ABSTRACT

INTRAMOLECULAR TRAPPING OF
CYCLOBUTADIENYLIRON TRICARBONYL
SYSTEMS

By

Taylor Albert Pancoast

Cyclobutadienyliron tricarbonyl complexes with pendent alkyne groups were prepared by treating either bromomethylcyclobutadienyliron tricarbonyl (56a) or 1-bromomethyl-2-methylcyclobutadienyliron tricarbonyl (56b) with the appropriate alkynol and triethylamine, or with the potassium salt of the alkynol. Treatment of (56a) with either potassium 3-pentyn-1-oxide or 3-pentyn-1-ol and triethylamine gave 1-(3-pentynoxymethyl)cyclobutadienyliron tricarbonyl (61) in up to 70% yield. Similar treatment of (56a) with 2-butyn-1-ol or its salt gave 1-(2-butynoxymethyl)cyclobutadienyliron tricarbonyl (79a) in up to 64% yield. Treatment of (56b) with 2-butyn-1-ol or its salt gave 2-methyl-1-(2-butynoxymethyl)cyclobutadienyliron tricarbonyl (79b) in up to 51% yield.

Acetone solutions of these complexes were decomposed by treating them with crystalline ceric ammonium nitrate (Ce IV) in 3.5 molar excess. Decomposition of (61) gave

5-methylisochroman, presumably via the Dewar-benzene system resulting from an intramolecular Diels-Alder reaction. Complexes (79a) and (79b) each gave two products when decomposed. The major products were 4-methylphthalan (82a) and 4,7-dimethylphthalan (82b) respectively. The minor products were 2-methyl-9-oxatricyclo[5.3.$2^{4,7}$.$o^{1,7}$]deca-1,5-dien-3-one (84a) and 2,7-dimethyl-9-oxatricyclo[5.3.$2^{4,7}$.$o^{1,7}$]deca-1,5-dien-3-one (84b) respectively.

When optically active samples of (*79b) were prepared and decomposed, the product (*84b) was found to be optically active also. The optical purity of the product (*84b) was the same as that of the starting complex (*79b).

Formation of the polycyclic products (84a) and (84b) involves insertion of a carbonyl group and must therefore take place on the metal. The finding that optically active product was obtained from the reaction of the cyclobutadiene ligand while it was still on the iron (provided you start with optically active complex) supports earlier conclusions that racemic products obtained from intermolecular trapping of optically active complex must result from a "free" cyclobutadiene intermediate.

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To that of the Spirit in
each of us.

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I wish to express my deep appreciation to Professor Robert H. Grubbs for his guidance and understanding which have helped me immensely both in the laboratory and outside of it.

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The support and strength I received from the people in the East Lansing Friends Meeting and Young Friends of North America made all of this possible.

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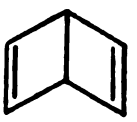
INTRODUCTION

Dewar Benzene

In 1867 Sir James Dewar[1] introduced planar bicyclo-[2.2.0]hexa-2,5-diene (1) as a possible alternative to Kekule's[12] formulation (2) for the structure of benzene.

(1)

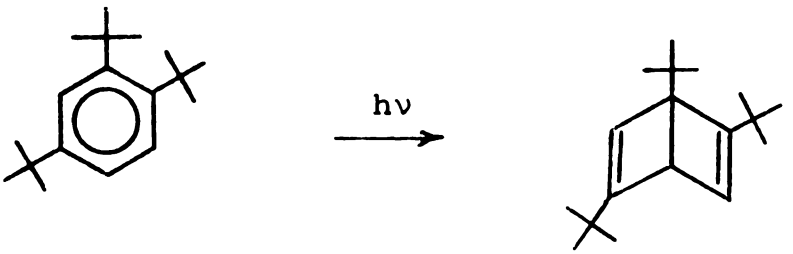
(2)



(3)

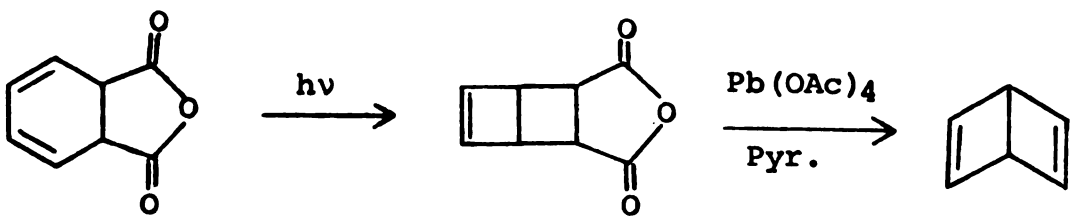
Despite its conceptualization as a minor resonance contributor to the structure of benzene,[3] there have been attempts to detect the Dewar ring system,[4,5] based on the assumption that the non-planar tautomer (3) should have at least a fleeting existence.

In 1961 van Tamelen and Pappas[6] became the first to isolate a derivative of (3) when they obtained 1,2,5-tri-t-butylbicyclo[2.2.0]hexa-2,5-diene (5) from the ultraviolet photolysis of 1,2,4-tri-t-butylbenzene (4).



(4) (5)

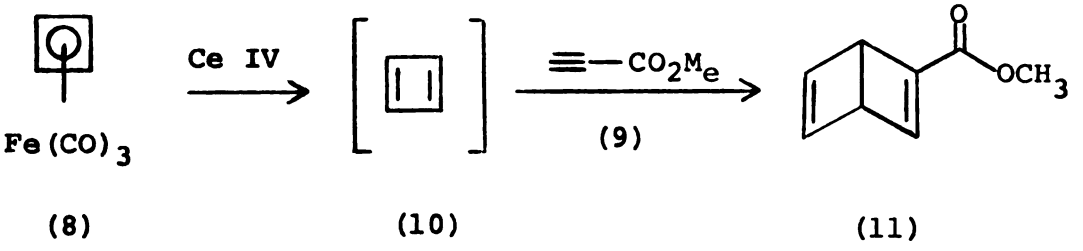
In 1963 these same workers reported making the parent compound (3)[7] by ultraviolet photolysis of cis-1,2-dihydrophthalic anhydride (6) to give bicyclo[2.2.0]hexa-5-ene-2,3-dicarboxylic acid anhydride (7). Treatment of (7) in pyridine solution with lead tetraacetate (43-45° for 20 min.) under partial vacuum gave ca. 20% yield of (3) in



(6) (7) (3)

the pyridine distillate.

Subsequently a number of other derivatives[8-17] have been reported, of which two are of particular interest. In 1965 Pettit et al.[8] reported using an acetylenic compound (9) to trap cyclobutadiene (10) generated by cerium IV oxidation of complex (8) as shown on the following page.



(8) (10) (11)

This method provides a good general route to derivatives of (3). The following year Schäfer[12] synthesized hexamethyl-Dewar-benzene (15) by trimerization of 2-butyne (12) in the presence of aluminum chloride catalyst as shown in Figure 1.

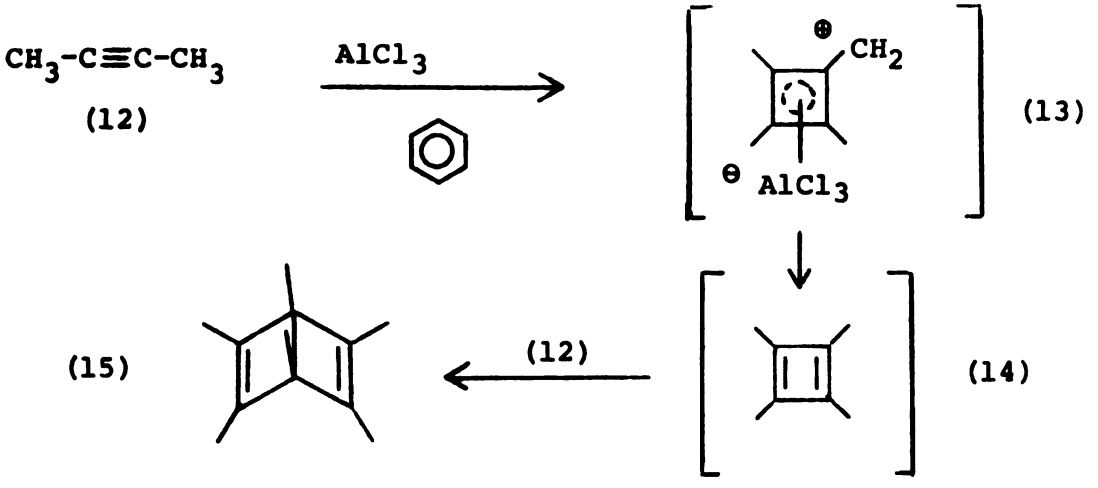


Figure 1. Synthesis of hexamethyl-Dewar-benzene.

This reaction, which is proposed[18] to involve generation of tetramethylcyclobutadiene (14) from complex (13), provided the first technical scale synthesis of a Dewar-benzene derivative, and made (15) available for study in large quantity.

It was initially expected that (3) and its derivatives would be very unstable with respect to the aromatic isomers, and consequently hard to isolate. The Dewar ring system is highly strained, while the benzene to which it goes is especially stable due to aromaticity. Furthermore, no skeletal rearrangement is required to get from the Dewar to the aromatic structure. Experimentally it has been found that (15) is unstable with respect to hexamethylbenzene (16) by ca. 62 Kcal mol^{-1} at room temperature.[12] Experimental values are lacking for the parent molecule, but Haller[19] has calculated that (3) is unstable with respect to (2) by some 66 Kcal mol^{-1}, and Latajka et al.[20] calculate a difference of 81 Kcal mol^{-1}.

