactivated as an electrophilic site by the epoxide). The product of this attack (79) could then react further to give a product still containing a carbonyl group.



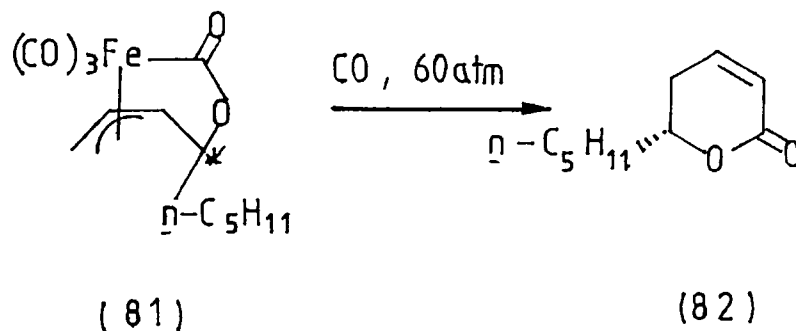
Variation of reaction conditions did not allow formation of the required epoxyalkene (73). Attempted reaction of the crude reaction product (which may have contained some of the required epoxyalkene) with nona-carbonyldiiron in tetrahydrofuran yielded none of the required iron complex (80) required for completion of the synthesis.



(80)

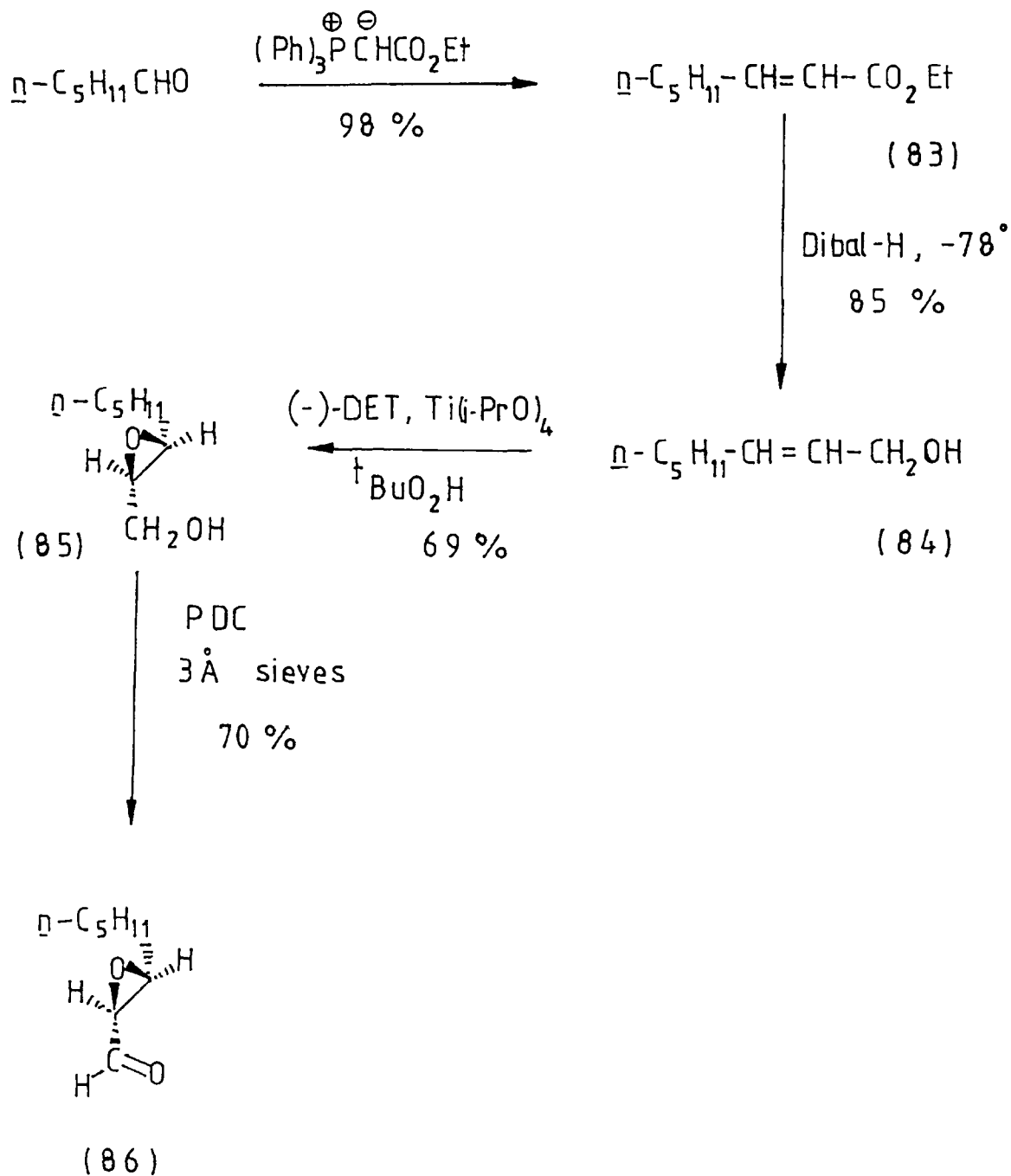
3.6 Attempted Synthesis of Massoia Lactone

Using a similar route to that used towards the synthesis of the oriental hornet pheromone, the chiral iron complex (81) was required for a synthesis of massoia lactone (82).



Hexanal was olefinated using the Wittig reagent (carbethoxymethylene)-triphenylphosphine to afford the α,β -unsaturated ester (83) in 98% yield (Scheme 20). Reduction with diisobutyl aluminium hydride at $-78^\circ C$ gave the allyl alcohol (84) in 85% yield. Epoxidation using the method of Sharpless²² with (-)-diethyl tartrate afforded the (R),(R)-epoxyaldehyde (85) in 69% yield ($[\alpha]_D^{23} = +28.4^\circ$). Oxidation using pyridine dichromate in the presence of powdered 3Å molecular sieves afforded the (R),(R)-epoxyaldehyde (86) $[\alpha]_D^{22} = -40.7^\circ$ in 70% yield. The problems encountered in olefination of epoxyaldehydes (71) and (72) applied when olefination of epoxyaldehyde (86) was attempted, and no epoxyalkene could be produced.

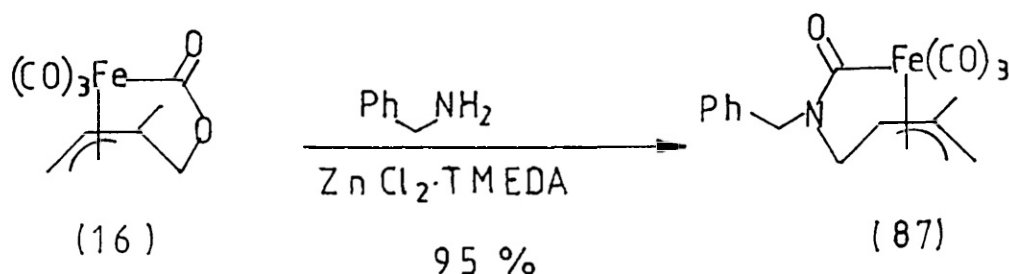
Scheme 20



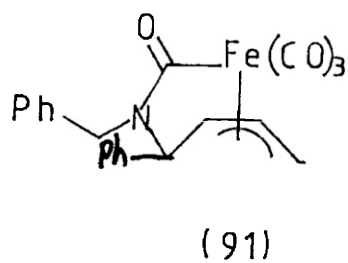
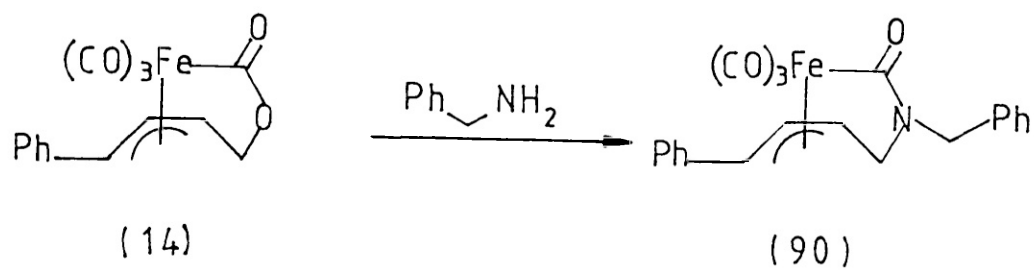
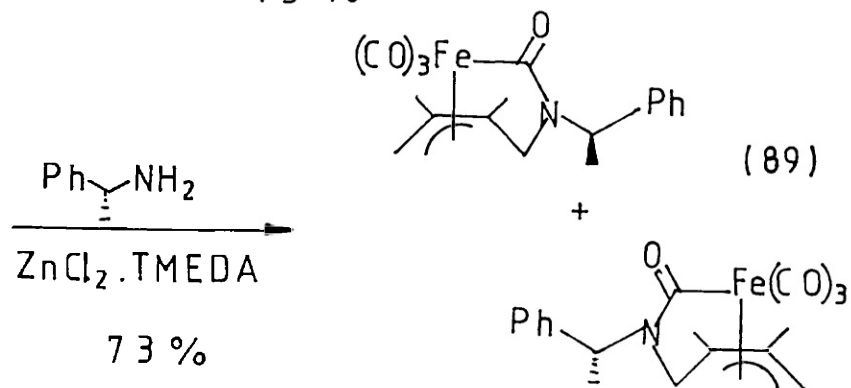
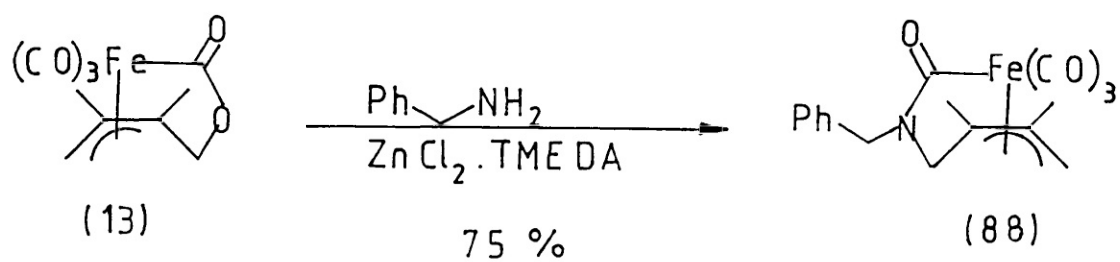
4. CHEMISTRY OF TRICARBONYLIRON COMPLEXES

4.1 Preparation of Tricarbonyliron Lactam Complexes

The action of amines on tricarbonyliron lactone complexes in the presence of Lewis acid catalysts has been shown to give tricarbonyliron lactam complexes.⁴⁰ For example, lactone complex (16) affords the

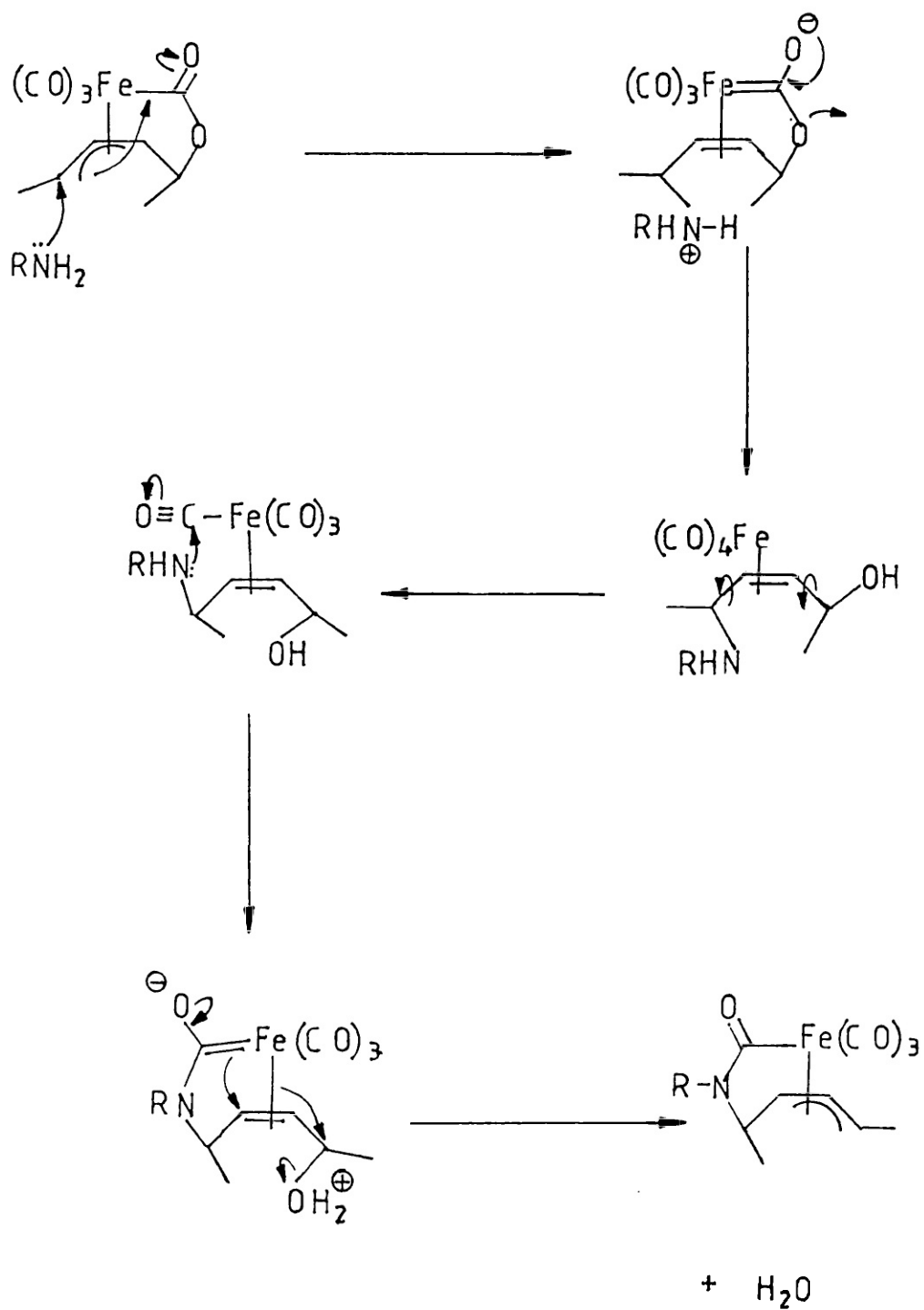


S_N' product, lactam complex (87) in 95% yield. Using this method, tricarbonyliron lactam complexes (88) and (89) (as a mixture of diastereoisomers) were also prepared from the tricarbonyliron lactone complex (13). However, tricarbonyliron lactone complex (14) reacted with benzylamine in the absence of a Lewis acid to give the tricarbonyliron lactone complex (90) in 56% yield. (Reaction in the presence of a Lewis acid is known to give the S_N' product (91)).¹⁹ Aumann³ has suggested the mechanism for this reaction involves nucleophilic attack by the amine on the allyl unit of the lactone complex (Scheme 21). Although this mechanism explains the inversion of the attacked carbon centre, and the shift of the allyl unit, it does not explain why the absence of a Lewis acid causes an alternative product to form. It is also not clear why the amine attacks the allyl unit, as it would be expected that the acyl carbonyl group would possess a much more electrophilic centre. Accordingly, another mechanism can be proposed (Scheme 22).

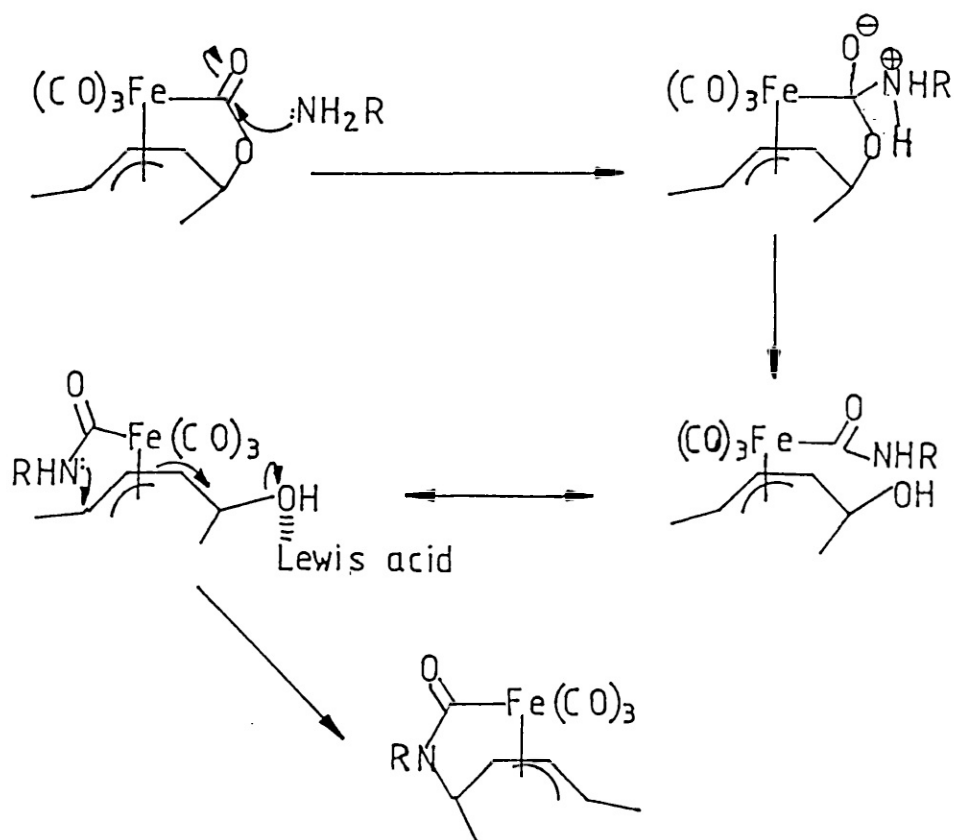


$\nu(\text{CO})$ 2078, 2020
 2010, 1582 cm^{-1}

Scheme 21

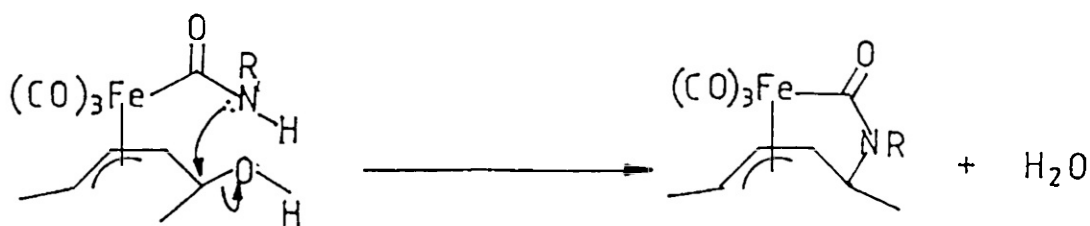


Scheme 22



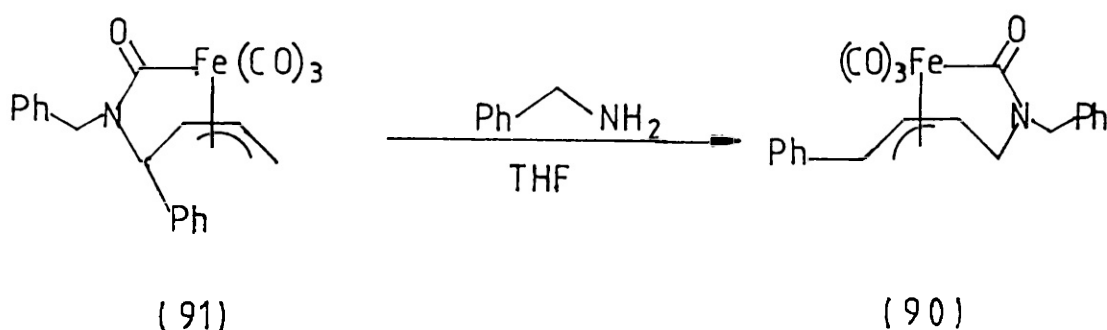
The reason for the formation of the regio-isomer in the absence of a Lewis acid in the reaction of lactone complex (14) with benzylamine is not clear. It is possible that hydrogen bonding between the $-\text{OH}$ and $-\text{NH}$ group favours a more rigid structure, which might then allow direct $\text{S}_{\text{N}}2$ displacement of the $-\text{OH}$ group to give the product in which no regio-reversal has occurred. (Scheme 23). Little experimental data are yet available to clarify the situation.