Surprisingly it was found that (3) had a half life of 2 days at room temperature,[7] while (15) has a half life of 105 hrs. at 120°,[18] and "can be kept for months in a refrigerator and for a long time even at room temperature."[12] Now it appears that most derivatives of (3) are stable enough to be readily isolable.

The Woodward Hoffman rules[21,22] provide a rationale for this stability. Van Tamelen[23] pointed out in 1965 that the isomerization of (3) to (2) is analogous to the opening of cyclobutene (17) to give butadiene (18). According to Woodward Hoffman rules, a (low-energy) concerted process must go with conrotatory bond rotations in the thermal

opening of (17). The cis and trans isomers give stereospecific products as shown in Figure 2.

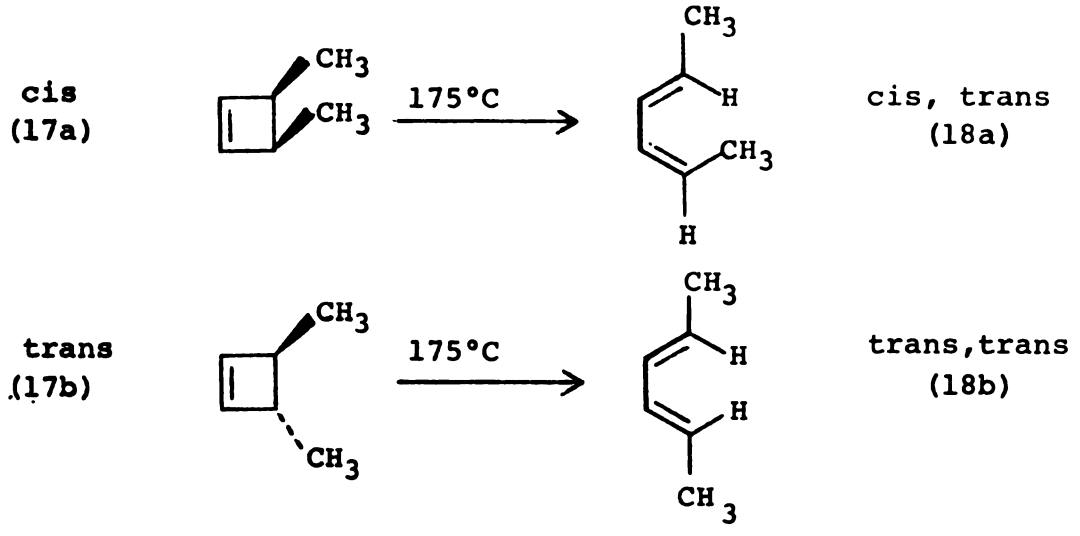
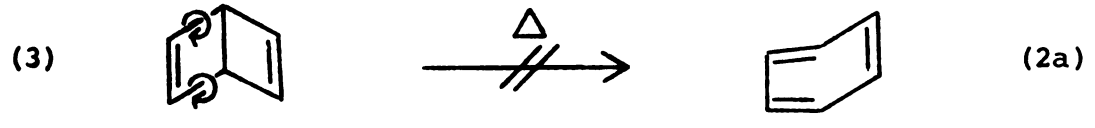


Figure 2. Allowed ring opening products for cyclobutene systems (thermal).

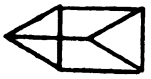
Conrotatory opening of the cyclobutene ring in (3), however, would give an incredibly strained trans double bond (2a).



Consequently the transformation is forced to go by some nonconcerted, higher energy process, such as through a biradical intermediate.[22]

Although derivatives of (3) are more stable than originally expected, they are nonetheless readily aromatized by heat,[8-17] light[8,24,25] and Lewis acids.[18]

Much of their chemistry has involved isomerization to prismane (19),[18,24] benzvalene (20)[24,25] and aromatic isomers by photolysis.



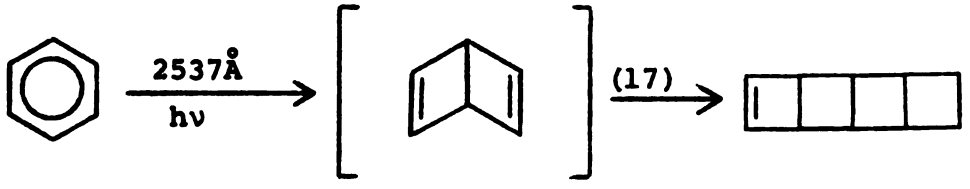
(19)

(20)

Only two compounds, (3) and (15), have received much study using standard reagents.[18,25] These investigations have centered on electrophilic additions to one or both double bonds, which proceed readily with little or no aromatization.

Diels-Alder cyclizations and [2+2] photochemical additions, however, are two potentially interesting classes of reactions which have received relatively little attention.

Srinivasan and Hill[26] reported a [2+2] cycloaddition in which irradiation of a 20 vol % solution of cyclobutene (17) in benzene gave tetracycle (21), presumably through generation of (3) <u>in situ</u> by photolysis of (2) as shown.



(2) (3) (21)

However, Wilzbach and Kaplan[27] subsequently reported obtaining polycycle (23) under similar conditions, using

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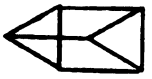

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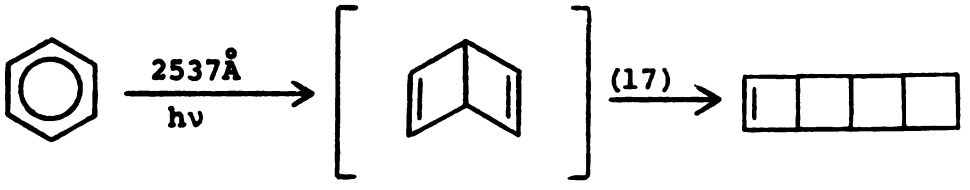
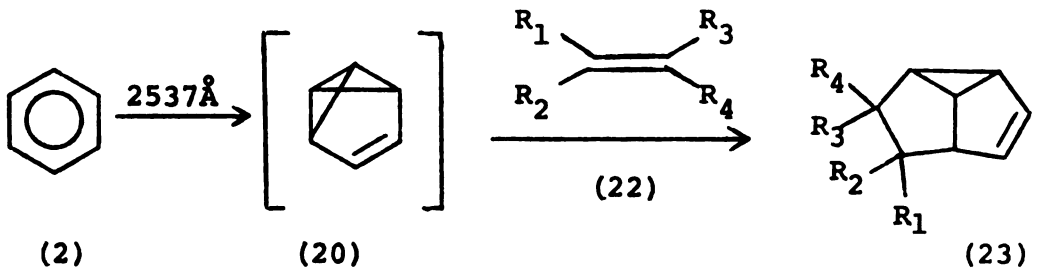


(2) (3) (21)

However, Wilzbach and Kaplan[27] subsequently reported obtaining polycycle (23) under similar conditions, using

cis-2-butene (a), cyclopentene (b) or 2,3-dimethyl-2-butene (c) as the olefin (22) instead of cyclobutene (17). The results indicate reaction with the benzvalene isomer (20), as shown in Figure 3, rather than with (3).

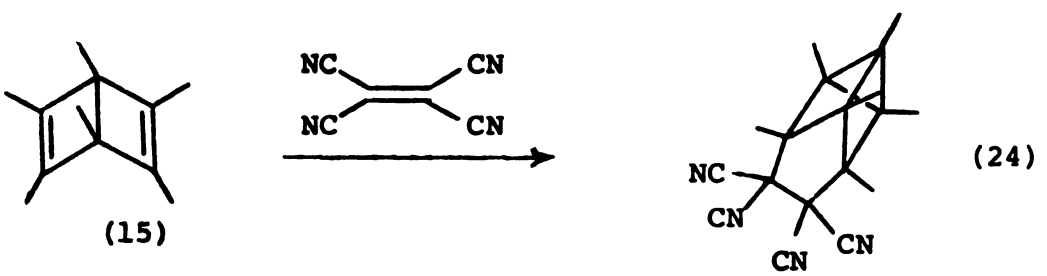


(2) (20) (23)

a) $R_1=R_3=CH_3$; $R_2=R_4=H$
b) $R_1=R_3=H$; $R_2=R_4= -(CH_2)_3-$
c) $R_1=R_2=R_3=R_4=CH_3$

Figure 3. Trapping of benzvalene from the photolysis of benzene.

Schäfer and Hellmann[18] obtained Diels-Alder adduct (24) by reaction of (15) with tetracyanoethylene.



(15) (24)

These examples indicate that the Dewar ring system can participate in cycloaddition reactions. However, the tendency of (3) and its derivatives to isomerize,[8-18,24,25] especially to aromatic systems, under the reaction

conditions of heat or light usually employed for cycloadditions in a serious drawback.

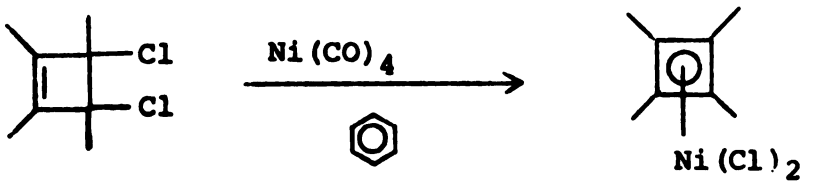
Cyclobutadiene

Cyclobutadiene (10) has long held special interest for chemists, both as the simplest antiaromatic compound, and

(10)

as one of the two possible C_4H_4 isomers.

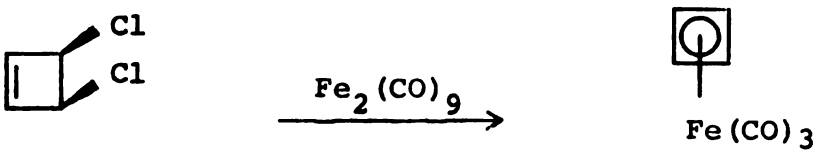
As early as 1956 Longuet-Higgins and Orgel[28] predicted that unstable (10) should be stabilized by complexation with a suitable transition metal. In 1959 Criegee and Schröder[29] obtained 1,2,3,4-tetramethylcyclobutadiene nickel dichloride (26) by treating 1,2,3,4-tetramethyl-3,4-dichlorocyclobutene (25) with nickel tetracarbonyl in benzene.



(25) (26)

The first complex of unsubstituted (10) was prepared by Pettit *et al.*[30] Treatment of *cis*-3,4-cyclobutenedichloride (27) with diiron nonacarbonyl gave a 40% yield of

cyclobutadienyliron tricarbonyl (8).



(27) (8)

Early workers found that (8) could undergo electrophilic aromatic substitution reactions.[31] Then Pettit et al.[8,32] reported that treatment of (8) with ceric ammonium nitrate (CeIV) gave products that would be expected if free cyclobutadiene (10) were present as shown in Figure 4.

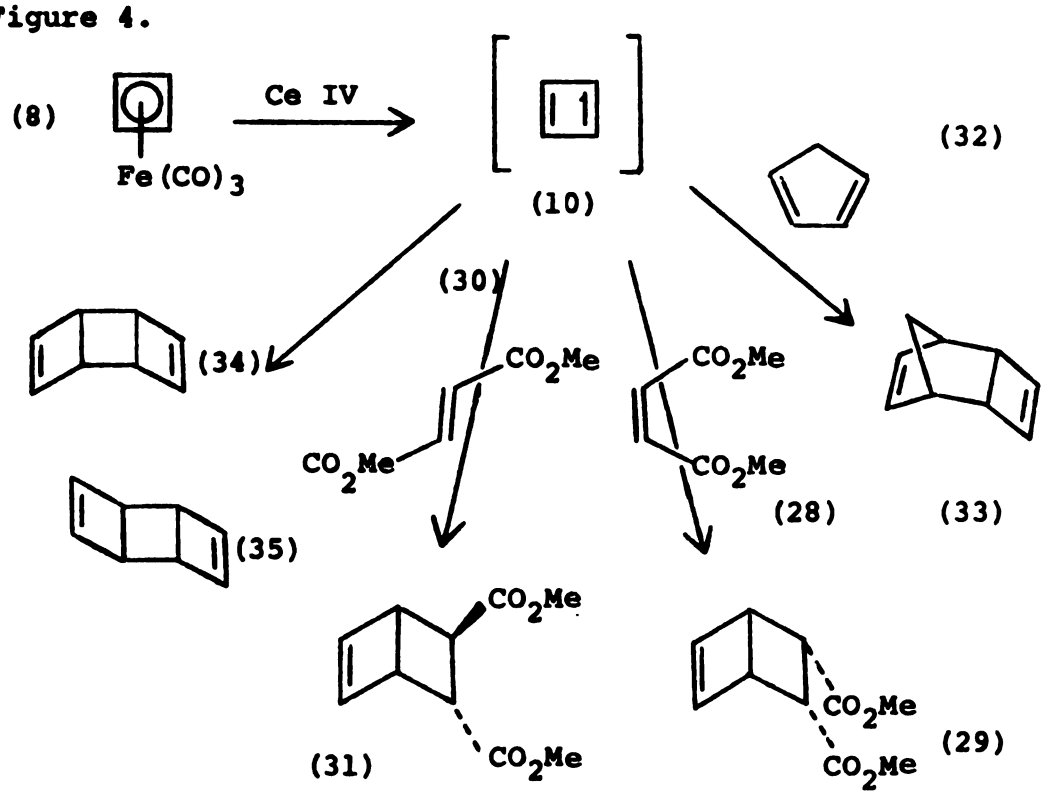
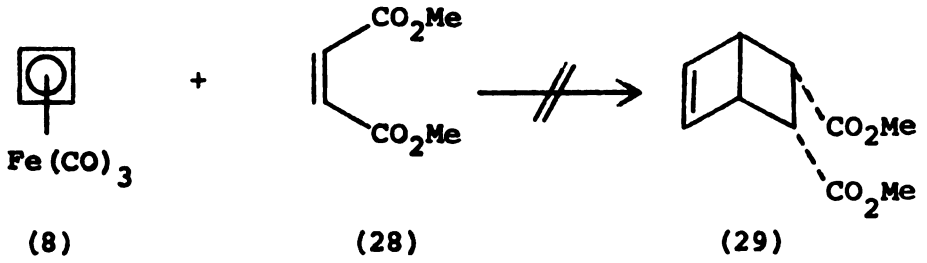


Figure 4. Reactions of cyclobutadiene with trapping reagents.

Oxidation (Ce IV) of (8) in the presence of dimethyl maleate (28) gave endo, cis-dicarbomethoxybicyclohexene (29), while dimethyl fumarate (30) yielded trans-dicarbomethoxybicyclohexene (31). Oxidation of (8) in the presence of cyclopentadiene (32) gave adduct (33), and in the absence of other dienes, dimers (34) and (35) were formed.

These results are consistent with a normal Diels-Alder mechanism, and led Pettit[32] to propose that the reacting species (10) is a singlet in the ground state. This is based on the assumption that (10) is free of the iron when it reacts.

In support of this assumption, Pettit[33] considered four possible alternative reaction pathways shown in Figures 5 through 8. The first possibility (Figure 5), direct reaction of (8) with the dienophile, e.g. (28), is eliminated by the finding that there is no reaction unless an oxidizing agent is present.



(8) (28) (29)

Figure 5. First possible reaction pathway (considered).

A second possibility (Figure 6) is replacement of CO by maleate (28) followed by intramolecular addition to the coordinated cyclobutadiene. Irradiation of (8) in the presence of (28) gives an iron coordinated maleate (36) which can be isolated. Complex (36) is indefinitely stable at 25° and shows no tendency to undergo a Diels-Alder reaction.

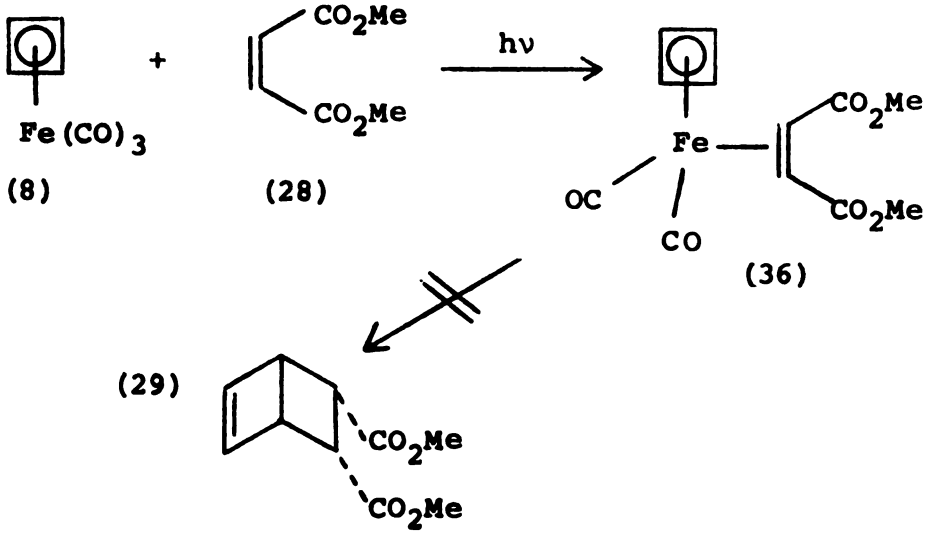


Figure 6. Second possible reaction pathway (considered).

A third possibility (Figure 7) is replacement of a CO by (28), which then adds to the coordinated cyclobutadiene during oxidation. Oxidation of complexes (36) and (37) gives adducts (29) and (31) respectively. However, if the maleate complex (36) is oxidized in the presence of excess free fumarate (30), both (31) and (29) are formed in a

ratio of 25:1. If the fumarate complex (37) is oxidized in the presence of free maleate (28), then (31) and (29) are obtained in a ratio of 50:1.

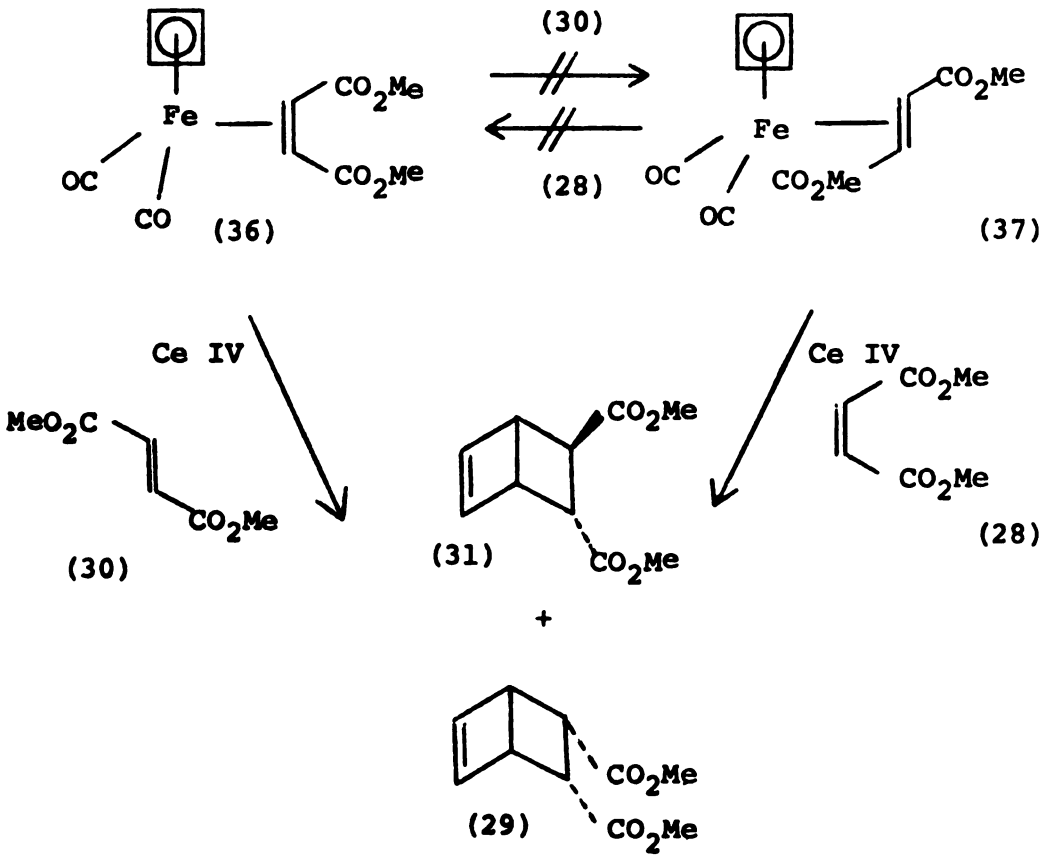


Figure 7. Third possible reaction pathway (considered).