Scheme 23



Reactions in the presence of a Lewis acid are faster than without one, -possibly evidence in favour of the second mechanism, as a hydroxide group activated by a Lewis acid is a better leaving group than $-OH$. This would ensure a faster overall reaction (if the elimination is the rate determining step), in the Lewis acid catalysed reaction.

Other workers¹⁹ suggest that the lactam complex (90) is formed by the action of the excess amine present in the reaction mixture on the lactam complex (91).



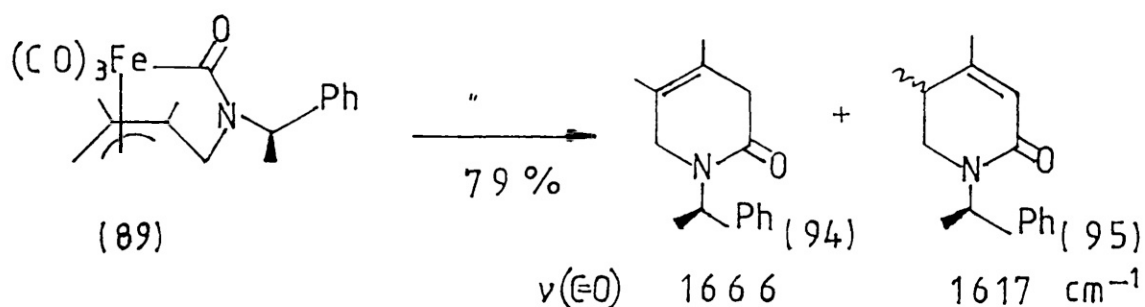
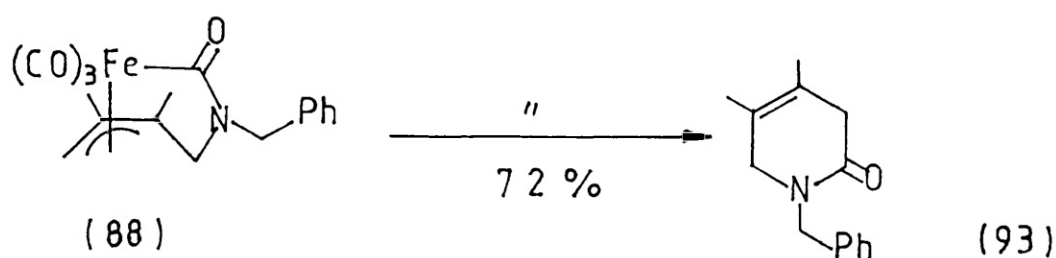
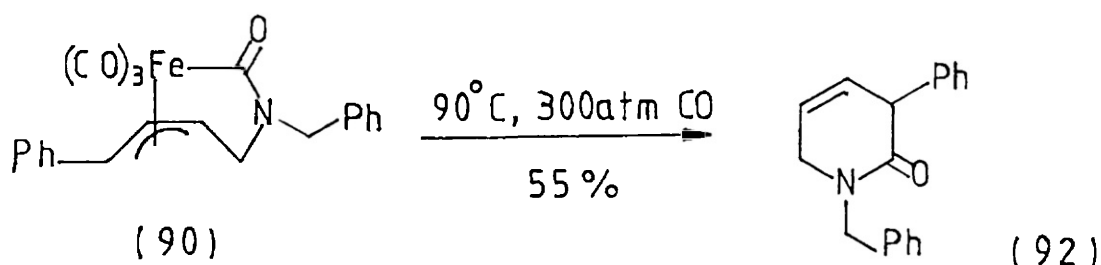
Although this conversion can be achieved by reacting lactam complex (91) with benzylamine, none of the S_N' lactam complex (91) is seen by tlc during the reaction of benzylamine on lactone complex (14) in the absence of a Lewis acid catalyst.

All these facts would suggest that the reaction of amines with lactone complexes is not as simple as first thought, and more work will have to be done in this area before the system can be thoroughly understood.

4.2 Carbonylation of Lactam Complexes

The preparation of lactones from tricarbonyliron lactone complexes by high pressure carbonylation has already been discussed (Section 2.5). Application of the same reaction conditions to lactam complexes (90)

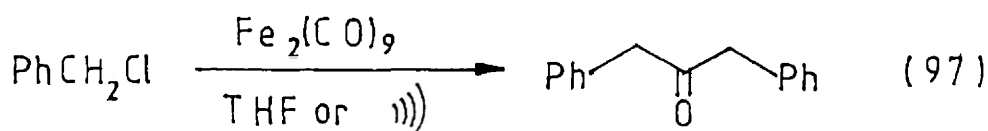
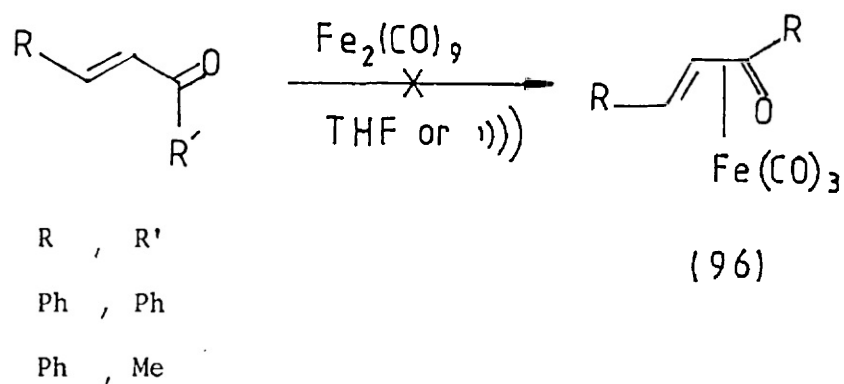
and (88) yielded the lactams (92) and (93) in reasonable yield.



Carbonylation of lactam complex (89) however gave the conjugated lactam (95) and the unconjugated lactam (94) (as a 1:1 inseparable mixture, determined by ^1H nmr). The reason for this is not clear, and the reaction was not investigated further.

4.3 Other Reactions of Nonacarbonyl Diiron

It has already been mentioned (Section 2.2) that tricarbonyliron diene complexes could not be prepared from nonacarbonyl diiron and dienes. Similarly, reaction of nonacarbonyl diiron with enones, did not produce any of the known⁴¹ complexes of type (96), although under the same conditions reaction with benzylchloride did give very small amounts (6%) of the carbonyl insertion product (97).



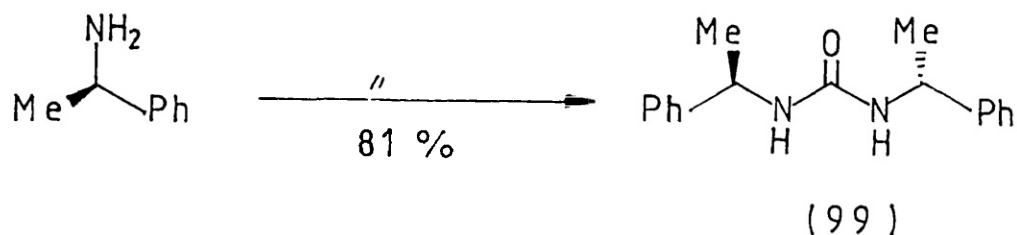
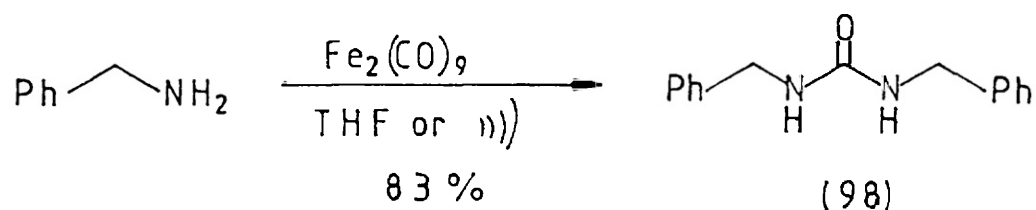
δ 7.38 10 H

4.8 4 H

ν_{max} (C=O) 1720

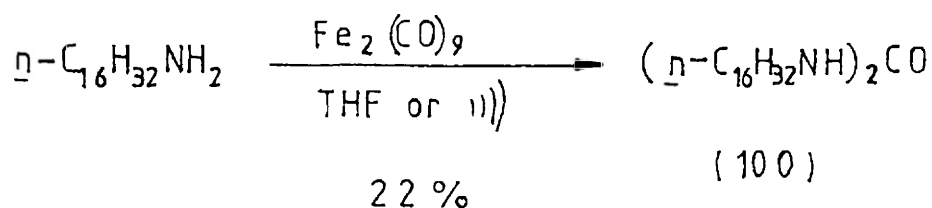
Attempts to prepare tricarbonyliron lactam complexes directly (see Section 4.1) by reacting an allyl epoxide with nonacarbonyl diiron in the presence of benzylamine gave a strong red colouration.

After concentration and purification by flash chromatography a white crystalline solid was obtained which contained none of the usual iron carbonyl stretches around $2,000 \text{ cm}^{-1}$. Examination of the mass spectrum and elemental analysis revealed that the product was dibenzylurea (98). A series of control reactions showed that the product was dependant only on the amine used, and that the allyl epoxide was not necessary to the process.



$$[\alpha]_D^{22} = -13.4^\circ$$

(R)- α -Methylbenzylamine under the same conditions afforded the analogous urea (99), but further attempts to prepare similar ureas from other amines - butylamine, imidazole, morpholine, pyrrolidine, aniline and triethylamine all gave no useful results. Hexadecylamine afforded the urea (100), but in only 22% yield.



These results are interesting because previous reports¹⁶ have stated that the reaction of pyridine in tetrahydrofuran with nonacarbonyl diiron under carbon monoxide, gives the substituted, tetracarbonyl iron complex (101).

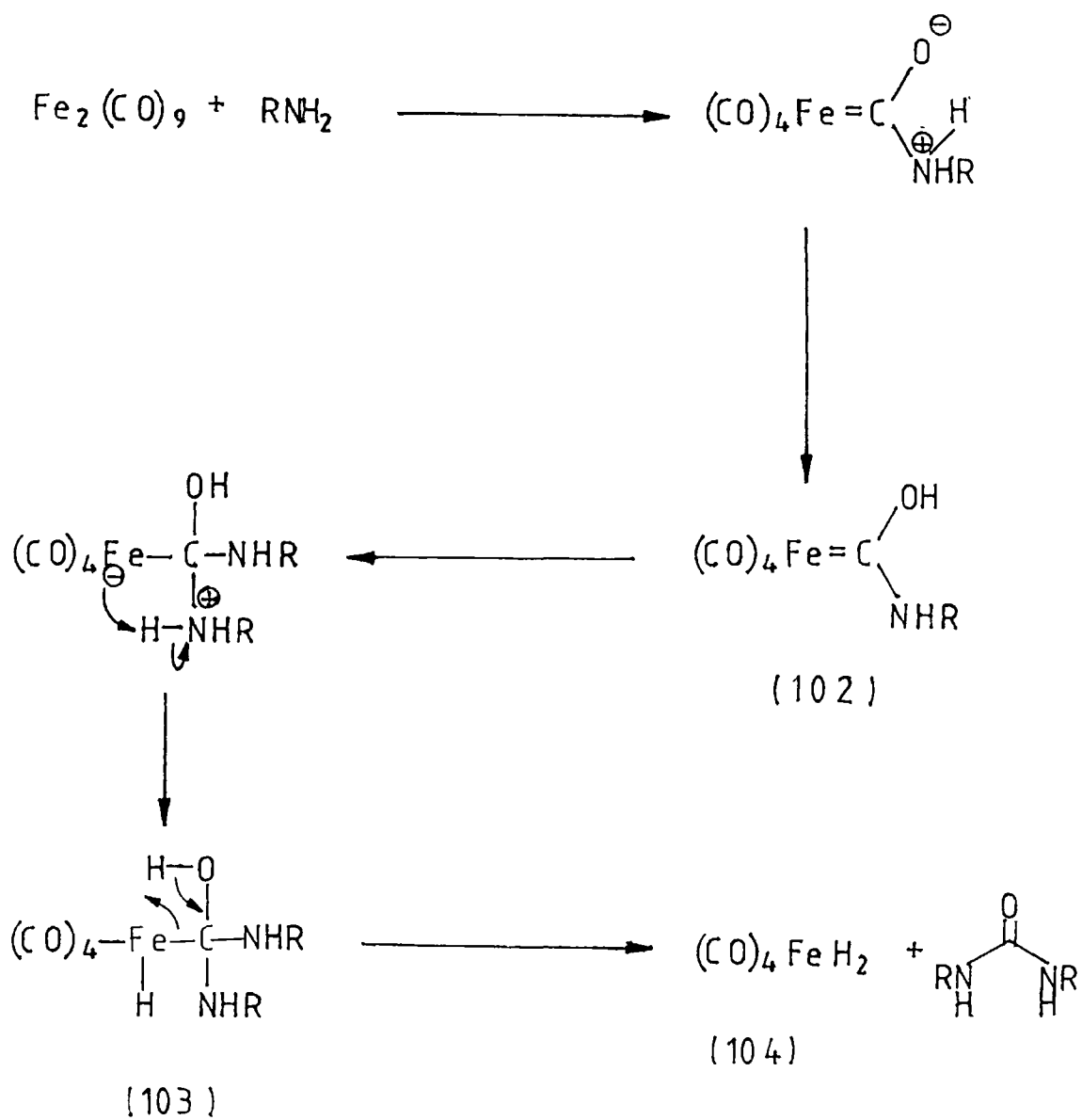


This result was confirmed, but if the reaction was carried out without an atmosphere of carbon monoxide, then no characterisable products could be obtained. Attempted preparation of ureas under a carbon monoxide atmosphere yielded neither urea or any isolable substitution complexes analogous to complex (101), though the red colouration was still observed. It was also found that carbonylation of nonacarbonyl diiron in benzene in the presence of amines also gave the red colouration, but no urea products.

The postulated mechanism (Scheme 24) involves nucleophilic attack of the amine onto a carbonyl ligand, probably a bridging carbonyl, to afford a carbene complex (102). Analogous reactions of nucleophiles with pentacarbonyl iron are known⁴² (Scheme 25), and carbene complexes of this type are known⁴³ to be dark red solids.⁴⁴ These carbene complexes are also known⁴³ to undergo nucleophilic attack at the carbene carbon, and in the presence of an amine this would give structure (103). Hydrogen transfer to the iron, which has been seen in similar systems⁴⁵ would then give the urea, and a tetracarbonyliron hydride species (104). This mechanism however does not explain why a carbon monoxide atmosphere inhibits the reaction.

Attempted isolation of the product responsible for the red colouration by flash chromatography using methanol yielded a very polar red solid, which, on removal of the solvent, decomposed very quickly to elemental iron. However, an i.r. solution spectrum of the solid

Scheme 24

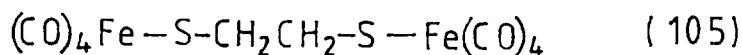


Scheme 25



(derived from α -methyl benzene) showed a sharp peak at 3438 cm^{-1} , and others at 2972, 2031, 1959, 1657, 1563, and 1490 cm^{-1} . ^1H nmr spectrum was extremely broad, due to the decomposition of the solid, but it did show peaks at δ 7.2 ($\sim 5\text{H}$), 4.4 ($\sim 3\text{H}$) and 1.3 ($\sim 3\text{H}$). The mass spectrum showed very weak peaks at 223 and 205, and stronger ones at 190 and 134, which do not correspond to any simple fragmentation, or loss of a carbon monoxide ligand. Most of this data then would seem to confirm the proposed carbene structure of the red solid.

Analogous reactions of benzylthiol with nonacarbonyl diiron gave no dithiocarbonate product, with or without a carbon monoxide atmosphere. Reaction of ethanethiol with pentacarbonyl iron or dodecacarbonyl tri-iron under carbon monoxide has been reported⁴⁶ as giving structure (105), a similar result to the reaction of pyridine with nonacarbonyl

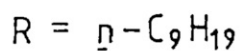
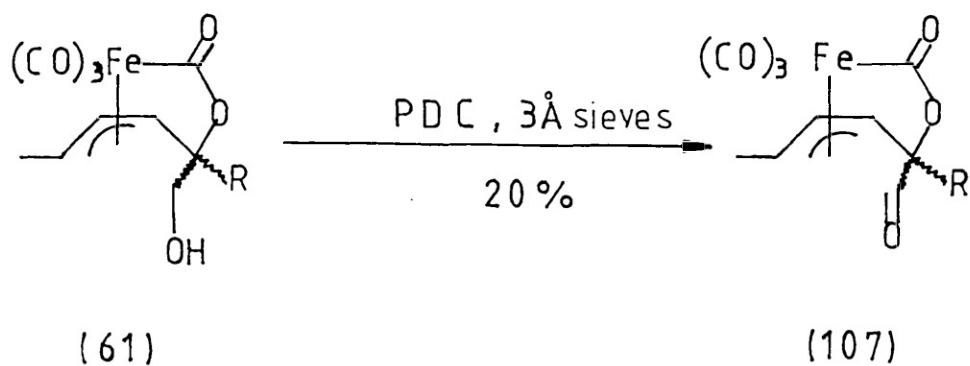


diiron under carbon monoxide.

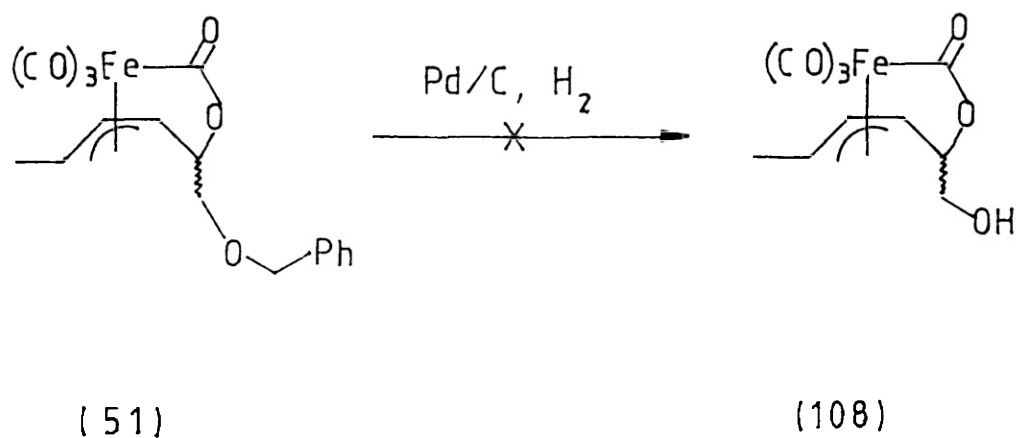
4.4 Reactions of Lactone Complexes

The tricarbonyliron lactone complexes are stable at room temperature, but decompose on heating, or long term storage (1 year) at room temperature to give finely divided iron, carbon monoxide and various organic products, depending on the original complex. Their reactivity with amines,⁴⁰ ceric ammonium nitrate,¹ ferric chloride,³ and alkalis³ have been reported elsewhere.

The complexes are stable to water and dilute acids, although with concentrated sulphuric acid a strong dark red colouration was observed,



However, attempted catalytic hydrogenolysis of complex (51) failed to yield the free hydroxy species (108) although no decomposition of the initial complex was observed.



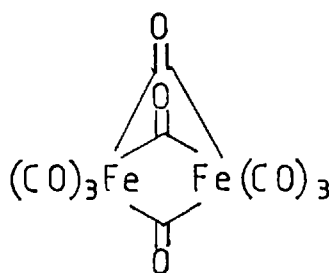
4.5 Attempted Use of Other Metal Carbonyls

The successful preparation of complexes using nonacarbonyl diiron in tetrahydrofuran, and under sonolysis conditions suggested that other metal carbonyl species may react with vinyl epoxides to give lactones directly. (It was already known⁴⁶ that both octacarbonyl dicobalt

(Co₂(CO)₈) and decacarbonyl dimanganese (Mn₂(CO)₁₀) react with tetrahydrofuran). To investigate this possibility a series of mono, di- and tri-metal carbonyls were stirred in tetrahydrofuran or sonolised in the presence of allyl epoxides, along with the appropriate control reactions in which no epoxide was present.

Hexacarbonyl molybdenum (Mo(CO)₆), hexacarbonyl chromium (Cr(CO)₆), decacarbonyl dimanganese, dodecacarbonyl triruthenium (Ru₃(CO)₁₂), (and *bis*-(triphenylphosphine) rhodium dichloride⁴⁷ ((PPh)₂RhCl₂)) all showed no reaction when stirred in tetrahydrofuran or when sonolised. Both octacarbonyl dicobalt and cyclopentadiene-tricarbonyl molybdenum when sonolised gave total decomposition, both in the presence and absence of an allyl epoxide. Cyclopentadiene-tricarbonyl molybdenum when stirred in tetrahydrofuran showed a slight shift of the carbonyl stretch in the i.r., but no further reaction, whereas octacarbonyl dicobalt in tetrahydrofuran resulted in total decomposition, to give a mixture of oxidation products, cobalt(II) carbonate, cobalt(II) oxide and cobalt(II) hydroxide.⁴⁶

All these results would suggest that the presence of the bridging carbonyl ligands in nonacarbonyl diiron (109) are important to its reactivity.



(109)

EXPERIMENTAL

Melting points were determined using a Kofler hot-stage apparatus and are uncorrected, boiling points were obtained using a Kugelröhr micro-distillation apparatus. Infrared spectra were recorded on a Perkin Elmer 298 and 983G spectrophotometer using a thin film between sodium chloride plates or a solution in sodium chloride solution cells. ^1H nmr Spectra were obtained in deuterated solvents using tetramethylsilane as an internal standard and were recorded on a Bruker WM 250 machine, or a Varian EM 360A. Rotations were determined with a Perkin Elmer 141 polarimeter and mass spectra were determined using a VG micromass 7070B instrument. Micro analyses were performed in the Imperial College Chemistry Department microanalytical laboratory.

Solvents were purified by standard techniques. Solutions were dried over anhydrous sodium sulphate, and concentrated with a rotary evaporator, followed by static evaporation on an oil pump.

Photolyses were carried out using a 450W Applied Photophysics lamp with a sodium bromide⁴⁸ filter and cooling solution. Sonolyses were carried out in a Semat 80W, 50 Hz ultrasound bath, which was also used to degas solvents.

Analytical thin layer chromatography (tlc) was performed on Merck precoated silica gel F₂₅₄ plates. Preparative chromatography was carried out on columns of MN kieselgel 60 (230-400 mesh) under pressure (flash chromatography), in a $\frac{1}{2}$ " or $1\frac{1}{2}$ " diameter glass column, using 25-40g of silica per gram of product. Columns were packed using a slurry of silica in petrol (b.p. 40-60°C) and the crude products, in a concentrated solution (1-5 ml) were transferred to the top of the column by pipette. Columns were run in a gradient of ether in petrol (0-100%, 10% steps) unless otherwise stated.

The following abbreviations are used:-

THF	tetrahydrofuran
ZnCl ₂ .TMEDA	zinc chloride/tetramethylethylenediamine complex. ¹⁹
¹ H nmr	proton nuclear magnetic resonance
s	singlet
d	doublet
m	multiplet
q	quartet
br	broad signal
J	value of the splitting constant
J _{AB}	value of the gem splitting constant in an AB quartet
Hz	Hertz
ν_{max}	wavenumber of bands in the infra-red spectrum
s	strong
m	medium
w	weak
sh	shoulder
glc	gas liquid chromatography
h	hour(s)
min	minute(s)
eq	equivalent(s)
ml	millilitre(s)
g	gram(s)
mmol	millimole(s)

decomp.	decomposition
m.p.	melting point
b.p.	boiling point
lit.	literature value
calc.	calculated
r.t.	room temperature
t.l.c.	thin layer chromatography
HCl	hydrochloric acid
i.r.	infra-red spectrum
dil.	dilute

General Method for Preparation of Epoxides A

To a solution of the diene (1 eq) in dichloromethane (3 ml per mmol of diene) with sodium carbonate (3.5 eq) at 0°C was added 35% peracetic acid (1 eq) at a rate which maintained the temperature below 5°C. The mixture was allowed to warm to room temperature, stirred for 5h, filtered, the filtrate concentrated and distilled to afford the epoxide.

General Method for Preparation of Epoxides B¹⁵

A suspension of sodium hydride (2 eq) in redistilled dimethylsulphoxide (2 ml per mmol of enone) under argon was heated at 70°C for 45 min, cooled to room temperature and diluted with an equivalent volume of THF. The mixture was cooled in an ice-salt bath and a solution of trimethylsulphonium iodide (2 eq) in dimethylsulphoxide (1 ml per mmol of iodide) was added over 3 min. The mixture was stirred for 1 min, the enone (1 eq, neat or in THF or dimethylsulphoxide) added and stirred for 15 min. After warming to room temperature the mixture was stirred for 15 min, diluted with water (20 ml per mmol of enone) and extracted with ether. The combined organic extracts were washed with water, dried and concentrated to afford the epoxide. Flash chromatography or distillation often caused decomposition, so the crude epoxide was usually used for preparation of the lactone complexes.

Preparation of 3,4-Epoxy-3-methylbutene (3)

Using method A, isoprene (4.76g, 70 mmol) in dichloromethane (210 ml) with sodium carbonate (26g, 245 mmol) and 35% peracetic acid (15.2g, 70 mmol) afforded 3,4-epoxy-3-methylbutene (3) (3.6g, 62%) identical by ¹H nmr to the previously prepared material.³

Preparation of 3,4-Epoxy-2,3-dimethylbutene (4)

Using method A, 2,3-dimethylbutene (1.4g, 17 mmol) in dichloromethane (50 ml) with sodium carbonate (6.3g, 59.5 mmol) and 35% peracetic acid (3.7 ml, 17 mmol) afforded 3,4-epoxy-2,3-dimethylbutene (4) (1.0g, 60%) identical by ¹H nmr to the previously prepared material.²

Preparation of 3,4-Epoxy-1-phenylbutene (5)

Using method B, cinnamaldehyde (1.5g, 11.4 mmol) afforded 3,4-epoxy-1-phenylbutene (5) (1.57g, 95%) pure by ^1H nmr; δ_{H} (60 MHz; CDCl_3) 2.6 - 2.9 (2H, m, 4- H_2), 3.3 (1H, m, 3-H), 5.7 (1H, dd, J 16 and 8 Hz, 2-H), 6.7 (1H, d, J 16 Hz, 1-H), and 7.2 (5H, s, aromatics); m/z 146 (m^+), 131 ($\text{m}^+ - \text{Me}$), 117 ($\text{m}^+ - \text{CHO}$), 105, 103, and 91.

Preparation of 3,4-Epoxy-3-methyl-1-phenylbutene (6)

Using method B, benzylidene acetone (500 mg, 3.42 mmol) afforded 3,4-epoxy-3-methyl-1-phenylbutene (6) (27.5 mg, 50%) as a thick yellow oil pure by ^1H nmr; δ_{H} (60 MHz; CDCl_3) 1.55 (3H, s, 3-Me), 2.8 (2H, s, 4- H_2), 6.2 (1H, d, J_{AB} 16 Hz, 1-H), 6.9 (1H, d, J_{AB} 16 Hz, 2-H), and 7.3 (5H, m, aromatics); m/z 160 (m^+), 147, and 131 ($\text{m}^+ - \text{CHO}$) (Found M^+ , 160.0886. Calc. for $\text{C}_{11}\text{H}_{12}\text{O}$, 160.0888).

Preparation of 1-(2-Naphthyl)-3-phenylpropen-3-one (7)

To a stirred solution of 2-naphthaldehyde (2g, 12.8 mmol) and acetophenone (3g, 25 mmol) in methanol (50 ml) was added dropwise sodium hydroxide (0.5g) in water (20 ml). After 2h the mixture was filtered and the solid recrystallised from methanol to afford 1-(2-naphthyl)-3-phenylpropen-3-one (7) (1.7g, 51%) m.p. 155-157°C (Found C, 88.17; H, 5.61. $\text{C}_{19}\text{H}_{14}\text{O}$ requires C, 88.34; H, 5.46%); ν_{max} (CDCl_3) 3060m, 1690w, 1660s, 1595s, 1575s, 1501w, 1436w, and 1355m cm^{-1} ; δ_{H} (60 MHz; CDCl_3) 7.3 - 8.3 (14H, m); m/z 258, (m^+), 229 ($\text{m}^+ - \text{CHO}$), 181 ($\text{m}^+ - \text{Ph}$), 152 ($\text{m}^+ - \text{PhCHO}$), 128 ($\text{m}^+ - \text{naphth}$), and 105.

Preparation of 1-(3-Pyridyl)-buten-3-one (8)

To a stirred solution of 3-pyridinecarboxaldehyde (2g, 0.9 mmol) in acetone (20 ml) was added a solution of sodium hydroxide (0.42g, 0.9 mmol) in water (5 ml). The mixture was stirred for 2h, acidified with dil. HCl, neutralised with sodium hydroxide, diluted with water and extracted with ether (3 x 10 ml). The combined organic extracts were dried, concentrated and distilled to afford 1-(3-pyridyl)-buten-3-one (8) (0.52g, 19%), b.p. 90°C, 0.06 mmHg (Found C, 73.38; H, 6.32; N, 9.34. $\text{C}_9\text{H}_9\text{ON}$ requires C, 73.45; H, 6.16, N 9.51%); ν_{max} (neat)

3080w, 3030m, 2920m, 2850w, 1690sh, 1670s, 1610s, 1585m, 1565, 1475s, 1415s, and 1355s cm^{-1} ; δ_{H} (60 MHz, CDCl_3) 2.4 (3H, s, 3-Me), 6.7 (2H, d, J_{AB} 17 Hz, 1-H or 2-H), 7.4 (2H, d, J_{AB} 17 Hz, 1-H or 2-H), 7.2 (1H, q, J 5 Hz, 5-H), 7.7 (1H, dt, J 8 and 1.5 Hz, 4-H), 8.5 (1H, dd, J 5 and 1.5 Hz, 6-H), and 8.65 (1H, d, J 3 Hz, 2-H); m/z 147 (m^+), 132 ($\text{m}^+ - \text{Me}$), 104 ($\text{m}^+ - \text{MeCO}$), and 77.

Preparation of 3-Phenyl-1-(3-pyridyl)-propen-3-one (9)

To a stirred solution of 3-pyridinecarboxaldehyde (3g, 2.82 mmol) and acetophenone (3.6g, 3.1 mmol) in methanol (40 ml) was added dropwise a solution of sodium hydroxide (1.2g, 3.1 mmol) in water (15 ml). After 1h the mixture was acidified with concentrated hydrochloric acid, stirred for 15 min, neutralised with sodium hydroxide and extracted with ether (3 x 20 ml). The combined organic extracts were dried, concentrated and the solid recrystallised from ether to afford 3-phenyl-1-(3-pyridyl)-propen-3-one (9) (1.54g, 26%) m.p. 96-97°C (Found C, 80.49; H, 5.30; N, 6.62. $\text{C}_{14}\text{H}_{11}\text{ON}$ requires C, 80.36; H, 5.40; N, 6.69%); ν_{max} (CDCl_3) 3060m, 3020m, 1670s, 1645m, 1605s, 1575m, 1565m, 1445w, and 1410m cm^{-1} ; δ_{H} (60 MHz; CDCl_3) 7.1 - 7.7 (7H, m, phenyl, 1-H and 2-H), 8.0 (2H, m, 4-H and 5-H on pyridine ring), 8.6 (1H, dd, J 6 and 2 Hz, 6-H on pyridine ring), and 8.8 (1H, d, J 3 Hz, 2-H on pyridine ring); m/z 209 (m^+), 180 ($\text{m}^+ - \text{CHO}$), 132 ($\text{m}^+ - \text{Ph}$), 131 ($\text{m}^+ - \text{py}$), and 122.

Preparation of 3,4-Epoxy-1-(2-naphthyl)-3-phenylbutene (10)

Using method B, enone (7) (300 mg, 1.2 mmol) afforded 3,4-epoxy-1-(2-naphthyl)-3-phenylbutene (10) (225 mg, 75%) as a yellow oil. Residual starting material was removed by precipitation from an ether solution with petrol. δ_{H} (60 MHz, CDCl_3) 3.1 (1H, d, J_{AB} 3 Hz, 4-H), 3.2 (1H, d, J_{AB} 3 Hz, 4-H), 6.3 (1H, d, J_{AB} 18 Hz, 2-H), 6.6 (1H, d, J_{AB} 18 Hz, 1-H), and 7.2 - 7.8 (12H, m, aromatics); m/z 272 (m^+), 270, 170 and 141 (Found M^+ , 272.1201. Calc. for $\text{C}_{20}\text{H}_{16}\text{O}$, 272.1196).

Preparation of 3,4-Epoxy-3-methyl-1-(3-pyridyl)-butene (11)

Using method B, the enone (8) (450 mg, 31 mmol) afforded 3,4-epoxy-3-methyl-1-(3-pyridyl)-butene (11) (100 mg, 20%); δ_{H} (60 MHz, CDCl_3) 2.7 (3H, d, $J < 1$ Hz, 3-Me), 3.2 (2H, s, 3- CH_2), 5.9 (1H, d, J_{AB} 17 Hz, 1-H or 2-H), 6.5 (1H, d, J_{AB} 17 Hz, 1-H or 2-H), 7.15 (1H, q, J 5 Hz, 5-H), 7.6 (1H, dt, J 7 and 2 Hz, 4-H), 8.4 (1H, dd, J 5 and 2 Hz, 6-H), and 8.5 (1H, d, J 4 Hz, 2-H); m/z 161 (m^+), 132, 131, 117, and 106.

Preparation of 3,4-Epoxy-3-phenyl-1-(3-pyridyl)-propene (12)

Using method B, the enone (9) (100 mg, 0.47 mmol) afforded 3,4-epoxy-3-phenyl-1-(3-pyridyl)-propene (12) (71 mg, 67%) as a yellow oil, δ_{H} (60 MHz; CDCl_3) 3.15 (2H, s, 3- CH_2), 6.50 (2H, s, 1-H and 2-H), 7.0-7.9 (7H, m, phenyl and 4-H and 5-H on pyridine ring), and 8.55 (2H, m, 2-H and 6-H on pyridine ring); m/z 223 (m^+), 206 ($\text{m}^+ - \text{OH}$), 194 ($\text{m}^+ - \text{CHO}$), and 106.

General Method for Preparation of Complexes (A)

A solution of the epoxide (1 eq) and nonacarbonyl diiron (1.1 - 1.5 eq) in benzene (10-40 ml per mmol of epoxide) in a round bottomed flask sealed with a suba-seal was sonolised until a green colour was visible (0.5 - 5 h). The mixture was concentrated and purified by flash chromatography and recrystallisation from ether/petrol to afford the tricarbonyliron lactone complex. Runs yielding more than 1g of complex were purified by dissolving the crude product in warm ether, filtering and inducing crystallisation in the filtrate by addition of petrol and cooling.

General Method for Preparation of Complexes (B)

A solution of the epoxide (1 eq) and nonacarbonyl diiron (1.1 - 1.5 eq) in THF (20-60 ml per mmol of epoxide) was stirred until a green colouration was visible (0.5 - 5 h). The mixture was concentrated and purified as in method A.

Preparation of π -Allyl-2,3,4- η^3 -(2,3-dimethyl-1-formyloxy-but-3-en-2-ylato)tricarbonyliron (13)

Using method A the epoxide (4) (150 mg, 0.51 mmol) and nonacarbonyl diiron (278 mg, 0.76 mmol) in benzene (20 ml) for 1h afforded π -allyl-2,3,4- η^3 -(2,3-dimethyl-1-formyloxy-but-3-en-2-ylato)tricarbonyliron (13) (56 mg, 44%) identical by ^1H nmr and ir to the previously prepared compound.² Using method B the epoxide (4) (50 mg, 0.51 mmol) and nonacarbonyl diiron (278 mg, 0.76 mmol) in THF (20 ml) for 2h afforded the complex (13) (54 mg, 42%).

Preparation of π -Allyl-2,3,4- η^3 -(1-formyloxy-4-phenylbut-3-en-2-ylato)-tricarbonyliron (14)

Using method A the epoxide (5) (0.67g, 4.6 mmol) and nonacarbonyl diiron (1.66g, 4.6 mmol) in benzene (50 ml) for 35 min afforded π -allyl-2,3,4- η^3 -(1-formyloxy-4-phenylbut-3-en-2-ylato)tricarbonyliron (14) (980 mg, 68%), m.p. 120°C (decomp) (Found C, 53.76; H, 3.21. $\text{C}_{14}\text{H}_{10}\text{O}_5$ Fe requires C, 53.54; H, 3.21%); ν_{max} (CDCl_3) 2950m, 2886m, 2084s, 2033s, 1656s, 1521w, 1490m, 1450m, and 1377s cm^{-1} ; δ_{H} (250 MHz, CDCl_3) 4.05 (1H, dd, J 12.5 and 5.5 Hz, 1-H_{endo}), 4.17 (1H, dd, J 12.5 and 1.5, 1-H_{exo}), 4.78 (1H, ddd, J 7.5, 5.5, and 1.5 Hz, 2-H), 4.82 (1H, d, J 12.5 Hz, 4-H), 5.62 (1H, dd, J 12.5 and 7.5 Hz, 3-H), and 7.28 - 7.42 (5H, m, aromatics); m/z 270 (m^+ -CO), 256 (m^+ -210), 242 (m^+ -3CO), 214, and 186. Using method B the epoxide (5) (100 mg, 0.62 mmol) and nonacarbonyl diiron (350 mg, 0.96 mmol) in THF (20 ml) for 0.5h afforded the complex (14) (0.53g, 100%).