These ratios simply reflect the fact that the more reactive dienophile (fumarate) goes to product faster than the less reactive maleate, regardless of which complex is used.

Since complexes (36) and (37) do not interconvert by ligand exchange, reaction <u>via</u> these complexes is unlikely. The fourth possibility (Figure 8) is external attack by maleate (28) on some oxidized form of (8) in which the cyclobutadiene is still bound to the iron. Decomposition of (8) in the presence of both maleate (28) and diphenylethylene (38) gives only adduct (29). Similarly, in competition between (30) and (38), only adduct (31) is obtained.

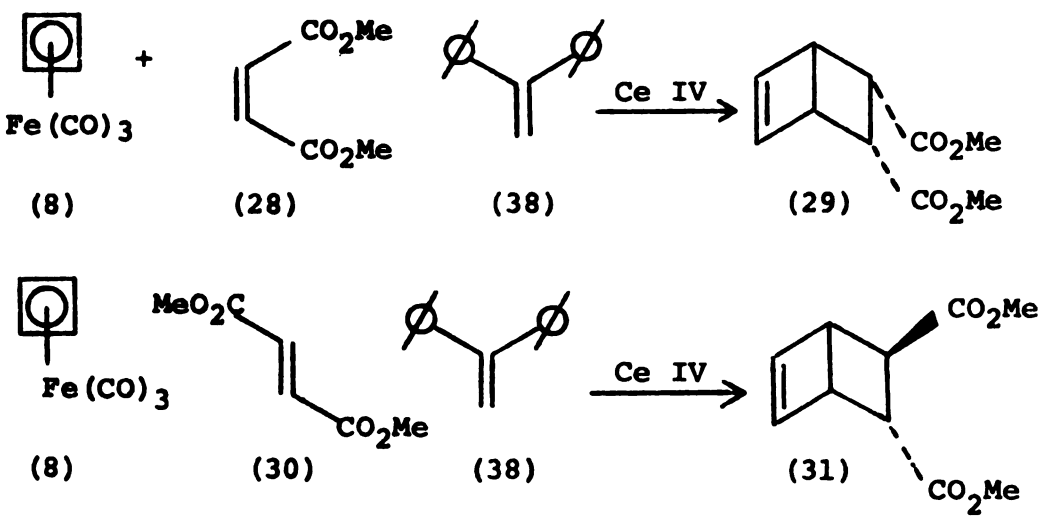


Figure 8. Fourth possible reaction pathway (considered).

Any reactive intermediate in the oxidation process must be either a cation or a cation radical, either of which would be more reactive to diphenylethylene (38) than to maleate or fumarate. The lack of any adduct derived from (38) makes the fourth possibility unlikely.

Following Pettit's work another possible mechanism, shown in Figure 9, was proposed by Grubbs and Grey.[34,35] Complex (8), which is coordinately saturated, could be oxidized to the unsaturated complex (39). Complexation of maleate (28) would give the saturated complex (40), which could then go on to react via intermediates such as (41).

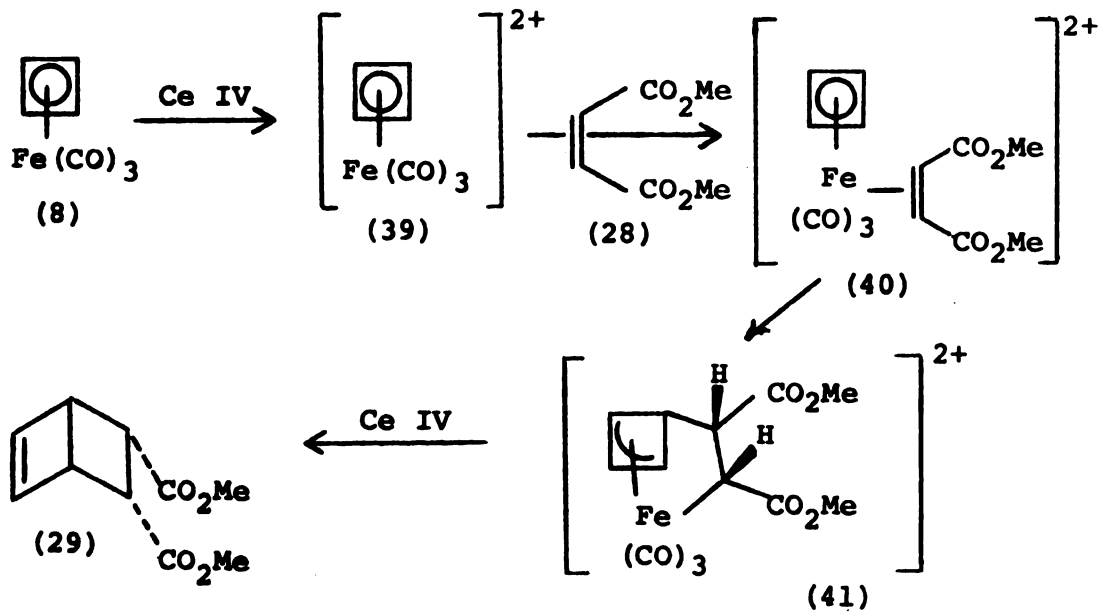
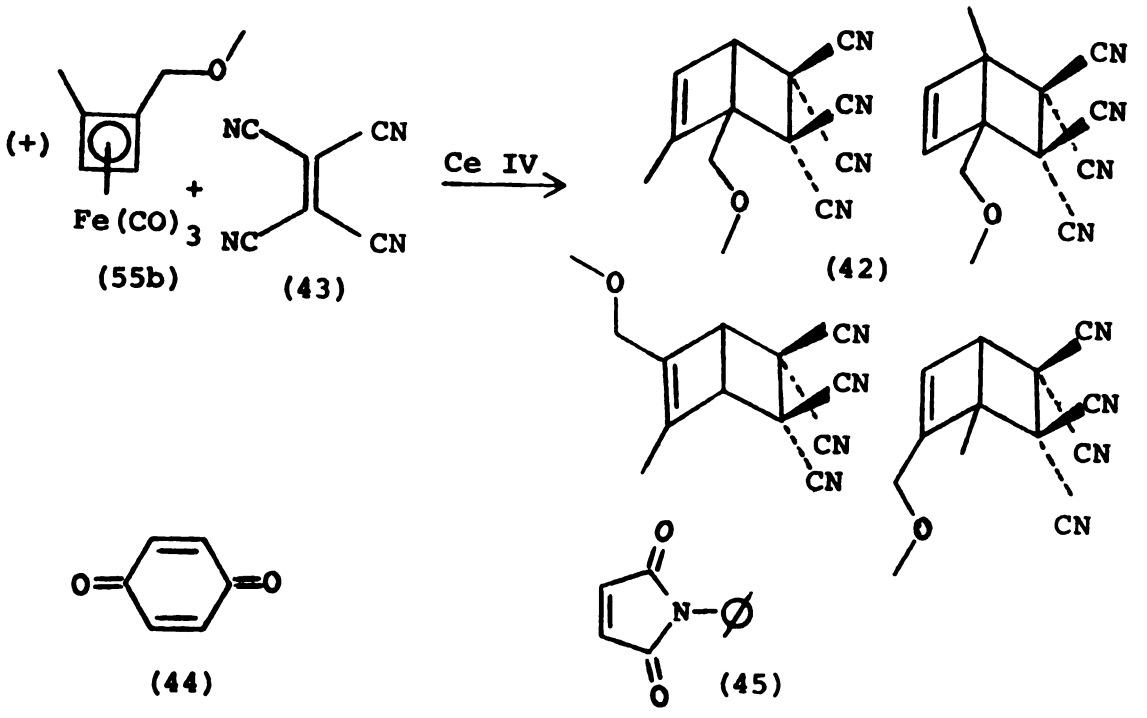


Figure 9. Grubbs's alternate reaction pathway (considered).

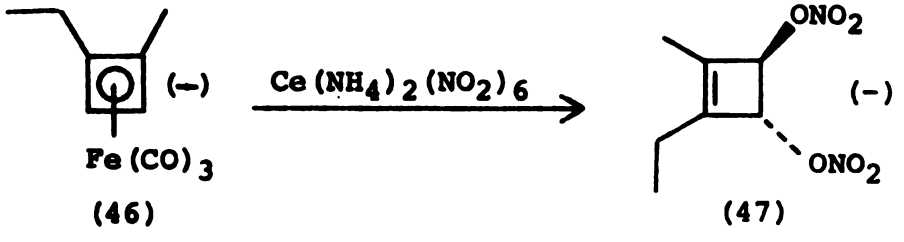
This mechanism is consistent with all of Pettit's results, since coordinating ability parallels dienophile strength for maleate, fumarate and diphenylethylene.