Preparation of π -Allyl-2,3,4- η^3 -(1-formyloxy-2-methyl-4-phenylbut-3-en-2-ylato)tricarbonyliron (15)

Using method A the epoxide (6) (100 mg, 0.62 mmol) and nonacarbonyl diiron (350 mg, 0.96 mmol) in benzene (20 ml) afforded π -allyl-2,3,4- η^3 -(1-formyloxy-(2-methyl-4-phenylbut-3-en-2-ylato)tricarbonyliron (15) (128 mg, 63%), m.p. 145-155°C (decomp). (Found C, 55.03; H, 3.46. $\text{C}_{15}\text{H}_{12}\text{O}_5\text{Fe}$ requires C, 54.91; H, 3.69%); ν_{max} (CDCl_3) 3020m, 2920m, 2070s, 2000s, 1710sh, 1655s, 1595w, 1440w, 1350w, and 970m cm^{-1} ; δ (250 MHz; benzene- d_6) 1.45 (3H, s, 2-Me), 3.37 (1H, d, J_{AB} 12.4 Hz, 1-H_{endo}), 3.57 (1H, d, J_{AB} 12.4 Hz, 1-H_{exo}), 4.67 (1H, d, J_{AB} 12.4 Hz,

4-H), 4.98 (1H, d, J_{AB} 12.4 Hz, 3-H), and 7.08 (5H, s, aromatics); m/z 328 (m^+), 300 ($m^+ - CO$), 284 ($m^+ - CO_2$), 272 ($m^+ - 2CO$), 256, 244 ($m^+ - 3CO$), 228, 216 ($m^+ - 4CO$), and 160. Using method B the epoxide (6) (100 mg, 0.62 mmol) and nonacarbonyl diiron (350 mg, 0.96 mmol) in THF (20 ml) after 2h afforded the complex (15) (130 mg, 64%).

Preparation of π -Allyl-2,3,4- η^3 -(1-formyloxy-2-methylbut-3-en-2-ylato)-tricarbonyliron (16)

Using method A, the epoxide (3) (2g, 23.6 mmol) and nonacarbonyl diiron (2.9g, 7.9 mmol) in benzene (800 ml) for 5h afforded π -allyl-2,3,4- η^3 -(1-formyloxy-2-methylbut-3-en-2-ylato)tricarbonyliron (16) (1.5g, 76%), identical by ^1H nmr and ir to the previously prepared compound.³ Smaller scale reactions gave a 90% yield. Using method B, the epoxide (3) (2.5g, 29.8 mmol) and nonacarbonyl diiron (10.9g, 30.0 mmol) in THF (75 ml) afforded the complex (16) (7.0g, 94%).

Preparation of π -Allyl-2,3,4- η^3 -(1-formyloxy-4-(2-naphthyl)-2-phenylbut-3-en-2-ylato)tricarbonyliron (17)

Using method A the epoxide (10) (100 mg, 0.37 mmol) and nonacarbonyl diiron (200 mg, 0.56 mmol) in benzene (20 ml) for 5h, afforded π -allyl-2,3,4- η^3 -(1-formyloxy-4-(2-naphthyl)-2-phenylbut-3-en-2-ylato)tri-carbonyliron (17) (108 mg, 65%) m.p. 146-9°C (decomp); ν_{max} (CDCl₃) 3060s, 2930s, 2080s, 2020s, 1720s, 1690s, 1600m, 1445m, and 1360w cm⁻¹; δ_H (250 MHz; CDCl₃) 4.40 (1H, d, J_{AB} 11.9 Hz, H-1_{endo}), 4.48 (1H, d, J_{AB} 11.9 Hz, H-1_{exo}), 5.12 (1H, d, J 12.0 Hz, H-4), 6.35 (1H, d, J 12.0 Hz, H-3), 7.25 (5H, s, 2-Ph), and 7.30 - 8.05 (7H, m, 4-naphthyl); m/z 396, 368, 340, 312, and 270. (Found $m^+ - 3CO - CO_2$, 312.0601. Calc. for C₂₀H₁₀Fe 312.0611). Using method B the epoxide (10) (100 mg, 0.37 mmol) and nonacarbonyl diiron (200 mg, 0.56 mmol) in THF (20 ml) for 2h afforded the complex (17) (96 mg, 59%).

General Method for Carbonylation of Complexes

The complex (0.1 - 10 mmol) was dissolved in benzene (50 ml) and heated to 90°C for 24h under 300 atm of carbon monoxide. Cooling, concentration and purification by flash chromatography afforded the lactones.

Preparation of 2,3-Dimethyl-3-penten-5-olide (18)

The lactone complex (13) (1.0g, 0.6 mmol) treated as above afforded 2,3-dimethyl-3-penten-5-olide (18) (0.59g, 79%) as an oil (Found: C, 66.58; H, 8.06. Calc. for $C_7H_{10}O_2$ C, 66.65; H, 7.99%); $\nu_{\max}$ (neat), 2875s, 1740s, 1620w, 1460m, 1440m, and 1380m cm^{-1} ; δ_H (60 MHz; $CDCl_3$) 1.76 (6H, s), 2.96 (2H, s, 2- H_2), and 4.72 (2H, s, 5- H_2).

Preparation of 2-Methyl-3-penten-5-olide (19)

The lactone complex (30) (2.3g, 9.13 mmol) treated as above afforded 2-methyl-3-penten-5-olide (19) (972 mg, 95%) b.p. 125°C, 2 mmHg (Found: C, 63.93; H, 7.21; $C_6H_8O_2$ requires C, 64.27; H, 7.19%); $\nu_{\max}$ (neat), 2980m, 2937m, 2883m, 1736s, 1461s, and 1398s cm^{-1} ; δ_H (60 MHz; $CDCl_3$) 1.34 (3H, d, J 8 Hz, 2-Me), 3.0 (1H, m, 2-H), 4.8 (2H, m, 5- H_2), and 5.8 (2H, m, 3-H and 4-H); m/z 112 (m^+), 97 (m^+ -Me), 84 (m^+ -CO), and 68 (m^+ -CO₂).

Preparation of 2-Phenyl-3-penten-5-olide (20)

The lactone complex (14) (530 mg, 1.84 mmol) treated as above afforded 2-phenyl-3-penten-5-olide (20) (237 mg, 74%); $\nu_{\max}$ ($CDCl_3$) 3033m, 1762s, 1684m, 1602w, 1492m, 1451m, 1379m, and 1228s cm^{-1} ; δ_H (60 MHz; $CDCl_3$) 2.6 (1H, m, 2-H), 3.8 (2H, d, J 8 Hz, 5- H_2), 5.3 (1H, m, 3-H), 6.5 (1H, m, 4H), and 7.0 - 7.5 (5H, s, aromatics); m/z 174 (m^+), 175, 146 (m^+ -CO), 131, 117, and 115.

Preparation of 3,4-Epoxy-pent-1-ene (28) and 1,2-epoxy-pent-3-ene (29)

To a stirred suspension of *trans*-penta-1,3-diene (2.5g, 36.1 mmol) and sodium carbonate (16g, 151 mmol) in dichloromethane (60 ml) at -5°C was added 35% peracetic acid (8.9 ml), the mixture warmed to room temperature overnight, filtered, and the filtrate concentrated to give the crude allyl epoxides (28) and (29) which were used without further purification.

Preparation of 4-*exo*- π -allyl-2,3,4- η^3 -(1-formyloxypent-3-en-2-ylato)-tricarboxyliron (30) and 2-*endo*- π -allyl-3,4,5- η^3 -(2-formyloxypent-4-en-3-ylato)tricarboxyliron (31)

Using method B for preparation of complexes the crude epoxides (28) and (29) and nonacarbonyl diiron (13.4g, 36.1 mmol) in THF (75 ml) afforded a mixture of 4-*exo*- π -allyl-2,3,4- η^3 -(1-formyloxypent-3-en-2-ylato)tricarboxyliron (30) and 2-*endo*- π -allyl-3,4,5- η^3 -(2-formyloxypent-4-en-3-ylato)tricarboxyliron (31) (3.8g, 42% from the diene) in a ratio of 1:3 separable by chromatography. Complex (30) m.p. 100-105°C (lit.³ 97-99°C) (Found: C, 42.82; H, 3.11; calc. for C₉H₈O₅Fe C, 42.90; H, 3.20%); $\nu_{\max}$ (CDCl₃) 2954w, 2886w, 2083s, 2028s, 1657s, 1443w, 1375w, and 986s cm⁻¹; δ_{H} (250 MHz; CDCl₃) 1.87 (3H, d, J 5.8 Hz, 4-Me), 3.90 - 4.10 (3H, m, 1-H₂ and 4-H), 4.63 (1H, m, 2-H), and 4.80 (1H, m, 3-H); m/z 224 (m⁺-CO), 196 (m⁺-2CO), 168 (m⁺-3CO), and 124. Complex (31) m.p. 115-117°C (lit.³ 110-111°C) (Found: C, 42.82; H, 3.14. calc. for C₉H₈O₅Fe C, 42.90; H, 3.20%); $\nu_{\max}$ (CDCl₃) 2983w, 2909w, 2087s, 2030s, 1665s, and 982w cm⁻¹; δ_{H} (250 MHz; CDCl₃) 1.38 (3H, d, J 6.3 Hz, 2-Me), 3.14 (1H, dd, J 12.6 and 1.9 Hz, 5-H_{endo}), 3.80 (1H, ddd, J 8.2, 1.9 and 1.9 Hz, 5-H_{exo}), 4.48 (1H, m, 2-H), and 4.67 - 4.90 (2H, m, 3-H and 4-H); m/z 224 (m⁺-CO), 196 (m⁺-2CO), 168 (m⁺-3CO), and 124.

Preparation of Parascorbic Acid (32)

The complex (31) (350 mg, 1.39 mmol) in degassed benzene (50 ml) was heated to 195°C for 4h under 60 atm of carbon monoxide, cooled, concentrated and purified by flash chromatography to afford 5-methyl-2-penten-5-olide (32) (114 mg, 73%) as a clear oil which yellowed on standing, b.p. 107°C, 16 mmHg, (Found: C, 64.12; H, 7.21. Calc. for C₆H₈O C, 64.27; H, 7.19%); $\nu_{\max}$ (neat) 2982s, 2937m, 2908m, 1721s, 1632w, 1451w, 1422m, and 1390s cm⁻¹; δ_{H} (60 MHz; CDCl₃) 1.45 (3H, d, J 7 Hz, 5-Me), 2.3 (2H, ddd, J 9, 5 and 2 Hz, 4-H₂), 4.5 (1H, tq, J 9 and 7 Hz, 5-H), 5.95 (1H, dt, J 9 and 2 Hz, 2-H), and 6.8 (1H, dt, J 9 and 5 Hz, 3-H); m/z 112 (m⁺), 68 (m⁺-CO), and 97 (m⁺-Me).

Preparation of *trans,trans*-2,3-Epoxyhex-4-ene (33)

To a stirred suspension of *trans,trans*-hexa-2,4-diene (3g, 36.6 mmol) and sodium carbonate (11.7g, 109 mmol) in dichloromethane (60 ml) at 0°C was added dropwise a 30% solution of peracetic acid (8.8 ml, 36.6 mmol). The mixture was allowed to warm to room temperature, stirred for 5h, filtered and the filtrate concentrated to afford *trans,trans*-2,3-epoxyhex-4-ene (33) (2.43g, 67%), b.p. 21-23°C, 0.05 mmHg (Found: C, 73.26; H, 10.37. Calc. for C₆H₁₀O C, 73.43; H, 10.27%); $\nu_{\max}$ (neat) 3020m, 2950s, 2920s, 2850m, 1655w, 1470w, 1440s, and 1370s cm⁻¹; δ_{H} (60 MHz; CDCl₃) 1.2 (3H, d, J 5 Hz, 2-Me), 1.7 (3H, dd, J 6.5 and 1.5 Hz, 4-Me), 2.5 - 3.0 (2H, m, 2-H and 3-H), 5.0 (1H, qdd, J 15.5, 7.5 and 1.5 Hz, 4-H), and 5.85 (1H, dq, J 15.5 and 6.5 Hz); *m/z* 98 (m⁺), 83 (m⁺-15), 69 (m⁺-29), and 53 (m⁺-43), (Found: M⁺, 98.2572. Calc. for C₆H₁₀O, 98.0731).

Preparation of 2-*exo*- and 2-*endo*- π -allyl-3,4,5- η^3 -(2-formyloxy-hex-4-en-3-ylato)tricarbonyliron (34) and (35)

A suspension of the allyl epoxide (33) (190 mg, 1.94 mmol) and nonacarbonyl diiron (920 mg, 2.5 mmol) in benzene (20 ml) was sonolised for 1h, filtered, the filtrate concentrated and purified by flash chromatography to afford 2-*endo*-3,4,5- η^3 -(2-formyloxy-hex-4-en-3-ylato)tricarbonyliron (35) and 2-*exo*-3,4,5- η^3 -(2-formyloxy-hex-4-en-3-ylato)tricarbonyliron (34) in a ratio of 4:1. 2-*endo*-Isomer (35), m.p. 124-126°C (lit., 115-116°C³ and 124-126°C²⁰) (Found: C, 45.41; H, 3.75. Calc. for C₁₀H₁₀O₅Fe C, 45.15; H, 3.79%); $\nu_{\max}$ (benzene) 3050m, 3020m, 2975m, 2070s, 2000s, 1950s, 1675s, 1460m and 1370m cm⁻¹; δ_{H} (250 MHz; benzene-d₆) 0.98 (3H, d, J 6.8 Hz, 2-Me), 1.14 (3H, d, J 5.8 Hz, 5-Me), 3.40 (1H, d, J 6.8 Hz, 5-H), and 3.70 (3H, m, 2-H, 3-H, and 4-H); *m/z* 238 (m⁺-CO), 222 (m⁺-CO₂), 210 (m⁺-2CO), 194, and 182, (Found: M⁺-CO 237.9920. Calc. for C₉H₁₀O₄Fe, 237.9928). 2-*exo*-Isomer (34), m.p. 108-109°C (lit., 102-103°C³ and 108-109°C²⁰) (Found: C, 44.51; H, 3.79. Calc. for C₁₀H₁₀O₅Fe C, 45.15; H, 3.79%); $\nu_{\max}$ (benzene) 3050m, 3020m, 2970m, 2080s, 2070s, 1670s, 1540m, and 1380m cm⁻¹; 0.92 (3H, d, J 5.8 Hz, 2-Me), 1.09 (3H, d, J 5.8 Hz, 5-Me), 3.46 (2H, m, 2-H and 5-H), 3.78 (2H, m, 3-H and 4-H); *m/z* 238 (m⁺-CO), 222 (m⁺-CO₂), 210 (m⁺-2CO), 194 and 182, (Found: M⁺-CO 237.9919. Calc. for C₉H₁₀O₄Fe, 237.9928).

Preparation of 2,5-Dimethyl-3-penten-5-olide (36)

A solution of the tricarbonyl iron complexes (34) and (35) (161 mg, 0.6 mmol) in degassed benzene (25 ml) was heated to 90°C for 24h under 300 atm of carbon monoxide. The mixture was concentrated and the product purified by flash chromatography to afford *2,5-dimethyl-3-penten-5-olide* (36) (98 mg, 89%) in a 1:1 ratio of *cis:trans*-diastereoisomers (determined by glc), b.p. 61-67°C, 42 mmHg (Found: C, 66.41; H, 8.11. Calc. for $C_7H_{10}O$ C, 66.65; H, 7.99%); $\nu_{\max}$ (neat) 2960s, 2920s, 2860s, 1715s, 1440m, and 1360m cm^{-1} ; δ_H (250 MHz; $CDCl_3$) 1.37 (3H, d, J 6.8 Hz, 2-Me), 1.44 (3H, d, J 7.4 Hz, 5-Me), 3.08 (1H, m, 2-H), 5.09 (1H, m, 5-H), and 5.78 (2H, m, 3-H and 4-H); m/z 126 (m^+) 111 ($m^+ - Me$), 98 ($m^+ - CO$), 96 ($m^+ - 2Me$), 83 ($m^+ - MeCO$), and 82 ($m^+ - CO_2$), (Found: M^+ , 126.0685. Calc. for $C_7H_{10}O_2$, 126.0678).

Preparation of 2,5-Dimethyl-5-pentanolide (37)

A solution of the lactone (36) (43 mg, 0.34 mmol) in ethyl acetate (3 ml) with 5% Pd/C (10 mg) was stirred for 1h at room temperature under 1 atm. of hydrogen. The solution was filtered and the filtrate concentrated to afford *2,5-dimethyl-5-pentanolide* (37) (40 mg, 92%) as a 1:1 mixture of *cis*- and *trans*-diastereoisomers (determined by glc), m.p. 50-51°C (lit., 49-50°C)²¹ (Found: C, 65.79; H, 9.32. Calc. for $C_7H_{12}O$ C, 65.90; H, 9.44%); $\nu_{\max}$ ($CDCl_3$) 2980s, 2930s, 2870s, 1720s, 1440w, and 1360w cm^{-1} ; δ_H (250 MHz; $CDCl_3$) 1.23 (3H, d, J 6.7 Hz, *cis*-2-Me), 1.31 (3H, d, J 7.4 Hz, *trans*-2-Me), 1.37 (3H, d, J 7.0 Hz, *cis*-5-Me), 1.38 (3H, d, J 6.3 Hz, *trans*-5-Me), 1.40 - 2.70 (5H, m), and 4.39 - 4.52 (1H, m, 5-H); m/z 128 (m^+), 113 ($m^+ - Me$), 94, 89, and 56, (Found: M^+ , 128.0832. Calc. for $C_7H_{12}O$, 128.0837).

Preparation of *trans,trans*-1-Hydroxyhexa-2,4-diene (42)

To a stirred suspension of lithium aluminium hydride (5.5g, 137 mmol) in dry ether (100 ml) at 0°C was added sorbic acid (13.8g, 123 mmol). The mixture was heated to 35°C for 1h, cooled, quenched with saturated sodium sulphate solution and filtered. The filtrate was concentrated and distilled to afford *trans,trans*-1-hydroxyhexa-2,4-diene (42) (2.13g, 18%), m.p. 30-31°C (lit.⁴⁹ 30.5 - 31.5°C); $\nu_{\max}$ (neat) 3400s, 3010m,

2960s, 2930s, 2870s, 1640m, 1450m, and 1380w cm^{-1} ; δ_{H} (60 MHz, CDCl_3) 0.9 (3H, d, J 6 Hz, 5-Me), 3.2 (1H, br s, OH), 3.9 (2H, d, J 5 Hz, 1- H_2), and 5.2 - 6.2 (4H, m, olefinics).

Preparation of 2,3-Epoxy-1-hydroxyhex-4-ene (43)

To a solution *trans-trans*-1-hydroxyhexa-2,4-diene (42) (3g, 30.6 mmol) in dichloromethane (60 ml) and vanadylacetoacetate (60 mg) under reflux was added *t*-butylhydroperoxide in benzene (47 ml, 1.3 M, 61.2 mmol). After 0.1h the mixture was cooled, concentrated and purified by flash chromatography to afford 2,3-epoxy-1-hydroxyhex-4-ene (43) (3.14g, 90%), b.p. 70°C, 0.1 mmHg; ν_{max} (neat) 3470s, 2960s, 2860s, 1710w, 1665m, 1440m, and 1375sh cm^{-1} ; δ_{H} (250 MHz, CDCl_3) 1.74 (3H, dd, J 6.5 Hz, 1.6 Hz, 5-Me), 3.07 (1H, m, 1-H), 3.35 (1H, dd, J 8.3, 2.2 Hz, 1-H), 3.40 (1H, br s, OH), 3.62 (1H, m, 2-H or 3-H), 3.90 (1H, m, 2-H or 3-H), 5.21 (1H, qdd, J 15.8, 8.3, 1.7 Hz, 4-H), and 5.96 (1H, dq, J 15.8, 6.6 Hz, 4-H); m/z 114 (m^+), 115 ($\text{m}^+ + 1$), 95 ($\text{m}^+ - \text{H}_3\text{O}$), and 85 ($\text{m}^+ - \text{CH}_2\text{OH}$) (Found: M^+ , 114.0674. Calc. for $\text{C}_6\text{H}_{10}\text{O}_2$ 114.0681).

Preparation of 1-Acetoxyhexa-2,4-diene (44)

To a stirred solution of 1-hydroxyhexa-2,4-diene (42) (0.5g, 5.1 mmol) in pyridine (5 ml) at 0°C was added acetic anhydride (0.76g, 7.5 mmol) and the mixture stirred for 1h. The mixture was warmed to r.t., stirred for 2h, diluted with water (10 ml), and extracted with ether (3 x 20 ml). The combined organic extracts were washed with water, 5% copper sulphate solution, dried, concentrated and purified by flash chromatography to afford 1-acetoxyhexa-2,4-diene (44) (0.41g, 80%), b.p. 30°C, 0.75 mmHg; ν_{max} (neat) 2990s, 2900s, 2860s, 2830m, 1720s, 1650w, 1430m, and 1360m cm^{-1} ; δ_{H} (60 MHz; CDCl_3) 1.7 (3H, d, J 5 Hz, 2-Me), 1.95 (3H, s, OAc), 4.45 (2H, d, J 6 Hz, 6- H_2), and 5.1 - 6.4 (4H, m, olefinics); m/z 140 (m^+), 112 ($\text{m}^+ - \text{CO}$), 99, and 95 (Found: M^+ , 140.0839. Calc. for $\text{C}_8\text{H}_{12}\text{O}_2$ 140.0837).

Preparation of 1-Benzyloxyhexa-2,4-diene (45)

To a stirred solution of 1-hydroxyhexa-2,4-diene (42) (5g, 51 mmol) in THF (100 ml) was added sodium hydride (2.5g, 50% suspension in oil, 52 mmol). After 0.5h, tetrabutyl ammonium iodide (200 mg, 0.6 mmol) was added followed by benzyl bromide (6 ml, 52 mmol). After 3h the mixture was diluted with water (50 ml), and extracted with ether (3 x 60 ml). The combined organic extracts were dried, concentrated and distilled to afford 1-benzyloxyhexa-2,4-diene (45) (6.7g, 70%), b.p. 103-104°C, 2 mmHg; $\nu_{\max}$ (neat) 3060m, 3020s, 2920s, 2850s, 1660m, 1600w, 1490m, 1450s, 1435sh, and 1360s cm^{-1} ; δ_{H} (60 MHz; CDCl_3) 1.7 (3H, d, J 6 Hz, 5-Me), 4.0 (2H, d, J 6 Hz, 1-H₂), 4.5 (2H, d, J 3 Hz, 1-OCH₂), 5.4 - 6.4 (4H, m, olefinics), and 7.3 (5H, s, aromatics); m/z 188 (m^+), 181, 170, 154 and 91 (Found: M^+ 188.1204. Calc. for $\text{C}_{13}\text{H}_{16}\text{O}$, 188.1201).

Preparation of 2,3-Epoxy-1-benzyloxymethyl-hex-4-ene (46)

To sodium hydride (317 mg, 13.1 mmol) was added THF (75 ml) and the epoxyalcohol (43) (1.38g, 12.1 mmol) in THF (15 ml) and the mixture stirred for 0.5h. To the mixture was added tetrabutylammonium iodide (270 mg) and benzylbromide solution in THF (14.6 ml, 0.84M, 12.1 mmol). The mixture was stirred overnight, concentrated and purified by flash chromatography to afford 2,3-epoxy-1-benzyloxymethyl-hex-4-ene (46) (1.5g, 66%) as an oil; $\nu_{\max}$ (neat) 3070w, 3040s, 2970w, 2860m, 1670w, 1610w, 1500m, 1470s, 1450s, and 1365m cm^{-1} ; δ_{H} (250 MHz; CDCl_3) 1.73 (3H, dd, J 6.6 and 1.6 Hz, 2-Me), 3.08 (1H, m, 5-H), 3.23 (1H, dd, J 8.0 and 1.8 Hz), 3.49 (1H, dd, J_{AB} 11.8 Hz, J 5.6 Hz, 6-H), 3.52 (1H, dd, J_{AB} 11.8 Hz, J 3.7 Hz, 6-H), 4.52 (1H, d, J_{AB} 11.4 Hz, 6-OCH), 4.59 (1H, d, J_{AB} 11.4 Hz, 6-OCH), 5.20 (1H, ddq, J 14.7, 8.0 and 1.6 Hz, 3-H), 5.98 (1H, dqd, J 14.7, 6.6 and 0.7 Hz, 2-H), and 7.30 (5H, s, aromatics); m/z 204 (m^+), 143, 142, 107 (m^+ -PhCH₂O), and 91 (PhCH₂), (Found: M^+ 204.1150. Calc. for $\text{C}_{13}\text{H}_{16}\text{O}$ 204.1152).

Preparation of π -Allyl-3,4,5- η^3 -(1-benzyloxy-2-formyloxyhex-4-en-3-ylato)tricarbonyliron (47) and (48)

A solution of the epoxide (46) (150 mg, 0.25 mmol) in benzene (20 ml) containing nonacarbonyldiiron (135 mg, 0.36 mmol) was sonolysed for 5h, concentrated and purified by flash chromatography and crystallisation

to afford π -allyl-3,4,5- η^3 -(1-benzyloxy-2-formyloxyhex-4-en-3-ylato)-tricarbonyliron (47) and (48) (73 mg, 79%) as a mixture of isomers at C-2, m.p. 64-65°C (Found C, 55.10; H, 4.35. $C_{17}H_{16}O_6Fe$ requires C, 54.87; H, 4.34%); $\nu_{\max}$ (CDCl₃) 3020w, 2950w, 2900w, 2850w, 2070s, 2005s, 1677s, and 1360w, cm⁻¹; δ_H (250 MHz; CDCl₃) 1.83 (3H, d, J 5.6 Hz, 5-Me), 3.53 (2H, m, 1-H₂), 3.50 (1H, m, 5-H), 4.15 - 4.40 (1H, m, 2-H), 4.57 (4H, m, 1-OCH₂, 3-H and 4-H), and 7.34 (5H, s, aromatics); m/z 328 (m^+ -CO₂), 316 (m^+ -2CO), 300 (328-CO), 288 (m^+ -3CO), 272 (328-2CO), 232 (m^+ -3CO), and 188 (m^+ -Fe(CO)₄O), (Found: M^+ 316.0988. Calc. for $C_{17}H_{16}O_6Fe$, 316.0998). Alternatively the epoxide (46) (50 mg, 0.25 mmol) and nonacarbonyl diiron (135 mg, 0.36 mmol) in THF (20 ml) was stirred for 2h, concentrated and purified as above to afford the complex (47) and (48) (31 mg, 34%). For a detailed analysis of the ¹H nmr spectrum of the separate isomers, see Section 3.3.

Preparation of 2-Methyl-5-benzyloxymethyl-3-penten-5-olide (50)

A solution of the complex (46) and (47) (200 mg, 0.54 mmol) in degassed benzene (8 ml) was heated to 130°C under 150 atm of carbon monoxide for 30h, cooled, concentrated and purified by flash chromatography to afford 2-methyl-5-benzyloxymethyl-3-penten-5-olide (50) (114 mg, 73%); $\nu_{\max}$ (CDCl₃) 3020w, 2850s, 1720s, 1610w, 1440m, 1350m, and 1080s cm⁻¹; δ_H (250 MHz; CDCl₃) 1.37 (3H, dd, J 7.4 and 2.0 Hz, 1-Me), 3.12 (1H, m, 1-H), 3.66 (2H, ddd, J 19.4, 10.4 and 4.0 Hz, 5-CH₂), 4.57 (2H, d, J 6.5 Hz, 5-CH₂OCH₂), 5.05 (1H, m, 5-H), 5.84 (2H, br s, 3-H and 4-H), and 7.31 (5H, m, aromatics); m/z 232 (m^+), 188 (m^+ -CO₂), 141 (m^+ -CH₂Ph) and 125 (m^+ -OCH₂Ph) (Found: M^+ 232.1100. Calc. for $C_{14}H_{16}O_3$ 232.1099).

Preparation of 2-Bromo-methylundecanoate (53)

To a stirred solution of undecanoic acid (5.2g, 28 mmol) in phosphorus tribromide (7.6g, 28.2 mmol) was added bromine (9.2g, 57.5 mmol) and the mixture heated to 100°C. After 15h the mixture was poured into methanol (50 ml) with vigorous stirring, diluted with water (20 ml) and extracted with petrol (4 x 20 ml). The combined organic extracts were washed with water (3 x 30 ml), dried, concentrated and distilled to afford 2-bromo-methylundecanoate (53) (6.3g, 80%) b.p. 115°C, 0.1 mmHg (Found: C, 51.33; H, 8.42. $C_{12}H_{25}O_2Br$ requires C, 51.61; H, 8.30%); $\nu_{\max}$ (neat) 2940s, 2920s, 2850s, 1740s, 1460s, 1430m, and 1360w cm⁻¹;

δ_{H} (60 MHz; CDCl_3) 0.8 (3H, m, 10-Me), 1.3 (14H, m), 2.0 (2H, m, 3-H₂), 3.6 - 3.7 (3H, 2s, OMe), and 4.2 (1H, t, J 9 Hz, 2-H); m/z 278/280 (m^+), 199 ($m^+ - \text{Br}$), and 154/152.

Preparation of Methyl Undecanoate (56)

To a stirred solution of undecanoic acid (10g, 53.7 mmol) in methanol (60 ml) was added 98% sulphuric acid (9 ml), and the mixture stirred for 3h. The mixture was cooled, neutralised with 5M sodium hydroxide solution, concentrated, diluted with water and extracted with ether (3 x 40 ml). The combined organic extracts were dried, concentrated and distilled to afford the ester (56) (10.4g, 97%), b.p. 90-95°C, 0.4 mmHg (Found: C, 71.67; H, 12.05. Calc. for $\text{C}_{12}\text{H}_{24}\text{O}_2$ C, 71.95; H, 12.08%); ν_{max} (neat) 2960s, 2920s, 2850s, 1740s, 1465m, 1455m, 1435m, and 1375m cm^{-1} ; δ_{H} (60 MHz; CDCl_3) 0.8 (3H, s, 2-Me), 1.2 (16H, s), 2.1 (2H, d, J 7 Hz, 10-H₂), and 3.6 (3H, s, 11-OMe); m/z 200 (m^+), 199 ($m^+ - 1$), 168 ($m^+ - \text{MeOH}$), 156 ($m^+ - \text{CO}_2$), 142 ($m^+ - \text{CO}_2\text{CH}_2$), and 128 ($m^+ - \text{CH}_2\text{CO}_2\text{Me}$).

Preparation of 5-Methoxycarbonyl-4-hydroxy-tetradec-2-ene (55)

To a stirred solution of lithiumdiisopropylamine (from diisopropylamine (2.6g, 26 mmol) and *n*-butyllithium (16.6 ml, 1.51M, 27 mmol)) in THF (16 ml) at -78°C under argon was added methyl undecanoate (56) (5g, 25 mmol) followed by crotonaldehyde (2.4g, 34 mmol) and the mixture warmed to room temperature. To this was added saturated ammonium chloride solution (30 ml) and the mixture extracted with ether (3 x 30 ml). The combined organic extracts were washed with water (2 x 20 ml), copper sulphate solution (2 x 50 ml, 5%), dried, concentrated and distilled to afford *5-methoxycarbonyl-4-hydroxy-tetradec-2-ene* (55) (6.17g, 88%) as a mixture of diastereoisomers, b.p. 140-141°C, 0.2 mmHg (Found: C, 70.86; H, 11.47. $\text{C}_{16}\text{H}_{30}\text{O}_3$ requires C, 71.07; H, 11.18%); ν_{max} (neat) 3440s, 2920s, 2840s, 1730s, 1680w, 1430m, and 1370m cm^{-1} ; δ_{H} (250 MHz; CDCl_3) 0.88 (3H, t, 13-Me), 1.25 (14H, m), 1.52 (2H, m, 9-H₂), 1.70 (3H, d, J 6 Hz, 2-Me), 2.45 (1H, m, 5-H), 2.57 (1H, br s, OH), 3.70 (3H, s, OMe), 4.15 (1H, t, J 7.5 Hz, 4-H), 5.43 (1H, m, 2-H or 3-H), and 5.70 (1H, m, 2-H or 3-H); m/z 270 (m^+), 271 ($m^+ + 1$), 253 ($m^+ - \text{OH}$), 252 ($m^+ - \text{H}_2\text{O}$), (Found: M^+ , 270.2189. Calc. for $\text{C}_{16}\text{H}_{30}\text{O}_3$, 270.2195).

Preparation of 5-Hydroxymethyl-tetradeca-2,4-diene (52)

A mixture of the ester (55) (5g, 18.5 mmol) and potassium hydrogen sulphate (25g, 185 mmol) in toluene (100 ml) was heated under reflux under Dean-Stark conditions for 48h, cooled, 1,8-diazobicyclo[5.4.0]-undecane (2.95g, 18.5 mmol) added and the mixture allowed to stand for 24h. To this was added ether (50 ml) and the mixture added to a suspension of lithium aluminium hydride (0.68g, 18.5 mmol) in ether (50 ml) at 0°C. After 0.2h the mixture was quenched with saturated sodium sulphate solution, filtered, the filtrate concentrated and distilled to afford *5-hydroxymethyl-tetradeca-2,4-diene* (52) (2.95g, 71%), b.p. 190°C, 0.05 mmHg (Found: C, 80.07; H, 12.84. $C_{15}H_{28}O$ requires C, 80.29; H, 12.58%); $\nu_{\max}$ (neat) 3420s, 3020s, 2950sh, 2920s, 2870s, 1653w, 1615w, 1460s, 1430m, and 1370w cm^{-1} ; δ_H (250 MHz; $CDCl_3$) 0.87 (3H, t, J 6.0 Hz, 13-Me), 1.27 (14H, m), 1.58 (1H, br s, OH), 1.79 (3H, dd, J 5.5 and <1 Hz, 2-Me), 2.18 (2H, t, J 7.5 Hz, 6-H₂), 4.06 (2H, s, 5-CH₂), 5.70 (1H, dq, J 15 and 9 Hz, 2-H), 6.00 (1H, d, J 11 Hz, 4-H), and 6.27 (1H, tq J 13, 11, and 1.5 Hz, 3-H); m/z 224 (m^+), 225 ($m^+ + 1$), 155, 151, 137, and 124, (Found: M^+ 224.2146. Calc. for $C_{15}H_{28}O$, 224.2140).

Preparation of 4,5-Epoxy-5-hydroxymethyl-tetradec-2-ene (59)

To a solution of the diene alcohol (52) (1.97g, 8.8 mmol) and vanadyl acetoacetate (150 mg) in benzene (50 ml) under reflux was added a solution of t -butyl hydroperoxide in benzene (5.0 ml, 3.5M, 17.6 mmol). After 0.1h the reaction was cooled, filtered through a short Florisil column (200-300 mesh), the filtrate concentrated and purified by flash chromatography or distillation to afford *4,5-epoxy-5-hydroxymethyl-tetradec-2-ene* (59) (1.85g, 88%), b.p. 190-195°C, 0.05 mmHg (Found: C, 74.76; H, 11.96. $C_{15}H_{28}O_2$ requires C, 74.95; H, 11.74%); $\nu_{\max}$ (neat) 3420s, 3020s, 2950s, 2920s, 2850s, 1660w, 1450m, 1435m, and 1370m cm^{-1} ; δ_H (250 MHz; $CDCl_3$) 0.88 (3H, t, J 6.0 Hz, 13-Me), 1.28 (16H, s), 1.78 (3H, dd, J 6.0 and 2.0 Hz, 2-Me), 1.88 (1H, br s, OH), 3.50 (1H, d, J 8.0 Hz, 4-H), 3.58 - 3.85 (2H, m, 5-CH₂), 6.38 (1H, qdd, J 15.0, 8.0, and 1.5 Hz, 3-H), and 6.79 (1H, dq, J 15.0, and 6.3 Hz, 2-H); m/z 240 (m^+), 209 ($m^+ - CH_2OH$), 155 (209-MeCH), 127 (C_9H_{19}), 95, 71, and 68, (Found: M^+ 240.2088. Calc. for $C_{15}H_{28}O_2$, 240.2089).

Preparation of 5-Benzyloxymethyl-4,5-epoxy-tetradec-2-ene (60)

To a stirred suspension of sodium hydride (142 mg, 3.0 mmol) in THF (30 ml) under argon was added the epoxyalcohol (59) (450 mg, 1.88 mmol). After 1h 1 drop of DMSO was added followed by redistilled benzylbromide (0.22 ml, 1.8 mmol). When tlc showed no further reaction, the mixture was diluted with petrol, filtered, the filtrate concentrated and purified by flash chromatography to afford 5-benzyloxymethyl-4,5-epoxy-tetradec-2-ene (60) (298 mg, 48%), b.p. 100°C, 0.01 mmHg; $\nu_{\max}$ (neat) 3090w, 3060w, 3030m, 2950s, 2920s, 2850s, 1660w, 1495m, 1450s, and 1375m cm^{-1} ; δ_{H} (250 MHz; CDCl_3) 0.88 (3H, t, J 7.0 Hz, 13-Me), 1.24 (16H, s), 1.77 (3H, dd, J 7.0 and 1.5 Hz, 2-Me), 3.30 (1H, d, J 7.9 Hz, 4-H), 3.47 (1H, d, J_{AB} 8.0 Hz, 5-CH), 3.63 (1H, d, J_{AB} 8.0 Hz, 5-CH), 4.53 (1H, d, J_{AB} 11.9 Hz, Ph-CH), 4.58 (1H, d, J_{AB} 11.9 Hz, Ph-CH), 5.36 (1H, ddq, J 14.7, 8.0, and 1.5 Hz, 3-H), 5.94 (1H, dq, J 14.7 Hz and 6.6 Hz, 2-H), and 7.34 (5H, s, aromatics); m/z 331 ($m^+ + 1$), 302 ($m^+ - \text{CO}$), 259, 249, and 209 (Found: M^+ 330.2572. Calc. for $\text{C}_{22}\text{H}_{34}\text{O}_2$, 330.2559).

Preparation of π -allyl-2,3,4- η^3 -(5-formyloxy-5-benzyloxymethyl-tetradec-3-en-4-ylato)tricarbonyliron (51)

A solution of the epoxide (60) (89 mg, 0.27 mmol) and pentacarbonyl iron (2 ml) in degassed benzene (300 ml) was irradiated for 9 min, concentrated and purified by flash chromatography to afford π -allyl-2,3,4- η^3 -(5-formyloxy-5-benzyloxymethyl-tetradec-3-en-4-ylato)tricarbonyliron (51) (56 mg, 37%) as a mixture of isomers at C-5 separable by chromatography. Isomer 1, m.p. 79-80°C (Found: C, 62.37; H, 6.87. $\text{C}_{26}\text{H}_{34}\text{O}_6\text{Fe}$ requires C, 62.60; H, 6.88%); $\nu_{\max}$ (benzene) 2910s, 2880m, 2850s, 2070s, 2000s, 1920m, 1675s, 1500w, 1440w, and 1370w cm^{-1} ; m/z 414 ($m^+ - 3\text{CO}$). Isomer 2, m.p. 81-82°C (Found C, 62.37; H, 6.87. $\text{C}_{26}\text{H}_{34}\text{O}_6\text{Fe}$ requires C, 62.60; H, 6.88%); $\nu_{\max}$ (benzene) 2900s, 2880s, 2850s, 2070s, 2000s, 1920m, 1672s, 1440w, and 1380w cm^{-1} ; δ_{H} (250 MHz; benzene- d_6) 0.52 (3H, t, J 6.7 Hz, 13-Me), 0.70 (3H, d, J 5.0 Hz, 2-Me), 0.8 - 1.6 (16H, m), 2.60 (1H, d, J_{AB} 9.2 Hz, 5-CH), 2.99 (1H, d, J_{AB} 9.2 Hz, 5-CH), 3.35 (2H, m, 2-H and 4-H), 3.56 (1H, d, J 6.7 Hz, 3-H), 3.77 (1H, d, J_{AB} 11.7 Hz, CHPh), 3.94 (1H, d, J_{AB} 11.7 Hz, CHPh), and 6.75 (5H, s, Ph); m/e 414 ($m^+ - 3\text{CO}$).