As a test of this mechanism an optically active complex (55b) was synthesized, then oxidized in the presence of a dienophile such as tetracyanoethylene (43) benzoquinone (44) or N-phenylmaleimide (45). No optical activity could be



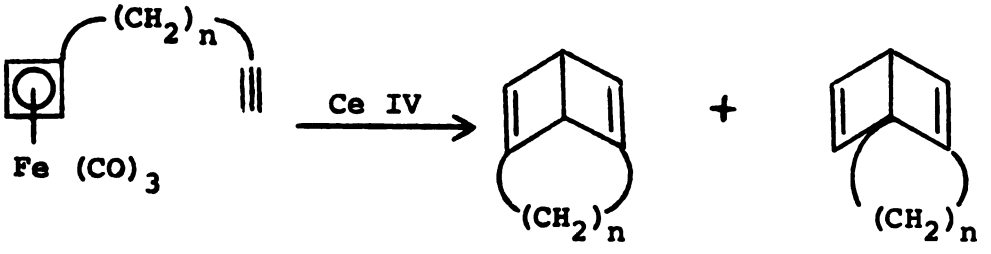
found in any of the adducts, indicating that the cyclobutadiene ligand is not near enough to the iron to have any chirality when it reacts.

In support of these findings E.K.G. Schmidt[36] reports finding optically active cyclobutene (47) when optically active cyclobutadienyliron tricarbonyl (46) is oxidized by ceric ammonium nitrate. He suggests the chiral product results from oxidation of cyclobutadiene bound to the metal, in contrast to the racemic products which result from Diels-Alder additions to free cyclobutadiene.



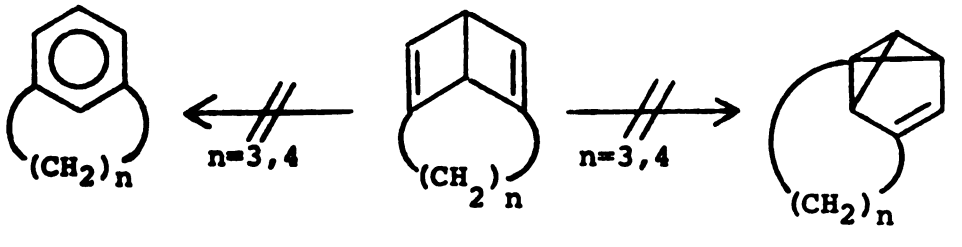
In the light of the above evidence it seems clear that the reactive species in the trapping reactions is free cyclobutadiene (10).

If a cyclobutadienyliron tricarbonyl complex could be synthesized with a pendent alkyne group, e.g. (48), it should be able to undergo an intramolecular Diels-Alder reaction to give a mixture of Dewar-benzene systems (49) and (50).



(48) (49) (50)

If the alkyl chain is short (n = 3,4) then (49) should be especially stable. It would be prevented from either flattening out to form the aromatic compound (51) or isomerizing to the benzvalene structure (52).



(51) (49) (52)

It should be possible for (49) to undergo [2+2] photochemical reactions and Diels-Alder reactions like those shown in Figure 10.

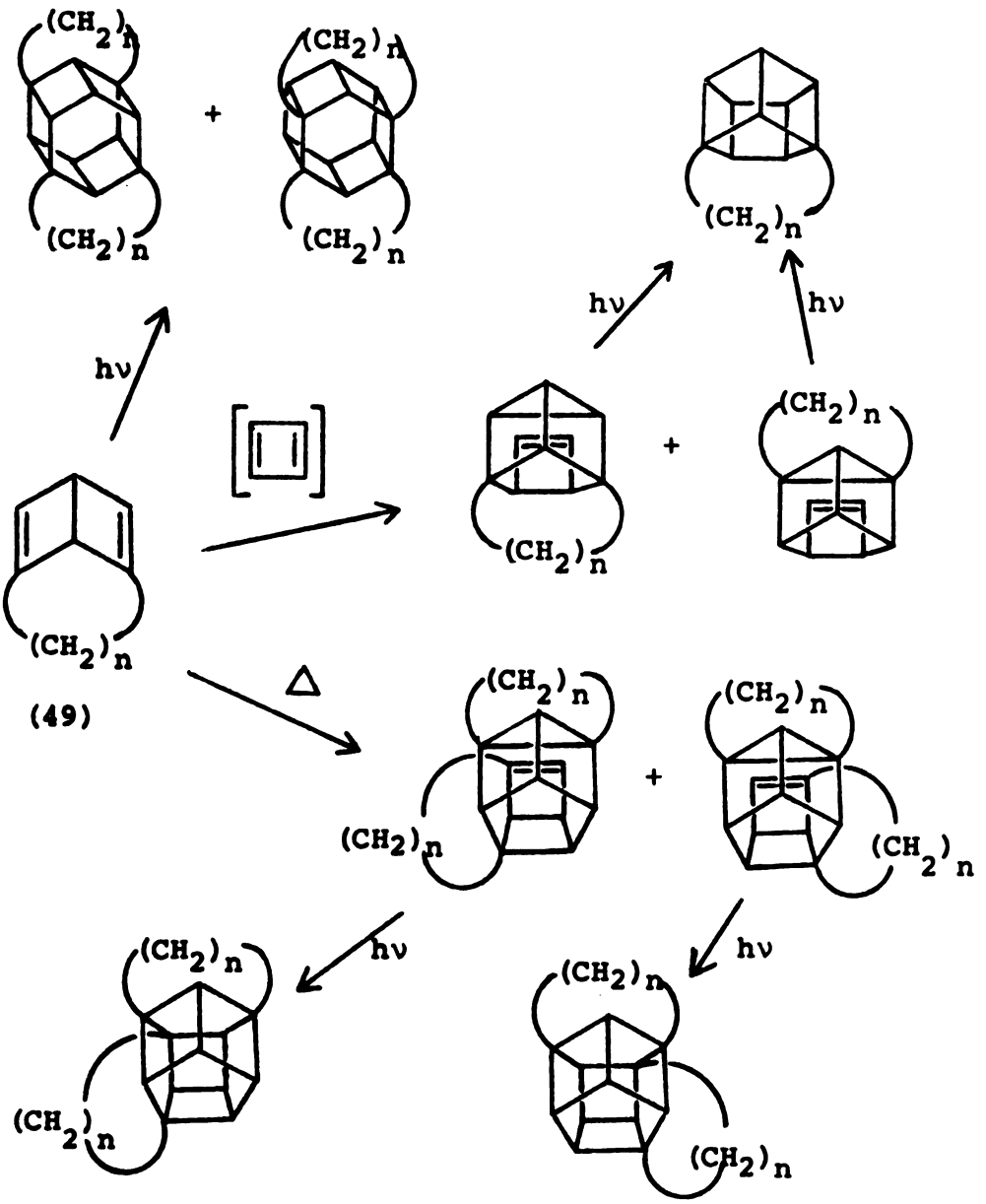


Figure 10. Possible photochemical and thermal reactions of isomerization hindered Dewar-benzenes.

It may also be possible to generate optically active Dewar-benzenes (53) by oxidation of optically active complex (54) as shown in Figure 11.

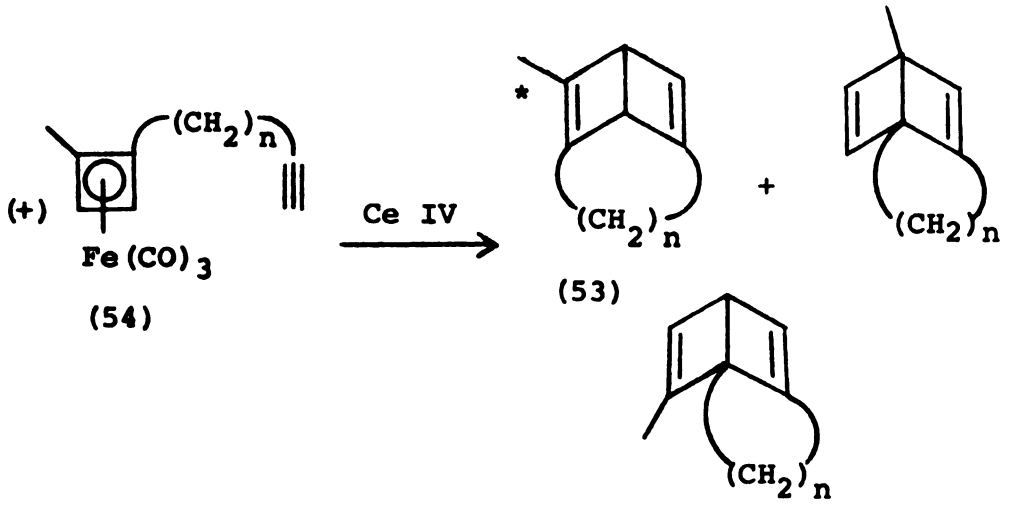


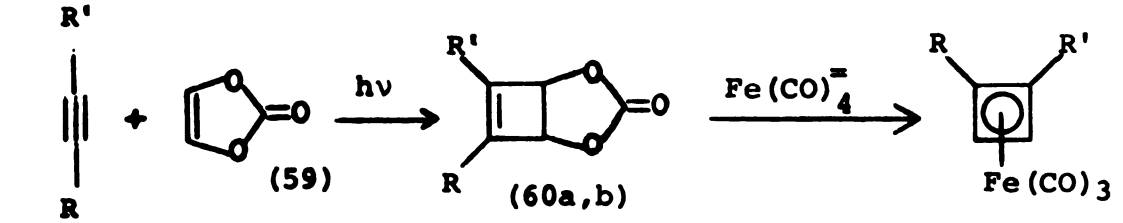
Figure 11. A proposed method for generating optically active Dewar-benzenes.