Preparation of π -Allyl-2,3,4- η^3 -(5-formyloxy-5-hydroxymethyl-tetradec-3-en-4-ylato)tricarbonyliron (61)

To a stirred solution of the epoxy alcohol (59) (100 mg, 0.47 mmol) in THF (20 ml) was added nonacarbonyldiiron (227 mg, 0.63 mmol). After 0.5h the mixture was concentrated and purified by flash chromatography and recrystallisation to afford π -allyl-2,3,4- η^3 -(5-formyloxy-5-hydroxymethyl-tetradec-3-en-4-ylato)tricarbonyliron (61) (136 mg, 71%) as a mixture of isomers at C-10, m.p. 95-99°C (Found: C, 55.54; H, 6.94.

$C_{19}H_{28}O_6Fe$ requires C, 55.90; H, 6.91%); $\nu_{\max}$ (CDCl₃) 2960s, 2940s, 2875s, 2860s, 2090s, 2030s, 1655s, 1450m, 1410w, 1400w, and 1370m cm⁻¹; δ_H (250 MHz; CDCl₃) 0.87 (3H, t, J 7.6 Hz, 13-Me), 1.15 - 1.80 (16H, m), 1.56 (1H, br s, OH), 1.87 (3H, d, J 6.3 Hz, 2-Me), 3.56 (1H, d, J_{AB} 7.5 Hz, 5-CH_{endo}), 3.61 (1H, d, J_{AB} 7.5 Hz, 5-CH_{endo}), 3.64 (1H, d, J_{AB} 5.0 Hz, 5-CH_{exo}), 3.68 (1H, d, J_{AB} 5.0 Hz, 5-CH_{exo}), 4.10 (1H, dq, J 11.9, and 6.4 Hz, 2-H), 4.58 (1H, d, J 7.6 Hz, 4-H), and 4.67 (1H, dd, J 11.9 and 7.6 Hz, 3-H); m/e 287, 265, and 263 (m^+ -Fe(CO)₃CH₂OH).

Preparation of 2-Methyl-5-hydroxymethyl-5-nonadecyl-3-penten-5-olide (62)

A solution of the complex (61) (450 mg, 0.11 mmol) in degassed benzene (50 ml) was heated to 90°C for 24h under 300 atm of carbon monoxide, cooled, concentrated and purified by flash chromatography to afford 2-methyl-5-hydroxymethyl-5-nonadecyl-3-penten-5-olide (62) (219 mg, 74%) as a mixture of diastereoisomers in the ratio of 3:1, separable by flash chromatography. Isomer 1 (least polar), m.p. 48-50°C (Found: C, 71.72; H, 10.86. $C_{16}H_{28}O_3$ requires C, 71.60; H, 10.52%); $\nu_{\max}$ (neat) 3460s, 2920s, 2880s, 1715s, 1685sh, 1455s, 1405w, and 1365m cm⁻¹; δ_H (250 MHz; CDCl₃) 0.85 (3H, t, J 7.4 Hz, 13-Me), 1.15 - 1.80 (17H, m), 1.40 (3H, d, J 7.8 Hz, 2-Me), 2.59 (1H, br s, OH), 3.08 (1H, m, 2-H), 3.59 (2H, m, 5-CH₂), 5.62 (1H, dd, J 10.4 and 2.3 Hz, 4-H), and 5.84 (1H, dd, J 10.4 and 3.3 Hz, 3-H); m/z 268 (m^+), 252 (m^+ -16), 237 (m^+ -CH₂OH), 227, 223, and 209. Isomer 2 (most polar), m.p. 48-51°C (Found: C, 71.36; H, 10.82. $C_{16}H_{28}O_3$ requires C, 71.60, H, 10.52%); $\nu_{\max}$ 3460s, 2920s, 2840s, 1740sh, 1723s, 1680sh, 1450m, and 1370w cm⁻¹; δ_H (250 MHz; CDCl₃) 0.87 (3H, t, J 6.7 Hz, 13-Me), 1.15 - 1.80 (17H, m), 1.41 (3H, d, J 7.8 Hz, 2-Me), 2.25 (1H, br s, OH), 3.10 (1H, m, 2-H), 3.62 (2H, m, 5-CH₂), 5.61 (1H, dd, J 10.1 and 2.5 Hz, 4-H), and 5.68 (1H, dd, J 10.1 and 3.0 Hz, 3-H); m/z 268 (m^+), 237 (m^+ -CH₂OH), 227, 223, and 209.

Preparation of *trans*-2-Methyl-5-hydroxymethyl-5-nonadecylpentan-5-olide (63)

A mixture of the lactone (62) (Isomer 1, least polar) (21 mg, 0.08 mmol) and platinum oxide (7 mg) in dry methanol (3 ml) was stirred under 1 atm of hydrogen until the orange colouration became black. The mixture was filtered, the filtrate concentrated and purified by flash chromatography to afford *trans*-2-methyl-5-hydroxymethyl-5-nonadecylpentan-5-olide (63) (18 mg, 80%) as a clear oil, $\nu_{\max}$ (CDCl₃) 3602m, 3511w, 2929s, 2857s, 1730sh, 1715s, 1461s, and 1378m cm⁻¹; δ_{H} (250 MHz; CDCl₃) 0.87 (3H, t, J 6.7 Hz, 2-Me), 1.27 (19H, br s), 1.50 - 2.20 (4H, m, 3-H₂ and 4-H₂), 2.30 - 2.70 (1H, m, 2-H), and 3.50 (2H, br s, 5-CH₂), identical by ir and nmr to the previously prepared compound.³⁰

Preparation of Malyngolide (38)

A mixture of the lactone (62) (Isomer 2, most polar) (7 mg, 0.02 mmol) and platinum oxide (3 mg) in dry methanol (1 ml) was stirred under 1 atm of hydrogen until the orange colouration became black. The mixture was filtered, the filtrate concentrated and purified by flash chromatography to afford *cis*-2-methyl-5-hydroxymethyl-5-nonadecylpentan-5-olide (38), (5.6 mg, 79%) as a clear oil, $\nu_{\max}$ (CDCl₃) 3601w, 2928s, 2857s, 1730sh, 1720s, 1459m, and 1377w cm⁻¹; δ_{H} (250 MHz; CDCl₃) 0.87 (3H, t, J 6.7 Hz, 2-Me), 1.30 (19H, br s), 1.50 - 2.20 (4H, m, 3-H₂ and 4-H₂), 2.40 (1H, m, 2-H), 3.47 (1H, d, J_{AB} 12.0 Hz, 5-CH), and 3.70 (1H, d, J_{AB} 12.0 Hz, 5-CH), identical by ir and nmr with the natural product.³⁰

Preparation of Ethyl 1,2-tridecanoate (67)

A solution of dodecanaldehyde (5g, 27.2 mmol) and (carbethoxymethylene) triphenylphosphorane (10.4g, 29.9 mmol) in benzene (75 ml) was stirred overnight, concentrated and the residue extracted with petrol (3 x 100 ml). The combined organic extracts were concentrated and distilled to afford *ethyl 1,2-tridecanoate* (67) (6.6g, 96%), b.p. 150°C, 0.25 mmHg (Found: C, 75.32; H, 12.01. $C_{16}H_{30}O_2$ requires C, 75.54, H, 11.85%); $\nu_{\max}$ (neat) 2925s, 2860s, 1722s, 1655m, 1465s, 1360m, and 720w cm^{-1} ; δ_H (60 MHz; $CDCl_3$) 0.6 - 1.8 (24H, m), 2.1 (2H, m, 11- H_2), 4.1 (2H, q, J 7 Hz, 13- CO_2CH_2), 5.7 (1H, dt, J 16 Hz, 1 Hz, 13-H), and 6.6 - 7.2 (1H, m, 12-H); m/z 254 (m^+), 255 (m^++1), 210 (m^+-CO_2), 209 (m^+-HCO_2), 167 ($m^+-CH_2CO_2Et$), 101 (167- CH_2), and 127, (Found: M^+ 254.2242. Calc. for $C_{16}H_{30}O_2$, 254.2246).

Preparation of 2,3-Tetradecen-1-ol (68)

To a stirred solution of the ester (67) (3g, 11.81 mmol) in dichloromethane (40 ml) and hexane (80 ml) at -78°C under argon was added a solution of diisobutylaluminium hydride in toluene (42.5 ml, 1M, 42.5 mmol) and the reaction mixture stirred for 0.6h. To this was added methanol (6 ml), the mixture warmed to room temperature, saturated sodium chloride solution (12 ml) added, the mixture poured into ether (1.2l) and magnesium sulphate (20g) and stirred for 1h. The solution was filtered, the filtrate concentrated and distilled to afford *2,3-tetradecen-1-ol* (68) (2.22g, 89%), b.p. 125°C, 0.25 mmHg (Found: C, 79.13; H, 13.40. $C_{14}H_{28}O$ requires C, 79.18; H, 13.29%); $\nu_{\max}$ (neat) 3300s, 2960s, 2940s, 2880s, 2860s, 1665w, 1460s, 1450s, 1370w, 905s, and 715w cm^{-1} ; δ_H (250 MHz, $CDCl_3$) 0.87 (3H, t, J 6 Hz, 13-Me), 1.23 (18H, s), 1.55 (1H, br s, OH), 2.03 (2H, m, 4- H_2), 4.08 (2H, d, J 5 Hz, 1- H_2), and 5.65 (2H, m, 2-H and 3-H); m/z 212 (m^+), 210, 194 (m^+-H_2O), 165, and 138, (Found: M^+ 212.2145. Calc. for $C_{14}H_{28}O$, 212.2140).

Preparation of 2(S),3(S),2,3-Epoxytetradecanol (69)

To stirred dichloromethane (80 ml) at -23°C under argon was added titanium (IV) isopropoxide (2.8 ml, 9.4 mmol) and (+)-diethyl tartrate (1.6 ml, 9.4 mmol). The mixture was stirred for 5 min, the allyl alcohol (68) (2g, 9.4 mmol) added followed by a solution of t -butyl-

hydroperoxide (4.8 ml, 4M, 18.8 mmol) in dichloromethane and the mixture stirred for 72h at -17°C . Tartaric acid solution (25 ml, 10%) was added, the mixture stirred for 0.5h then for 1h at room temperature. The organic layer was separated, concentrated, dissolved in ether (150 ml) and stirred with sodium hydroxide solution (50 ml) for 0.5h at 0°C . The organic layer was separated, washed with water (3 x 20 ml), brine (1 x 30 ml), dried, concentrated and crystallised from ether to afford *2(S),3(S),2,3-epoxytetradecanol* (69) (1.89g, 88%), m.p. $68-69^{\circ}\text{C}$ (Found: C, 73.63; H, 12.43. $\text{C}_{14}\text{H}_{28}\text{O}_2$ requires C, 73.63; H, 12.36%); $[\alpha]_{\text{D}}^{24} -21.0^{\circ}$ (c 1.57 in CHCl_3); ν_{max} (CDCl_3) 3630s, 3500m, 2960s, 2880s, 1455s, 1385m, 1205m, 920w, and 870w cm^{-1} ; δ_{H} (250 MHz; CDCl_3) 0.88 (3H, t, J 6.25 Hz, 13-Me), 1.27 (18H, s), 1.56 (2H, m, 4-H₂), 2.60 (1H, br s, OH), 2.87 - 3.00 (2H, m, 2-H and 3-H), 3.61 (1H, d, J_{AB} 12.6 Hz, 1-H), and 3.91 (1H, d, J_{AB} 12.6 Hz, 1-H); m/z 197 (m^+ -CH₂OH), 186, and 166, (Found: M^+ -CH₂OH, 197.1902. Calc. for $\text{C}_{13}\text{H}_{25}\text{O}$, 197.1905).

Preparation of 2(R),3(R),2,3-epoxytetradecanol (70)

As for *2(S),3(S),2,3-epoxytetradecanol* (69), using the allyl alcohol (68) (2g, 9.4 mmol) and (-)-diethyl tartrate to afford *2(R),3(R),2,3-epoxytetradecanol* (70) (1.75g, 82%), m.p. $68-69^{\circ}\text{C}$ (Found: C, 73.75; H, 12.62. $\text{C}_{14}\text{H}_{28}\text{O}_2$ requires C, 73.63, H, 12.36%); $[\alpha]_{\text{D}}^{22} +26.4^{\circ}$ (0.95 in CHCl_3), otherwise identical to the *2(S),3(S)-epoxyalcohol*.

Preparation of 2(S),3(S)-2,3-Epoxytetradecanal (71)

To a vigorously stirred suspension of pyridinium dichromate (3.29g, 11.1 mmol) and powdered 3Å molecular sieves³⁴ (8.8g, 2g per mmol) in dichloromethane (40 ml) was added a solution of the epoxyalcohol (69) (1g, 4.38 mmol). When tlc indicated a complete reaction (about 1h) the mixture was diluted with ether (120 ml) and filtered through a pad of silica containing 15% calcium sulphate. The filtrate was concentrated and purified by flash chromatography to afford *2(S),3(S)-2,3-epoxytetradecanal* (71) (0.69g, 70%), m.p. $41-43^{\circ}\text{C}$ (Found: C, 74.06; H, 11.66. $\text{C}_{14}\text{H}_{28}\text{O}$ requires C, 74.29; H, 11.58%); $[\alpha]_{\text{D}}^{22} +47.7^{\circ}$ (2.43 in CHCl_3); ν_{max} 2970s, 2930s, 2860s, 1730s, 1430m, and 1370m cm^{-1} ; δ_{H} (250 MHz; CDCl_3) 1.87 (3H, t, J 6.6 Hz, 13-Me), 1.15 - 1.75 (21H, m), 3.13 (1H, dd, J 6.1 and 1.8 Hz, 2-H), 3.33 (1H, dt, J 6.7 and 1.8 Hz, 3-H), and 9.03 (1H, d, J 6.6 Hz, 1-H); m/z 226 (m^+), 197 (m^+ -CHO), 179, and 149.

Preparation of 2(R),3(R)-2,3-Epoxytetradecanal (72)

As for 2S,3S-2,3-epoxytetradecanal (71), using the epoxyalcohol (70) (70 mg, 0.31 mmol) to afford 2R,3R-2,3-epoxytetradecanal (72) (45 mg, 64%), m.p. 41-43°C (Found C, 74.50; H, 11.83. $C_{14}H_{26}O_2$ requires C, 74.29; H, 11.58%); $[\alpha]_D^{22}$ -50.53° (0.75 in $CHCl_3$), otherwise identical to the 2(S), 3(S)-epoxyaldehyde.

Preparation of Ethyl-1,2-heptenoate (83)

A solution of hexanal (20g, 0.20 mmol) and (carbethoxymethylene)tri-phosphorane (76g, 0.22 mmol) in benzene (500 ml) was stirred overnight, concentrated, and the residue extracted with petrol (3 x 150 ml). The combined organic extracts were concentrated and distilled to afford ethyl-1,2-heptenoate (83) (33.3g, 98%), b.p. 68-69°C, 0.01 mmHg, (Found: C, 70.34; H, 10.78. $C_{10}H_{18}O_2$ requires C, 70.55; H, 10.66%); ν_{max} (neat) 2920s, 2850s, 1715s, 1655m, 1460m, and 1365m cm^{-1} ; δ_H (60 MHz; $CDCl_3$) 0.9 (3H, t, J 8.4 Hz, 6-Me), 1.0 - 1.5 (9H, m), 2.1 (2H, t, J 8.4 Hz, 3-H₂), 4.1 (2H, q, J 8.4, CO_2CH_2-), 5.7 (1H, dt, J 19.2 and 1.9 Hz, 1-H), and 6.9 (1H, dt, J 19.2 and 8.4 Hz, 2-H); m/z 170 (m^+), 141 ($m^+ - Et$), 142 ($m^+ - CO$), and 125 ($m^+ - OEt$).

Preparation of 2,3-Octen-1-ol (84)

To a stirred solution of the ester (83) (5g, 29.4 mmol) in dichloromethane (160 ml) and hexane (200 ml) at -78°C under argon was added a solution of diisobutylaluminium hydride in toluene (106 ml, 1M, 106 mmol) and the reaction stirred for 0.6h. To this was added methanol (10 ml), the mixture warmed to room temperature, saturated sodium chloride solution (20 ml) added, the mixture poured into ether (1.5ℓ) and magnesium sulphate (25g) and stirred for 1h. The solution was filtered, the filtrate concentrated and distilled to afford 2,3-octen-1-ol (84) (3.2g, 85%), b.p. 101°, 0.01 mmHg (Found: C, 74.64; H, 12.78. $C_8H_{16}O$ requires C, 74.94; H, 12.58%); ν_{max} (neat) 3400s, 2920s, 2850s, 1665w, 1465s, and 1375m cm^{-1} ; δ_H (250 MHz; $CDCl_3$) 0.88 (3H, t, J 6.3 Hz, 7-Me), 1.20 - 1.45 (8H, m), 1.90 (1H, br s, OH), 2.03 (2H, m, 4-H₂), 4.07 (2H, d, J 5.4 Hz, 1-H₂), and 5.55 (2H, m, 2-H and 3-H); m/z 128 (m^+), 110 ($m^+ - H_2O$), and 99 ($m^+ - CHO$).

Preparation of 2(R),3(R)-2,3-Epoxyoctanol (85)

To stirred dichloromethane (200 ml) at -23° under argon was added titanium (IV) isopropoxide (7 ml, 23.4 mmol) and (-)-diethyl tartrate (4 ml, 23.4 mmol). The mixture was stirred for 5 min, the allyl alcohol (84) (3g, 23.4 mmol) added followed by a solution of t -butylhydroperoxide (12 ml, 4M, 48 mmol) in dichloromethane and the mixture stirred overnight at -23°C . Tartaric acid solution (60 ml, 10%) was added, the mixture stirred for 0.5h, then for 1h at room temperature. The organic layer was separated, concentrated, dissolved in ether (250 ml) and stirred with sodium hydroxide solution (125 ml) for 0.5h at 0°C . The organic layer was separated, washed with water (3 x 20 ml), brine (1 x 30 ml), dried, concentrated and crystallised from ether to afford 2(R),3(R)-2,3-epoxyoctanol (85) (2.33g, 69%), m.p. $23-25^{\circ}\text{C}$ (Found: C, 66.49; H, 11.23. $\text{C}_8\text{H}_{16}\text{O}_2$ requires C, 66.63; H, 11.18%). $[\alpha]_{\text{D}}^{23} 28.4^{\circ}$ (1.05 in CHCl_3); ν_{max} (neat) 3300m, 2920s, 2840m, 1730w, 1450m, 1400w, and 1360w cm^{-1} ; δ_{H} (250 MHz; CDCl_3) 0.90 (3H, t, J 6.5 Hz, 7-Me), 1.20 - 1.70 (8H, m), 1.85 (1H, m, br t, J 7.0 Hz, OH), 2.95 (2H, m, 2-H and 3-H), 3.44 (1H, m, 1-H), and 3.92 (1H, m, 1-H); m/z 143, 101 and 83.

Preparation of 2(R),3(R)-2,3-Epoxyoctanal (86)

To a vigorously stirred suspension of pyridinium dichromate (5.62 mg, 1.9 mmol) and powdered 3Å molecular sieves (1.5g, 2g per mmol) in dichloromethane (7 ml) was added a solution of the epoxyalcohol (85) (110 mg, 0.76 mmol). When tlc indicated a complete reaction (about 1h) the mixture was diluted with ether (20 ml) and filtered through a pad of silica containing 15% calcium sulphate. The filtrate was concentrated and purified by flash chromatography to afford 2(R),3(R)-2,3-epoxyoctanal (86) (77 mg, 70%), m.p. $53-55^{\circ}\text{C}$ (Found: C, 67.38; H, 9.59. $\text{C}_8\text{H}_{14}\text{O}$ requires C, 67.57; H, 9.62%); $[\alpha]_{\text{D}}^{22} -40.7^{\circ}$ (1.05 in CHCl_3); ν_{max} (neat) 2920s, 2850s, 2815w, 1725sh, 1715s, 1685m, 1470(m), 1430(m), and 1375 cm^{-1} ; δ_{H} (250 MHz; CDCl_3) 0.90 (3H, t, J 6.3 Hz, 7-Me), 1.20 - 1.75 (8H, m), 3.16 (1H, dd, J 6.25 and 2.2 Hz, 2-H), 3.25 (1H, dt, J 15.6 and 2.2 Hz, 3-H), and 9.02 (1H, d, J 6.3 Hz, 1-H); m/z 125 ($\text{m}^+ - \text{OH}$), 113 ($\text{m}^+ - \text{CHO}$), 95 ($\text{m}^+ - \text{OCH}_2\text{OH}$), 83, and 71.

General Method for Amine Insertion

A solution of the tricarbonyliron lactone complex (1 eq) and the amine (2-10 eq) in THF (10 ml per mmol of iron complex) were stirred with $\text{ZnCl}_2 \cdot \text{TMEDA}$ complex (2 eq) until tlc indicated a complete reaction (0.5 - 2h). The mixture was filtered, the filtrate concentrated and purified by flash chromatography and recrystallisation from ether/petrol mixtures to afford the tricarbonyliron lactam complex.

Preparation of π -Allyl-2,3,4- η^3 -[1-(formyl(benzyl)-amino)-3-methylbut-3-en-2-ylato]tricarbonyliron (87)

The lactone complex (16) (100 mg, 0.4 mmol), benzylamine (510 mg, 4.7 mmol) and $\text{ZnCl}_2 \cdot \text{TMEDA}$ complex (202 mg, 0.8 mmol) in THF (40 ml) treated as above afforded π -allyl-2,3,4- η^3 -[1-(formyl(benzyl)-amino)-3-methylbut-3-en-2-ylato]tricarbonyliron (87) (128 mg, 95%) identical by ^1H nmr and ir to the previously prepared compound.⁵

Preparation of π -Allyl-2,3,4- η^3 -[1-(formyl(benzyl)-amino)-2,3-dimethylbut-3-en-2-ylato]tricarbonyliron (88)

The lactone complex (13) (1g, 3.7 mmol), benzylamine (8g, 7.7 mmol) and $\text{ZnCl}_2 \cdot \text{TMEDA}$ (1.85g, 7.4 mmol) in THF (40 ml) treated as above afforded π -allyl-2,3,4- η^3 -[1-(formyl(benzyl)-amino)-2,3-dimethylbut-3-en-2-ylato]tricarbonyliron (88) (1g, 75%) identical by ^1H nmr and ir to the previously prepared compound.⁵

Preparation of π -Allyl-2,3,4- η^3 -[1-(formyl((R)- α -methylbenzyl)amino)-2,3-dimethylbut-3-en-2-ylato]tricarbonyliron (89)

The lactone complex (13) (500 mg, 1.9 mmol), (R)- α -methylbenzylamine (920 mg, 7.63 mmol) and $\text{ZnCl}_2 \cdot \text{TMEDA}$ complex (950 mg, 3.8 mmol) in THF (20 ml) treated as above afforded π -allyl-2,3,4- η^3 -[1-(formyl((R)- α -methylbenzyl)amino)-2,3-dimethylbut-3-en-2-ylato]tricarbonyliron (89) (514 mg, 73%) as a mixture of diastereoisomers, m.p. 86-88°C (decomp) (Found: C, 58.81; H, 5.19; N, 3.79. $\text{C}_{19}\text{H}_{18}\text{O}_4\text{NFe}$ requires C, 58.56; H, 5.19; N, 3.79%); ν_{max} (CDCl_3) 2978m, 2901m, 2070s, 2010s, 1561s, 1421m, 1379m, and 1171s cm^{-1} ; δ_{H} (250 MHz; CDCl_3) 1.30 and 1.43 (3H, d, J 7.1 Hz, N-CHMe), 1.78 and 1.88 (3H, s, 2-Me), 2.00 and 2.05 (3H, s,

3-Me), 2.31 and 2.47 (1H, d, J 1.8 Hz, 4-H_{endo}), 2.84 and 2.86 (1H, d, J 10.7 Hz, 1-H_{exo}), 3.10 and 3.20 (1H, d, J 10.7 Hz, 1-H_{endo}), 3.38 and 3.49 (1H, d, J 1.8 Hz, 4-H_{exo}), 5.52 and 5.89 (1H, q, J 7.1 Hz, N-CH), and 7.10 - 7.40 (5H, m, aromatics); m/z 341 (m^+ -CO), 313 (m^+ -2CO), and 285 (m^+ -3CO).

Preparation of π -Allyl-2,3,4- η^3 -[1-(formyl(benzyl)amino)-4-phenylbut-3-en-2-ylato]tricarbonyliron (90)

The lactone complex (14) (202 mg, 0.64 mmol), and benzylamine (278 mg, 2.6 mmol) in THF (10 ml) (without $ZnCl_2$.TMEDA complex) treated as above afforded π -allyl-2,3,4- η^3 -[1-(formyl(benzyl)amino)-4-phenylbut-3-en-2-ylato]tricarbonyliron (90) (145 mg, 56%), m.p. 117-121°C (Found: C, 62.35; H, 3.78; N, 3.88. $C_{21}H_{17}O_4NFe$ requires C, 62.55; H, 4.25; and N, 3.97%); ν_{max} ($CDCl_3$) 2980w, 2860w, 2080s, 2000s, 1990s, 1580s, and 1410w cm^{-1} ; δ_H (250 MHz; $CDCl_3$) 3.21 (1H, d, J 12.0 Hz, 1-H_{endo}), 3.38 (1H, dd, J 12.0 and 5.5 Hz, 1-H_{exo}), 4.32 (2H, s, Ph-CH₂), 4.33 (1H, m, 2-H), 4.58 (1H, d, J 12.4 Hz, 4-H), 5.49 (1H, dd, J 12.5 and 7.5 Hz, 3-H), and 7.16 - 7.40 (10H, m, aromatics); m/z 375 (m^+ -CO), 319, and 291.

Preparation of 1-Benzyl-6-dihydro-3-hydro-3-phenyl-2-pyridone (92)

Using the general method for carbonylation, the lactam complex (90) (142 mg, 0.35 mmol) afforded 1-Benzyl-6-dihydro-3-hydro-3-phenyl-2-pyridone (92) (51 mg, 55%) as an oil; ν_{max} ($CDCl_3$) 3068m, 3033m, 2931s, 1661s, 1601m, 1494m, 1447m, and 1387s cm^{-1} ; δ_H (60 Hz; $CDCl_3$) 2.1 - 2.3 (2H, m, 6-H₂), 3.3 (1H, m, 3-H), 4.3 (2H, s, N-CH₂), 5.6 (2H, m, 4-H and 5-H), and 6.85 (10H, m, aromatics); m/z 263 (m^+), 172 (m^+ -CH₂Ph), and 146.

Preparation of 1-Benzyl-3,6-dihydro-4,5-dimethyl-2-pyridone (93)

Using the general method for carbonylation, the lactam complex (88) (347 mg, 0.98 mmol) afforded 1-benzyl-3,6-dihydro-4,5-dimethyl-2-pyridone (93) (152 mg, 72%) as an oil; ν_{max} (neat) 3031w, 2967s, 2918s, 1665s, 1619m, 1438w, and 1388m cm^{-1} ; δ_H (60 MHz; $CDCl_3$) 1.70 (6H, s, 4-Me and 5-Me), 3.03 (2H, br s, 6-H₂), 3.73 (2H, br s, 3-H₂), 4.73 (2H,

s, N-CH₂), and 7.18 - 7.35 (5H, m, aromatics); m/z 215 (m^+), 200 (m^+ -Me), and 91 (PhCH₂).

General Method for Preparation of Ureas

A solution of the amine (1 eq) and nonacarbonyl diiron (1.1 eq) was stirred in THF (15 ml per mmol of amine) until tlc indicated a complete reaction (1-4 days). The mixture was concentrated and purified by flash chromatography to give the urea.

Preparation of Dibenzyl Urea (98)

Benzylamine (0.45 ml, 4.12 mmol) and nonacarbonyl diiron (1.6g, 4.5 mmol) in THF (50 ml) treated as above afforded *dibenzyl urea* (98) (550 mg, 83%), m.p. 170-171°C, (Found: C, 74.85; H, 6.71; N, 11.63. C₁₅H₁₆N₂O requires C, 74.97; H, 6.71 and N, 11.66%); $\nu_{\max}$ (CDCl₃) 3446m, 2951m, 1742m, 1669s, 1528s, 1488m, and 1380m cm⁻¹; δ_H (60 MHz; CDCl₃) 3.9 - 4.5 (6H, m) and 7.1 (10H, s, aromatics); m/z 240 (m^+), 149 (m^+ -CH₂Ph), 106 (PhCH₂NH), and 91 (PhCH₂).

Preparation of (R)-Di-(α -methylbenzyl)urea (99)

(R)-(α)-Methylbenzylamine (0.5g, 4.13 mmol) and nonacarbonyl diiron (1.6g, 4.5 mmol) in THF (50 ml) treated as above afforded (*R*)-*Di-(α -methylbenzyl)urea* (99) (442 mg, 81%), m.p. 199-202° (Found: C, 76.02; H, 7.58; N, 10.30. C₁₇H₂₀N₂O requires C, 76.09; H, 7.51; N, 10.44%); $[\alpha]_D^{22}$ -13.4° (0.78; CHCl₃); $\nu_{\max}$ (CDCl₃) 3436m, 2976m, 1749w, 1657s, 1520s, 1450s, and 1375m cm⁻¹; δ_H (250 MHz; CDCl₃) 1.41 (6H, d, J 7.1 Hz, Me), 4.52 (2H, ν d, J 6.0 Hz, NH), 4.77 (2H, m, N-CH), and 7.13 (10H, m, aromatics); m/z 268 (m^+), 163 (m^+ -PhCHMe), 120 (m^+ -PhCHMeNH), and 106 (PhCH₂Me).

Preparation of Dihexadecyl Urea (100)

Hexadecyl amine (1g, 4.17 mmol) and nonacarbonyl diiron (1.7g, 4.6 mmol) in THF (50 ml) treated as above afforded dihexadecyl urea (100) (114 mg, 22%), m.p. ν r.t.; $\nu_{\max}$ (CDCl₃) 3400s, 2927s, 2855s, 1792vw, 1658s, 1512w, 1464s, 1378m, and 929w cm⁻¹; δ_H (60 MHz; CDCl₃) 0.7 - 1.4 (66H

m) and 5.2 (2H, s, NH); m/z 508 (m^+), 283 ($m^+ - C_{16}H_{33}$), and 268 ($m^+ - C_{16}H_{33}NH$).

Preparation of Pyridinetetracarbonyliron (101)

A mixture of nonacarbonyl diiron (1g, 2.75 mmol) and pyridine (0.32 ml, 4.12 mmol) in THF under carbon monoxide was stirred overnight, concentrated and the solid recrystallised from petrol to give *pyridine tetracarbonyliron* (101) (556g, 82%) as an orange solid, m.p. 64.5 - 65.0°C (Found: C, 43.43; H, 1.93; N, 5.53. Calc. for $C_9H_5O_4NFe$ C, 43.77; H, 2.04; N, 5.67%); ν_{max} (CDCl₃) 2334m, 2051s, 1927s, and 1603m cm^{-1} (lit.¹⁶ (hexane) 2942, 1970 and 1943 cm^{-1}); δ_H (60 MHz; CDCl₃) 6.9 - 7.7 (3H, m, 3-H, 4-H and 5-H), and 8.4 - 8.8 (2H, m, 2-H and 6-H); m/z 247 (m^+), 219 ($m^+ - CO$), 191 ($m^+ - 2CO$), 163 ($m^+ - 3CO$), 135 ($m^+ - 4CO$), 79, and 52.

Preparation of π -Allyl-2,3,4- η^3 -(5-formyloxy-5-carboxaldehyde-tetradec-3-en-4-ylato)tricarbonyliron (107)

To a stirred suspension of PDC (87 mg, 0.21 mmol) and powdered 3Å molecular sieves (245 mg, 2g per mmol), in dichloromethane (4 ml) was added the complex (61). After 15h tlc showed complete reaction the mixture was diluted with ether (10 ml) filtered through celite, the filtrate concentrated and purified by flash chromatography to afford π -allyl-2,3,4- η^3 -(5-formyloxy-5-carboxaldehyde-tetradec-3-en-4-ylato)tricarbonyliron as a mixture of isomers at C-5 (107) (17 mg, 20%), (Found: C, 55.94; H, 7.04. $C_{19}H_{26}O_6Fe$ requires C, 56.17; H, 6.48%); ν_{max} (neat) 2929s, 2857s, 2086s, 2043s, 1736m, 1674s, 1455m, 1379m, and 985m cm^{-1} ; δ_H (250 MHz; CDCl₃) 0.87 (3H, t, J 7.4 Hz, 14-Me), 1.23 (16H, m), 1.92 (3H, d, J 5.7 Hz, 2-Me), 4.12 (1H, m, 2-H), 4.60 - 4.75 (2H, m, 3-H, 4-H); 7.35 (1H, s, 5-CHO_{endo}), and 9.48 (1H, s, 5-CHO_{exo}); m/z 378 ($m^+ - CO$), 350 ($m^+ - 2CO$), 349 ($m^+ - CO - CHO$), 321 ($m^+ - 2CO - CHO$), 306, 294, and 278.

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PUBLICATIONS

Fe₂(CO)₉ IN TETRAHYDROFURAN OR UNDER SONOCHEMICAL CONDITIONS AS CONVENIENT PRACTICAL ROUTES TO π -ALLYLTRICARBONYLIRON LACTONE COMPLEXES

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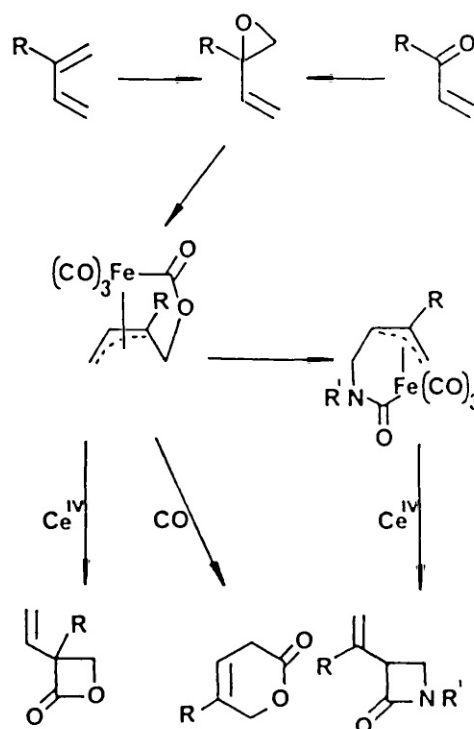
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Abstract:— A series of alkenyl epoxides were converted into their corresponding π -allyltricarbonyliron lactone complexes by either treatment with tetrahydrofuran solutions of Fe₂(CO)₉ at room temperature, or in hydrocarbon solvents with Fe₂(CO)₉ under ultrasonification conditions. The new routes constitute convenient practical alternatives to presently existing methodology.

π -Allyltricarbonyliron lactone complexes have been shown to be useful precursors for the synthesis of lactones and lactams. For example, oxidation of these species with ceric ammonium nitrate leads predominantly to alkenyl substituted β -lactones,¹ whilst exhaustive carbonylation affords δ -lactones.² Treatment of these lactone complexes with amines in the presence of Lewis acids, gives the corresponding lactam complexes by an S_N' like mechanism. These upon oxidation with Ce(IV) provide a novel route to β -lactams,³ a structural unit common to many important antibiotics (Scheme).

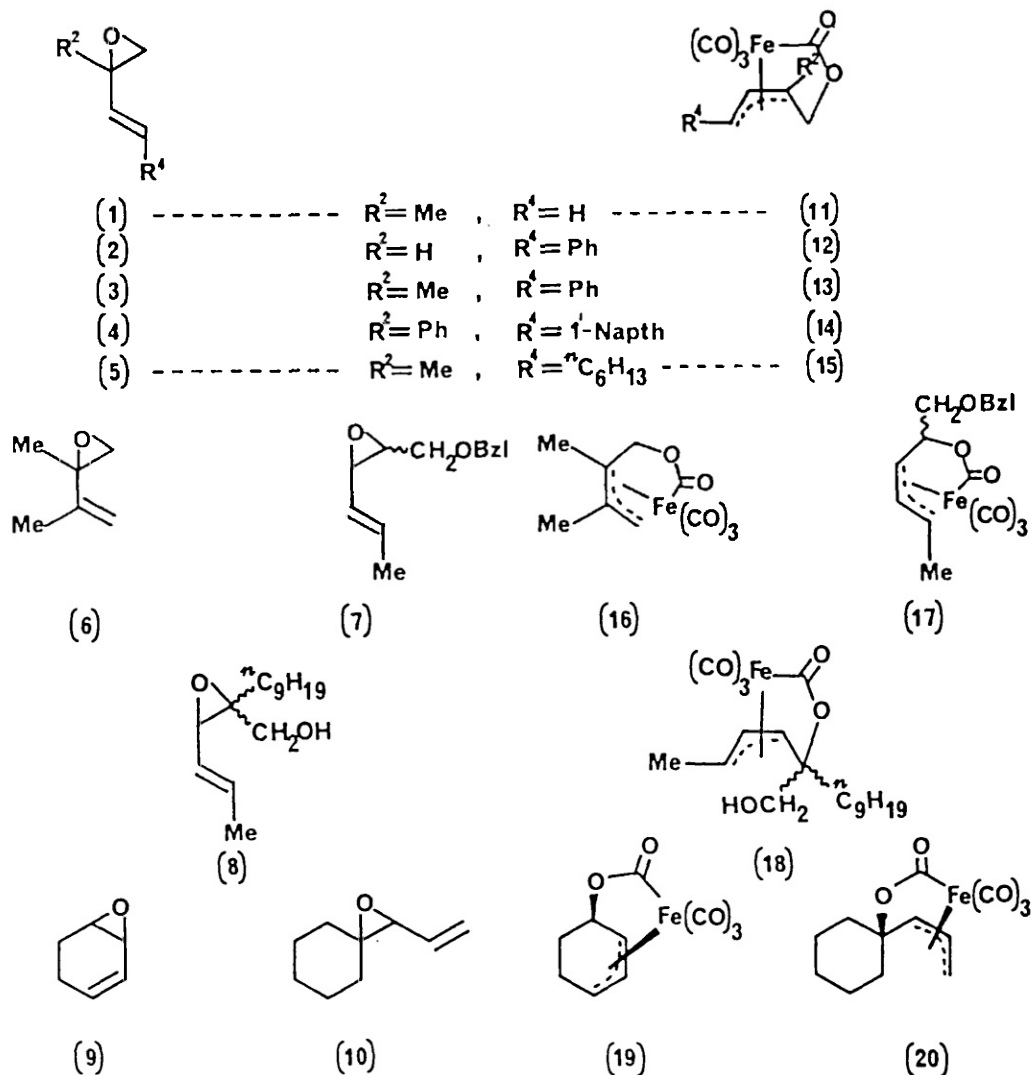
π -Allyltricarbonyliron lactone complexes are prepared by treatment of alkenyl epoxides with coordinatively unsaturated iron carbonyl species, generated under thermal or photochemical conditions.⁴ The thermal reactions however, are not amenable to more sensitive or complex substrates,^{2b} while the photo-

chemical route inevitably involves high dilutions and use of the volatile and toxic pentacarbonyliron, (Fe(CO)₅).