My intention in beginning this research was to synthesize cyclobutadienyliron tricarbonyl complexes with pendent alkyne groups. I hoped to produce stable Dewar-benzene systems by intramolecular trapping of the cyclobutadiene ligand. I also hoped to see if optically active products could be obtained from chiral complex via the faster intramolecular process when similar intermolecular trappings had yielded only racemic products.

RESULTS AND DISCUSSION

I. Synthesis of 1-(3-pentynoxymethyl)-cyclobutadienyliron Tricarbonyl (61)

The initial goal of this project was to synthesize a suitable cyclobutadienyliron tricarbonyl containing a pendant alkyne. A general method for making mono- or di-substituted cyclobutadienyliron tricarbonyls, shown in Figure 12, had already been developed by Grubbs.[37]

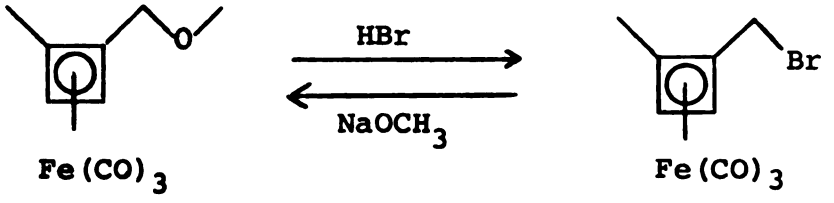


a) R = H, R'=CH_2OCH_3
b) R = CH_3, R'=CH OCH_3

Figure 12. Grubbs's general route to cyclobutadienyliron tricarbonyl systems.

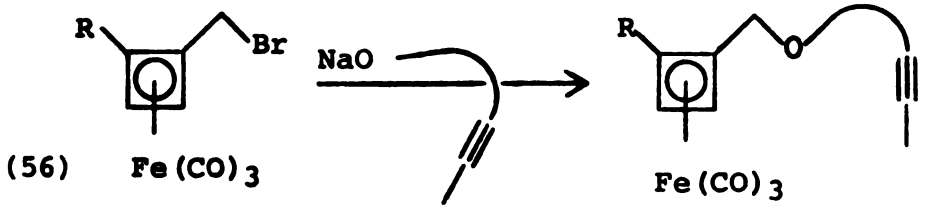
Using Grubbs's method, Grey[35] prepared 1-methoxymethyl-2-methylcyclobutadienyliron tricarbonyl (55b) and methoxymethylcyclobutadienyliron tricarbonyl (55a) in this laboratory.

Grey found that the ether linkage in (55a) was readily cleaved by hydrobromic acid to give the bromide (56b). Subsequent reaction of (56b) with sodium methoxide regenerated (55b) in essentially quantitative yield.



(55b) (56b)

The above reaction suggested that treatment of either (56b) or the bromide (56a), obtained from (55a), with the appropriate sodium alkoxide would give cyclobutadienyliron tricarbonyl with a pendent alkyne as shown below.



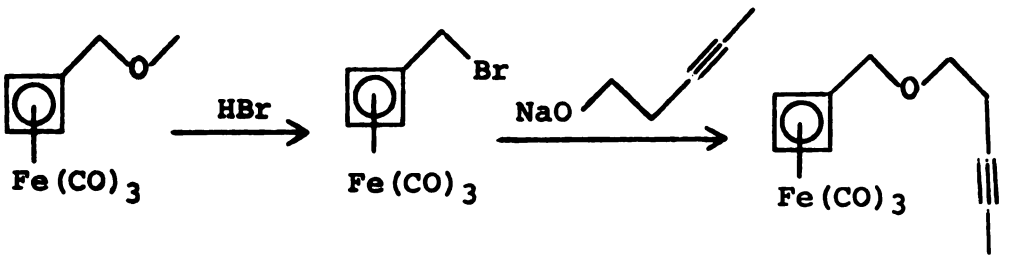
(56)

a) R = H
b) R = CH_3

Since (55a) was available in slightly higher yield, and was a simpler system, it became the initial target. Starting with ethylene carbonate (57),[39] methoxymethylcyclobutadienyliron tricarbonyl (55a) was obtained in 3.3% overall yield following the procedure of Grubbs and Grey.

Treatment of a pentane solution of (55a) with 48% hydrobromic acid gave (56a) as expected. The bromide was not isolated, but the pentane solution was dried and filtered before use.

The initial attempt to convert (55a) to (61) by the reaction sequence shown below was inconclusive.



(55a) (56a) (61)

The pentane solution of (56a) was treated with sodium-3-pentyn-1-oxide, freshly prepared from the alcohol and sodium metal, and allowed to stir overnight. The formation of a white precipitate and the appearance of a product peak on the gas chromatograph indicated that a reaction took place. The reaction mixture was dried, filtered and condensed, giving 170 mg of yellow oil presumed to be (61).

The oil was dissolved in 95% ethanol and treated with aqueous ceric ammonium nitrate in hopes that Dewar ring systems could be observed as products. However, no identifiable products were found.

One likely explanation for the lack of products is that the desired product (61) was not ever formed. Accordingly,

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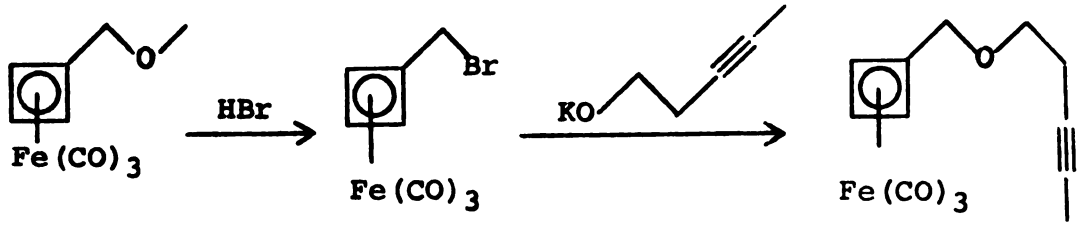
another attempt was made to synthesize (61) using the potassium alkoxide, as shown below, instead of the sodium salt.



(55a) (56a) (61)

When freshly prepared potassium-3-pentyn-1-oxide was added to a pentane solution of (56a) prepared as before, up to 90% glc yields of 1-(3-pentynoxymethyl)cyclobutadienyl-iron tricarbonyl (61) were obtained. Passage through a silica gel column and/or vacuum distillation gave isolated yields of up to 71% of the air sensitive yellow liquid (b.p. 85-90° at 0.1 mm).

The nmr spectrum showed a triplet (J = 2.2 Hz) at δ 1.73 for the three methyl hydrogens. The two methylene hydrogens next to the triple bond gave a triplet of overlapping quartets (J = 6.7 Hz, J = 2.2 Hz) at δ 2.34. The two methylene hydrogens between the first methylene group and the oxygen gave a triplet (J = 6.7 Hz) at δ 3.48. The two methylene hydrogens next to the ring gave a sharp singlet at δ 3.74. The ring hydrogen furthest from the substituent gave a sharp singlet at δ 4.00. The two equivalent ring hydrogens gave a sharp singlet at δ 4.07.

The mass spectrum of (61) showed no parent peak m/e 288. However, peaks of m/e 232 and m/e 204 corresponding to loss of two and three carbonyls respectively were observed. There was also a large peak of m/e 148 from loss of three carbonyls and iron. Successive loss of the carbonyls and iron is characteristic for ironcarbonyl complexes.

Although the above synthesis gave sufficient quantities of material for the decomposition studies, described in Parts II and IV, it has two major drawbacks. The overall yields are low and the final coupling reaction gives small amounts of side product which cannot easily be separated from the desired product (61).

There are two steps in particular which go in low yield. The photolysis of methyl propargyl ether and vinylene carbonate (59) in acetone sensitizer (Figure 12) gives at best a 17% yield of (60a) as an air sensitive yellow oil. The subsequent treatment of (60a) with iron dianion in tetrahydrofuran to give (55a) went in 25% yield once, but usually goes in 10-20% yields. Attempts to improve these yields met with only partial success.

In the case of the photolysis, it was observed that the product (60a) reacts further with both methyl propargyl ether and acetone.[35] There is a steady increase in the concentration of (60a) until finally, after two or three days, it is reacting as fast as it is formed. The concentration of (60a) then steadily decreases. Attempts to

replace the acetone with xylene as sensitizer gave no reaction. When acetone was added to the solution the yield of (60a) increased until a maximum was reached using just acetone with no xylene. Varying the concentrations was equally unproductive, so attempts to improve the photolysis were abandoned.

Efforts were turned instead toward improving the conversion of (60a) to the complex (55a). Grey's procedure, shown in Figure 12, was to add a tetrahydrofuran solution of sodium tetracarbonyl ferrate, prepared from iron pentacarbonyl and sodium mercury amalgam, to a tetrahydrofuran solution of (60a). Flash distillation of the solution at 150° followed by another vacuum distillation gave (55a) as an air sensitive yellow oil.

Although Grey observed large apparent yields of (55b) on the glc trace , he found it was very difficult to isolate the complex. The work-up he finally used, although the result of much trial and error gave only 12% yields of (55b) and 10-20% yields of (55a). Rather than spend more time on the work-up, it was decided to change the reaction conditions in hopes of getting a cleaner reaction.

An alternative to the sodium/mercury amalgam method previously used was provided by a procedure developed by Collman[40] for preparing disodium tetracarbonyl ferrate as a white pyrophoric powder. Following Collman's procedure,

sodium metal and benzophenone were allowed to react in refluxing dioxane to form the blue ketyl. Iron pentacarbonyl was then slowly added to the hot solution, giving a white precipitate. After cooling, the solvent was removed and the remaining precipitate was rinsed several times with petroleum ether before being vacuum dried. Collman reagent is extremely pyrophoric and must be prepared in a total absence of oxygen. Nitrogen from the cylinder was passed through a BASF catalyst oxygen scrubber as well as a ketyl scrubber to prevent decomposition of the reagent.

Despite its sensitivity to oxygen, the Collman reagent was more convenient to use than the amalgam since it could be made on a large scale and stored in a dry box for future use.

When a tetrahydrofuran solution of Collman reagent was added to an almost equimolar solution of carbonate (60a) there was only a small cyclobutadienyliron tricarbonyl peak on the gas chromatograph. When the carbonate solution was cooled to -78° prior to addition of the dianion, a much larger product peak was formed. As the solution was allowed to warm the product peak became smaller. Upon recooling, the peak regained its former size. If the solution warmed to room temperature for a period of time, subsequent cooling had little effect.

A possible explanation for these and subsequent results is shown in Figure 13.

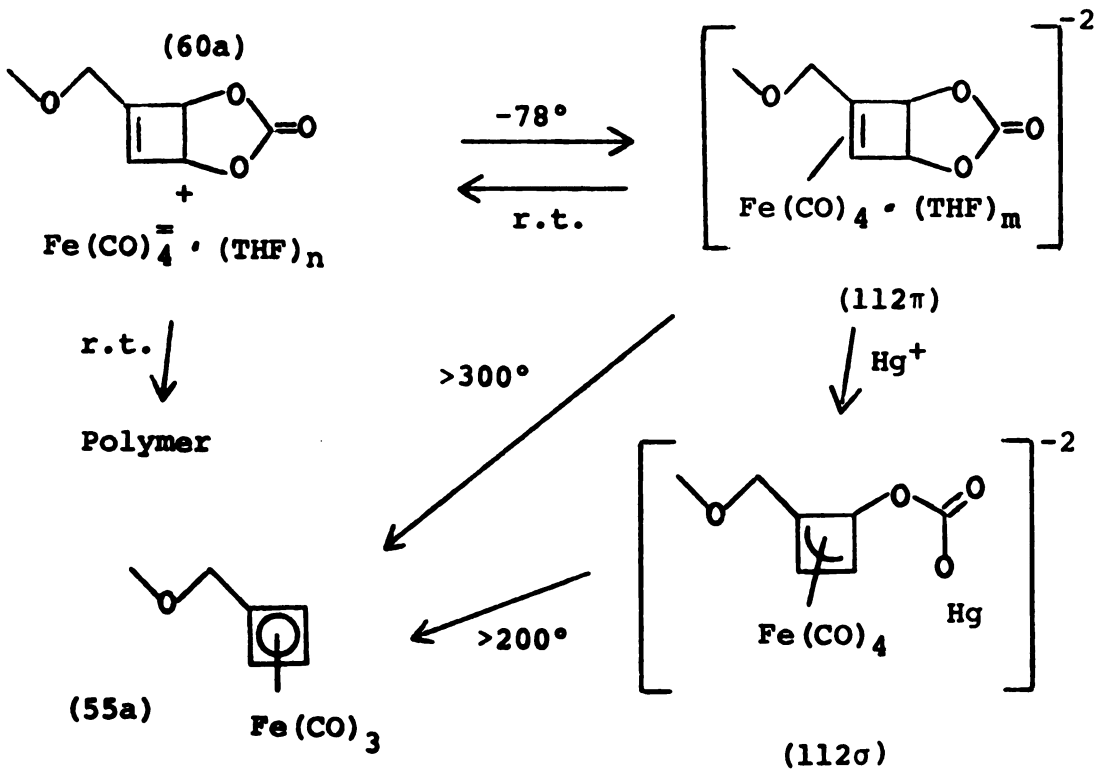


Figure 13. A possible mechanism for the formation of (55a) from (60a).

At -78° there is a reversible replacement of solvent by (60a) to give a π-complexed intermediate (112 π) which is thermally unstable. At room temperature the equilibrium is reversed and base catalyzed polymerization of (60a) and (112 π) takes place. On the glc (> 300°) the intermediate goes on to produce (55a). When the amalgam was used to make the dianion, mercurous ions were present and reacted

with the π-complex to form a thermally stable intermediate (112 σ) which neither reverts back to starting materials nor polymerizes. The difficulty in finding a good work-up stemmed from having not the product but an intermediate. The product was not formed until the flash distillation.

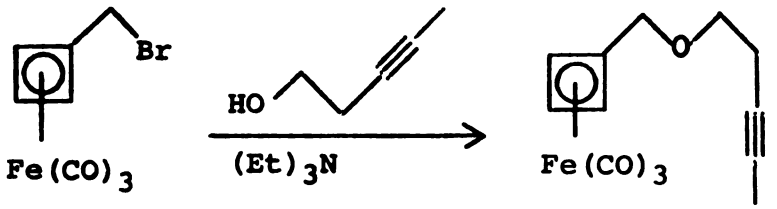
The first runs which used Collman's reagent and a flash distillation work-up gave only 3% yield of (55a). Some (60a) was also recovered. An attempt to catalyze the conversion of the π-complex to (55a) by addition of acetic acid gave back starting material, which polymerized. Refluxing the reaction mixture gave a similar result. When the ratio of dianion to carbonate was varied the yields were still poor.

Since (112 π) apparently went to (55a) in good yield on the gas chromatograph, attempts were made to approximate those conditions with the work-up. The cold solution of π-complex was dropped into a hot (300°) column filled with glass helices while a slow stream of nitrogen was blown through the column. This raised the yields to about 14%, which was about what the amalgam procedure usually gave. Unfortunately, the pyrolysis took three times as much time and energy as the old work-up, so instead the temperature of the flash distillation was raised from 150 to 210° using a sand bath.

Part of the difficulty was due to the reaction mixture warming partially in the addition funnel. It was clear that the intermediate formed by the amalgam procedure (112 σ) being stable at room temperature, was different from the intermediate obtained by using the Collman reagent (112 π). The obvious change in replacing the amalgam generated dianion with Collman reagent was the lack of mercury in the system. Addition of one mole equivalent of mercurous chloride to the reaction mixture gave an intermediate (112 σ) which was stable at room temperature, as measured by glc, and improved the isolated yields.

The final form of the procedure was to treat a tetrahydrofuran solution of (60a) with a slight excess of Collman reagent at -78°. An excess of mercurous chloride was added and the solution was flash distilled at 200-215° to give 20-25% yields of (55a). This procedure was a small but significant improvement over the amalgam procedure.

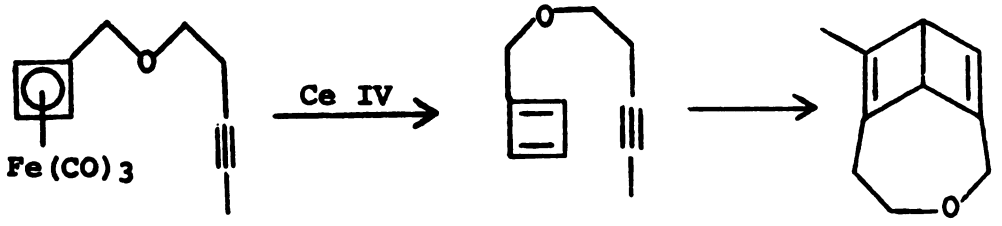
The remaining problem of unwanted side products in the final coupling reaction giving (61) was less difficult to solve. Treatment of the bromide (56a) with equimolar amounts of 3-pentyne-1-ol and triethylamine gave (61) in somewhat lower yield than the alkoxide coupling reaction, but without the side product.



(56a) (61)

II. Decomposition Studies on (61)

Treatment of cyclobutadienyliron tricarbonyl systems with ceric ammonium nitrate (Ce IV) normally oxidizes the iron and releases the cyclobutadiene to react with whatever dienophile is present in solution.[41] It was hoped that oxidation of (61) would give (63) via an intramolecular Diels-Alder reaction as shown below.



(61) (62) (63)

When a solution of (61) in 95% ethanol was treated with aqueous Ce IV in 3.5 molar excess, no identifiable products were obtained. Addition of (61) to the Ce IV solution gave similar results.

Since iron carbonyl compounds are generally light sensitive, it was decided to try a photodecomposition of (61) instead. A tetrahydrofuran solution of the complex was photolyzed until glc analysis showed no more starting material present. The solution was condensed and put through a silica gel column. Analysis of the resultant fraction by nmr disclosed no vinyl peaks such as (63) would be expected to give. Two fractions, however, gave peaks consistent with a methyl isochroman structure. In particular, 5-methylisochroman (68) and 7-methylisochroman (66) can be rationalized as being formed by the two Diels-Alder pathways shown in Figure 14.