Scheme

1738

A. M. HORTON *et al.*

Alternatively these complexes can be prepared by a less general method and in low yield from 1,4-dihydroxybut-2-enes, 1,4-hydroxyaminobut-2-enes or oxazines.⁵ Clearly these reaction conditions are unsatisfactory for large scale synthesis, therefore new and convenient methods of preparation are required if these complexes are to find more general synthetic use. Here we report upon two new methods which we believe satisfy these criteria.

The first of these involves the use of nonacarbonyl diiron ($\text{Fe}_2(\text{CO})_9$), an orange crystalline and easily handled solid, in tetrahydrofuran solution. Dissolution of $\text{Fe}_2(\text{CO})_9$ in tetrahydrofuran is known⁶ to produce solutions which are thought to contain the carbonyl complex, $\text{Fe}(\text{CO})_4 \cdot \text{THF}$. It is not unreasonable to expect that these solutions would react with alkenyl epoxides to give the corresponding π -allyltricarbonyl-iron lactone complexes. This indeed was found to be the case. The alkenyl epoxides

$\text{Fe}_2(\text{CO})_9$ in tetrahydrofuran or under sonochemical conditions

1739

(1) to (8) were smoothly converted to the iron complexes (11) to (18) in moderate to excellent yields upon reaction at room temperature (Table).

be prepared by a variety of methods involving selective epoxidation of dienes,⁷ methylation of enones or enals using dimethylsulphonium methylide⁸, or from carbonyl

Table: *Reaction of Alkenyl Epoxides with $\text{Fe}_2(\text{CO})_9$.*

Epoxide	Product	Method ^a	Reaction time h	Yield %
(1)	(11)	A	0.75	94 ^d
		B	5	76 ^d
(2)	(12)	A	0.5	100 ^d
		B	0.6	68
(3)	(13)	A	2	64
		B	0.6	63
(4)	(14)	A	2	59
		B	5	65
(5)	(15)	A	0.75	56
		B	1.2	66
(6)	(16)	A	2	42
		B	1	44
(7)	(17)	A	2	34
		B	5	79
(8) ^b	(18)	A	0.5	71
(9) ^c	(19)	B	1.5	34
(10) ^c	(20)	B	1.5	50

a) Method A: $\text{Fe}_2(\text{CO})_9$ in THF; Method B: $\text{Fe}_2(\text{CO})_9$ in benzene or ether under ultrasonification

b) This epoxide failed to react using method B.

c) This epoxide was not studied under method A conditions.

d) Yield based on $\text{Fe}_2(\text{CO})_9$.

During these reactions it was noticed that compounds using arsonium ylides.⁹

the initially red coloured solutions turned green on completion of reaction, presumably due to formation of $\text{Fe}_3(\text{CO})_{12}$. Attempted reaction with $\text{Fe}_3(\text{CO})_{12}$ or $\text{Fe}(\text{CO})_5$ in THF, failed to afford the complexes with alkenyl epoxides. The starting alkenyl epoxides can

The reaction conditions using $\text{Fe}_2(\text{CO})_9$ /THF were satisfactory for most substrates, however a complimentary process was also investigated which would allow reaction at room temperature in hydrocarbon solvents such as benzene, hexane, petroleum ether etc.,

but still using $\text{Fe}_2(\text{CO})_9$ as the convenient source of carbonyliron species. As the alkenyl epoxides failed to react with $\text{Fe}_2(\text{CO})_9$ alone in these solvents (over a period of up to two weeks), we subjected the reaction mixtures to ultrasonification using a Semat 80 Watt, 50 kHz ultrasonic bath. Under these conditions it was now possible to readily convert the alkenyl epoxides (1) - (7) and (9) - (10) to the corresponding complexes (11) - (17) and (19) - (20) in a synthetically acceptable fashion (Table). The use of ultrasonification methods in chemistry is of considerable current interest¹⁰ and reactions of metal carbonyls under these conditions has proved particularly topical.^{11,12}

The reaction is carried out in suba-sealed round bottomed flask immersed in the ultrasonic bath, until disappearance of $\text{Fe}_2(\text{CO})_9$, or t.l.c. indicates the reaction to be complete. The product was isolated by filtration using a 'Celite' pad, followed by chromatography on a silica gel column or recrystallisation. With volatile alkenyl epoxides, it was expedient to use an excess of the epoxide over $\text{Fe}_2(\text{CO})_9$ in order to ensure high yields of complex.

In control reactions, neither $\text{Fe}(\text{CO})_5$ nor $\text{Fe}_3(\text{CO})_{12}$ in hydrocarbon solvents were found to react with alkenyl epoxides under sonochemical conditions. Exposure of $\text{Fe}_2(\text{CO})_9$ alone to ultrasonification gave $\text{Fe}(\text{CO})_5$, precipitated elemental iron and carbon monoxide. Dienes in the presence of $\text{Fe}_2(\text{CO})_9$ failed to afford complexes under similar reaction conditions, though in a

separate experiment, tricarbonyliron diene complexes were shown to be stable to the sonochemical method. On the other hand the π -allyltricarbonyliron lactone complexes were slowly decomposed in benzene solution under prolonged ultrasonification ($\approx 25\%$ decomposition after 18 h).

These results strongly suggest that the conclusions presented by Suslick¹² on related systems are highly debatable, and that alternative pathways could be operating during these sonochemical procedures. Clearly more work is required to properly define possible reactive intermediates and the effect of varying reaction conditions.

Nevertheless, we believe that above procedures constitute practically useful methods for the preparation of π -allyltricarbonyliron lactone complexes, further uses of which will be reported in detail later.

EXPERIMENTAL

Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer 298 spectrometer for solutions in CHCl_3 unless otherwise stated. ^1H NMR spectra were recorded at 60 MHz using a Varian EM 360A, or at 250 MHz using a Bruker WH250 spectrometer, for solutions in deuteriochloroform with tetramethylsilane as internal standard. Mass spectra were obtained using a V.G. Micromass 7070 B spectrometer. Solvents were dried using standard methods. Chromatography was performed on MN-Silica gel 60 (230-400 mesh) under pressure.

General Procedure for the Preparation of π -Allyltricarbonyliron Lactone Complexes using $\text{Fe}_2(\text{CO})_9$ in Tetrahydrofuran. $\text{Fe}_2(\text{CO})_9$ was added to a stirred solution of the alkenyl epoxide in THF. Upon formation of a green solution (or complete dissolution of $\text{Fe}_2(\text{CO})_9$), solvent was removed under reduced pressure. The residue was dissolved in the minimum quantity of benzene and eluted through a short column of silica gel with benzene-ether to afford the pure ferrilactone complex.

2-4-n³-(1-Formyloxy-2-methylbut-3-en-2-ylato)tricarbonyliron (11). To a solution of (1) (2.5g, 0.03mol) in THF (75ml) was added Fe₂(CO)₉ (9.2g, 0.03mol). Work up after 0.75 h as above and elution of the column with 20% ether-benzene gave the complex (11) (7.0g, 94%) m.p. 101°C, identical to the previously prepared compound.^{2a}

2-4-n³-(1-Formyloxy-4-phenylbut-3-en-2-ylato)tricarbonyliron (12). To a solution of (2) (0.29g, 2.0mmol) in THF (30ml) was added Fe₂(CO)₉ (0.62g, 1.7mmol). After 0.5 h, work up in the usual manner and elution of the column with 25% ether-benzene gave the complex (12) (0.53g, 100%), m.p. >120°C (decomp.); IR 2080, 2030, 1665 and 984 cm⁻¹; NMR δ 4.05 (1H, dd, J = 12.5, 5.5 Hz, H-1), 4.17 (1H, dd, J = 12.5, 1.5 Hz, H-1), 4.78 (1H, ddd, J = 7.5, 5.5, 1.5 Hz, H-2), 4.82 (1H, d, J = 12.5 Hz, H-4), 5.62 (1H, dd, J = 12.5, 7.5 Hz, H-3), and 7.28-7.42 (5H, m, Ph) (Found: C, 53.76; H, 3.21%. C₁₄H₁₀FeO₅ requires C, 53.54; H, 3.21%).

2-4-n³-(1-Formyloxy-2-methyl-4-phenylbut-3-en-2-ylato)tricarbonyliron (13). To the epoxide (3) (100mg, 0.62mmol) in THF (20ml) was added Fe₂(CO)₉ (350mg, 0.96mmol). After 2 h, work up as above gave the complex (13) (130mg, 64%), m.p. 150°C; IR 3020, 2920, 2070, 2000, 1710, 1655, 1595, 1440 and 970 cm⁻¹; NMR δ 1.45 (3H, s, Me), 3.38 (1H, d, J_{AB} = 12.4 Hz, H-1), 3.57 (1H, d, J_{AB} = 12.4 Hz, H-1), 4.67 (1H, d, J = 12.4 Hz, H-3), 4.98 (1H, d, J = 12.4 Hz, H-4), and 7.08 (5H, s, Ph) (Found: C, 55.03; H, 3.46%. C₁₅H₁₂O₅Fe requires C, 54.91; H, 3.69%).

2-4-n³-(1-Formyloxy-2-phenyl-4-naphthylbut-3-en-2-ylato)tricarbonyliron (14). To a solution of (4) (100mg, 0.37mmol) in THF (20ml) was added Fe₂(CO)₉ (200mg, 0.56mmol). After 2 h, work up as above gave the complex (14) (96mg, 59%), m.p. 146-90°C (decomp.); IR 3060, 2930, 2080, 2020, 1720, 1690 and 1600 cm⁻¹; NMR δ 4.40 (1H, d, J_{AB} = 10 Hz, H-1), 4.48 (1H, d, J_{AB} = 10 Hz, H-1), 5.12 (1H, d, J = 12 Hz, H-4), 6.35 (1H, d, J = 12 Hz, H-3), 7.25 (5H, s, Ph), and 7.30-8.05 (7H, m, naphthyl).

2-4-n³-(1-Formyloxy-2-methyldec-3-en-2-ylato)tricarbonyliron (15). A solution of (5) (195mg, 1.16mmol) in THF (22ml) with Fe₂(CO)₉ (0.43g, 1.2mmol) was stirred for 0.75 h. Work up as above and elution with 15% ether-benzene gave the complex (15) (211mg, 56%) as an oil, IR 2930, 2860, 2080, 2030, 2010, 1665, 1460, 1385 and 985 cm⁻¹; NMR δ 0.98 (3H, t, J = 6.7 Hz, 10-Me), 1.20-1.78 (9H, m), 1.97 (3H, s, 2-Me), 2.22 (1H, ddd, J = 13.2, 8.4, 4.8 Hz, H-5), 3.75 (1H, ddd, J = 11.9, 8.4, 4.8 Hz, H-4), 3.85 (1H, dd, J = 12.0, 1.1 Hz, H-1), 4.08 (1H, d, J = 12.0 Hz, H-1), and 4.71 (1H, d, J = 11.9 Hz, H-3) (Found: C, 52.05; H, 5.94%. C₁₄H₂₀FeO₅ requires C, 51.87; H, 6.22%).

2-4-n³-(2,3-Dimethyl-1-formyloxybut-3-en-2-ylato)tricarbonyliron (16). To the alkenyl epoxide (6) (50mg, 0.51mmol) in THF (20ml)

was added Fe₂(CO)₉ (278mg, 0.76mmol). Work up as above after 2 h gave the complex (16) (54mg, 42%), m.p. 104°C, identical to the previously prepared compound.¹

2-4-n³-(1-Benzoyloxymethyl-1-formyloxy-pent-3-en-2-ylato)tricarbonyliron (17). To the epoxide (7) (50mg, 0.25mmol) in THF (20ml) was added Fe₂(CO)₉ (135mg, 0.37mmol). After 2 h, work up as above gave the complexes (17) (31mg, 34%) as a mixture of isomers at C-1, m.p. 64-65°C; IR 3020, 2950, 2850, 2070, 2005 and 1667 cm⁻¹; NMR δ 1.83 (3H, d, J = 5.6 Hz, 4-Me), 3.53 (2H, m, CH₂OBN), 4.07 (1H, m, H-4), 4.40 (1H, dd, J = 10.3, 4.5 Hz, H-3), 4.57 (4H, m, PhCH₂, H-2, H-1) and 7.34 (5H, s, Ph) (Found: C, 55.10; H, 4.35%. C₁₇H₁₆FeO₆ requires C, 54.87; H, 4.34%).

Preparation of 2-4-n³-(5-Formyloxy-5-hydroxymethyltetradec-3-en-4-ylato)tricarbonyliron (18). To a solution of (8) (100mg, 0.47mmol) in THF (20ml) was added Fe₂(CO)₉ (227mg, 0.63mmol). After 0.5 h, work up as above gave the complexes (18) as a mixture of isomers at C-5, (100mg, 71%), m.p. 95-99°C; IR 2960, 2940, 2875, 2860, 2090, 2030 and 1655 cm⁻¹; NMR δ 0.87 (3H, br t, J = 7.6 Hz, 15-Me), 1.15-1.80 (17H, m), 1.56 (1H, br s, OH), 1.87 (3H, d, J = 6.4 Hz, 1-Me) 3.64 (2H, m, 6-CH₂) 4.10 (1H, dq, J = 11.9, 6.4 Hz, H-2), 4.58 (1H, d, J = 7.6 Hz, H-4), and 4.67 (1H, dd, J = 11.9, 7.6 Hz, H-3) (Found: C, 55.54; H, 6.94%. C₁₉H₂₈O₆Fe requires C, 55.90; H, 6.91%).

General Procedure for the Preparation of π-Allyltricarbonyliron Lactone Complexes using Ultrasonification. A solution of the alkenyl epoxide in an inert solvent (usually benzene) with Fe₂(CO)₉ was subjected to ultrasonification until dissolution of the iron carbonyl occurred (0.5 - 5 h). Filtration of the mixture through a pad of 'Celite' and removal of the solvent under reduced pressure (taking care not to heat the solution above room temperature), gave a residue which was purified by column chromatography and/or recrystallisation to give the ferrilactone complex.

2-4-n³-(1-Formyloxy-2-methylbut-3-en-2-ylato)tricarbonyliron (11). A solution of isoprene epoxide (1) (2g, 23.6mmol) in benzene (800ml) containing Fe₂(CO)₉ (2.9g, 7.9mmol) was reacted ultrasonically for 5 h. Work up gave the complex (11) (1.5g, 76%) (based on Fe₂(CO)₉) identical in all respects to the previously prepared material. Conducting the reaction on a smaller scale gave an improved (90%) yield.

2-4-n³-(1-Formyloxy-4-phenylbut-3-en-2-ylato)tricarbonyliron (12). The epoxide (2) (0.67g, 4.6mmol) in ether (50ml) containing Fe₂(CO)₉ (1.66g, 4.6mmol) was reacted ultrasonically for 0.6 h. Work up gave the complex (12) (0.98g, 68%) identical to the material prepared above.

2-4-n³-(1-Formyloxy-2-methyl-4-phenylbut-3-en-2-ylato)tricarbonyliron (13). A solution

of the epoxide (3) (100mg, 0.62mmol) in benzene (20ml) containing $\text{Fe}_2(\text{CO})_9$ (350mg, 0.96mmol) was reacted ultrasonically for 0.6 h. Work up gave the complex (13) (128mg, 63%) identical to the material prepared above.

2-4- η^3 -(1-Formyloxy-2-phenyl-4-naphthylbut-3-en-2-ylato)tricarbonyliron (14). A solution of the epoxide (4) (100mg, 0.37mmol) in benzene (20ml) containing $\text{Fe}_2(\text{CO})_9$ (200mg, 0.56mmol) was reacted ultrasonically for 5 h. Work up gave the complex (14) (108mg, 65%), identical to the material prepared above.

2-4- η^3 -(1-Formyloxy-2-methyldec-3-en-2-ylato)tricarbonyliron (15). A solution of the epoxide (5) (131mg, 0.78mmol) in benzene (35ml) containing $\text{Fe}_2(\text{CO})_9$ (0.28g, 0.8mmol) was reacted ultrasonically for 1.2 h. Work up gave the complex (15) (166mg, 66%) identical to that prepared above.

2-4- η^3 -(2,3-Dimethyl-1-formyloxy-but-3-en-2-ylato)tricarbonyliron (16). A solution of the epoxide (6) (150mg, 0.51mmol) in benzene (20ml) containing $\text{Fe}_2(\text{CO})_9$ (278mg, 0.76mmol) was reacted ultrasonically for 1 h. Work up gave the complex (16) (56mg, 44%), identical to that prepared previously.

2-4- η^3 -(1-Benzylloxymethyl-1-formyloxy-pent-3-en-2-ylato)tricarbonyliron (17). A solution of the epoxide (7) (50mg, 0.25mmol) in benzene (20ml) containing $\text{Fe}_2(\text{CO})_9$ (135mg, 0.36mmol) was reacted ultrasonically for 5 h. Work up gave the complex (17) (73mg, 79%) identical to the previously prepared material.

2-4- η^3 -(Cyclohex-3-en-2-ylato)-1-oxycarbonyl-tricarbonyliron (19). The epoxide (9) (438mg, 5.0mmol) in benzene (60ml) with $\text{Fe}_2(\text{CO})_9$ (1.82g, 5.0mmol) was reacted ultrasonically for 1.5 h. Work up gave the complex (19) (448mg, 34%), m.p. 74°C (decomp.) (Lit. ^{30} 80°C); IR 2900, 2100, 1990, 1650, 1460, 1375, 1340, 1325, 1060, 1010, 995 and 975 cm^{-1} ; NMR δ 1.10-1.37 (1H, m), 1.48-1.73 (1H, m); 2.18 (1H, ddd, $J = 18, 11.5, 5.5$ Hz, H-5a), 2.44 (1H, dddd, $J = 18, 6.5, 6.5, 1$ Hz, H-5a), 4.52 (1H, dm, $J = 7$ Hz, H-1), 4.70 (1H, ddd, $J = 6.5, 5.5, 2$ Hz, H-4), 5.44 (1H, dd, $J = 6.5, 6.5$ Hz, H-3), and 5.75 (1H, ddd, $J = 7, 6.5, 2$ Hz, H-2).

2-4- η^3 -Spiro(cyclohexane-1,1'-but-3-en-2-ylato)-1-oxycarbonyl-tricarbonyliron (20). A solution of the epoxide (10) (293mg, 2.2mmol) in benzene (80ml) containing $\text{Fe}_2(\text{CO})_9$ (0.86g, 2.4mmol) was reacted ultrasonically for 1.5 h. Work up gave the complex (20) (333mg, 50%) m.p. 96°C (decomp.) identical to the previously prepared material.¹

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