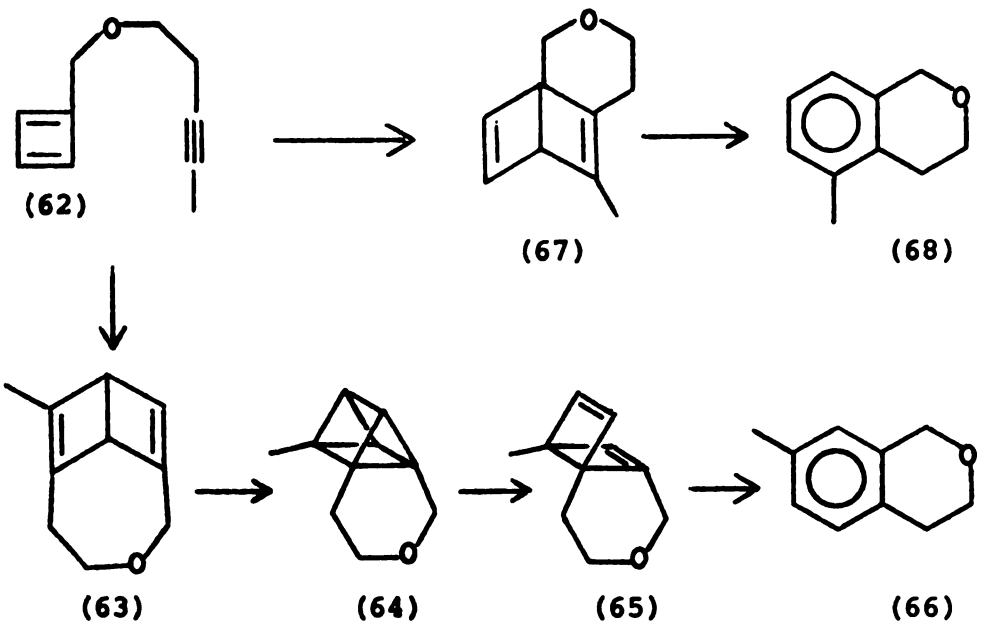


Figure 14. Possible mechanisms for the formation of (66) or (68) from (62).

In order to identify which, if either, of these two isochromans was the product, both of them were prepared by independent synthesis.

The 7-methylisochroman was prepared from p-bromotoluene (69), as shown in Figure 15.

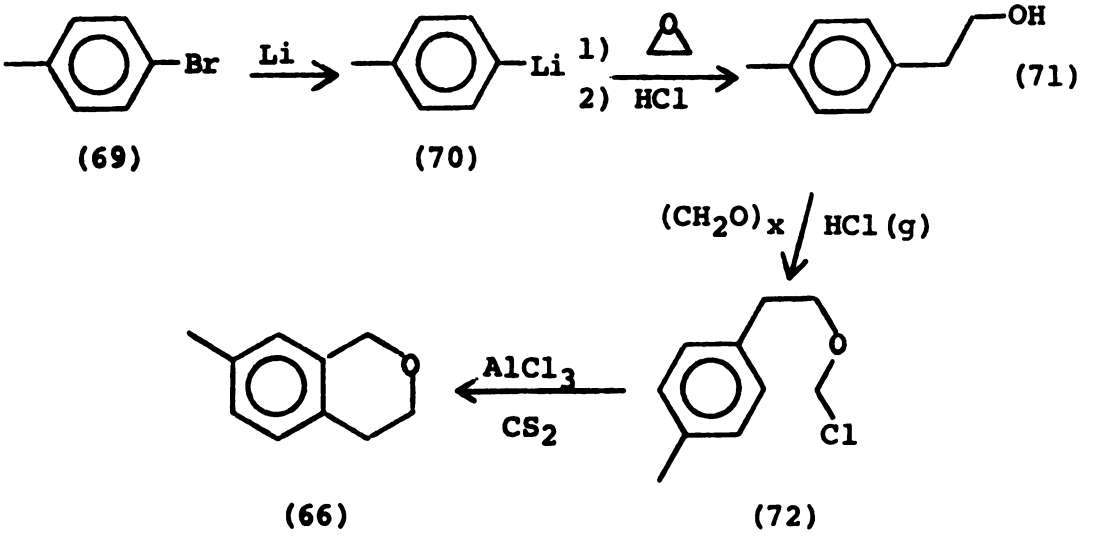


Figure 15. Reaction scheme for the independent synthesis of (66).

The nmr spectrum of (66) has a singlet at δ 2.29 for the three methyl hydrogens. The two methylene hydrogens <u>para</u> to the methyl group give a triplet at 2.77 (J = 5.5 Hz). The two methylene hydrogens next to the oxygen give a triplet at δ 3.94 (J = 5.5 Hz). The two methylene hydrogens between the ring and the oxygen give a singlet at δ 4.73. The three ring hydrogens give a multiplet at δ 7.0.

The 5-methylisochroman (68) was prepared by the same reaction sequence starting with o-bromotoluene (73) as shown in Figure 16.

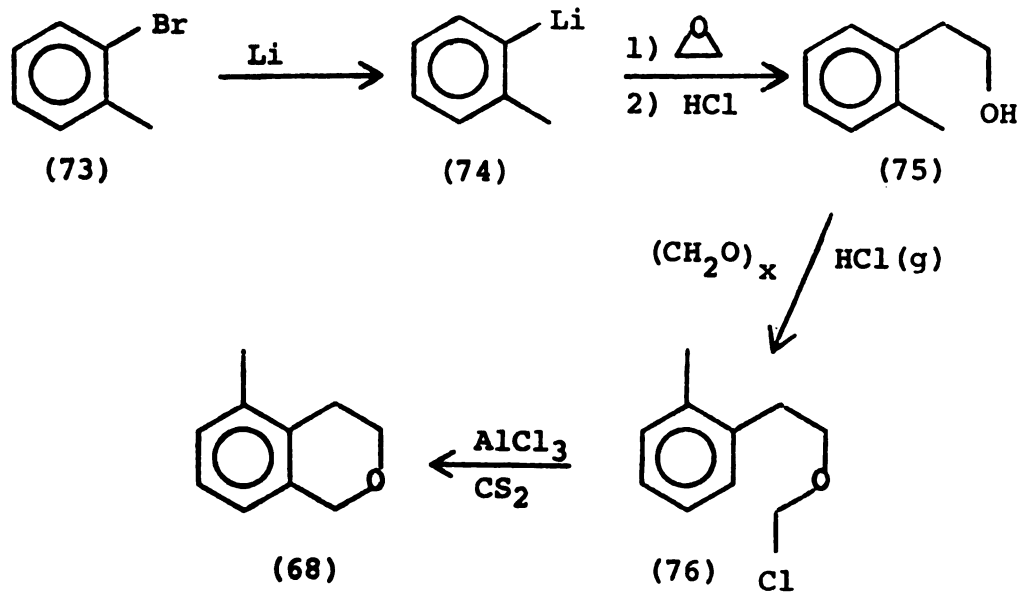


Figure 16. Reaction scheme for the independent synthesis of (68).

Cyclization of (76) with aluminum trichloride in carbon disulfide gave 5-methylisochroman (68) (78% yield), which turned out to have the same nmr spectrum and glc retention time as the photolysis product from (61). Although the nmr of 7-methylisochroman (66) was very similar to that of (68), a mixture of the photolysis product and 7-methylisochroman gave two glc peaks just as a mixture of the prepared isomers did. The photolysis product and 5-methylisochroman gave a single glc peak.

In addition to a small yield of 5-methylisochroman, the photodecomposition yielded a substantial amount of starting material (61). This occurred even though no starting complex could be detected by glc when the reaction was stopped. Nor was there any peak for the product isochroman prior to work-up. These results suggest that the photolysis forms some intermediate complex which can, on work-up, either go on to product or back to starting material.

It was previously noted (see Figure 6) that photolysis of (8) with olefin (28) or (30) gives respectively (36) and (37) as stable isolable complexes. Photolysis of (61) could give intermediate (78) by an analogous reaction as shown in Figure 17.

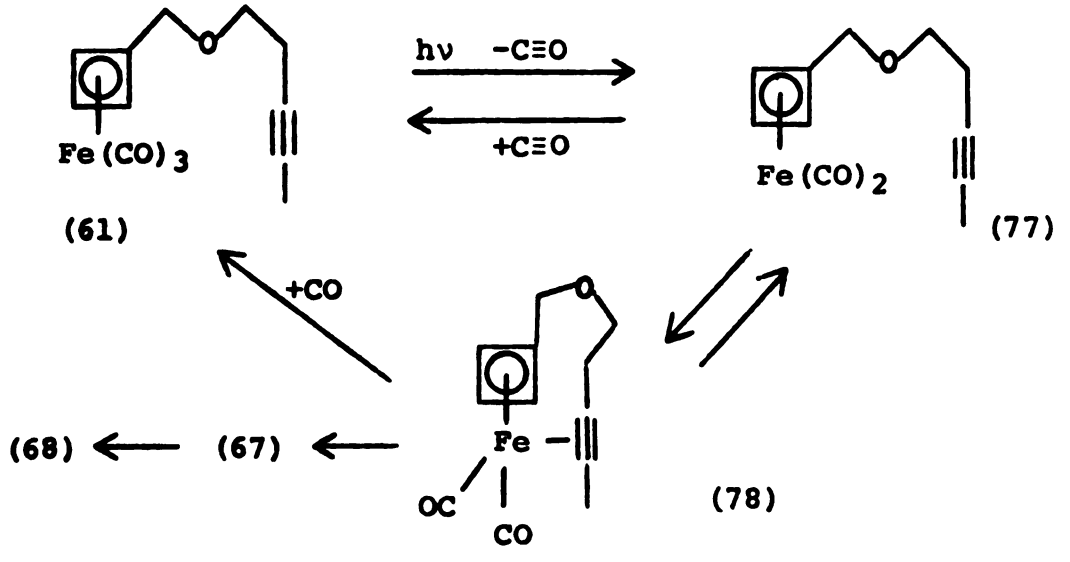


Figure 17. A partial mechanism for the photochemical decomposition of (61).

Light induced reversible loss of carbon monoxide from the iron leaves an open coordination site (77). Subsequent π-complexation of the triple bond to the iron would give (78), which could either go back to (61) or decompose to the isochroman *via* (67).

If the above scheme is correct, then a solution of intermediate (78) placed under a carbon monoxide atmosphere should revert back to (61). Also, treatment of (78) with Ce IV should give mostly isochroman (68) or other trapping products and very little (61).

When a photolyzed solution of (61) which gave no glc peaks was placed under 44 psi of carbon monoxide for 22 hr, peaks appeared for both (61) and the isochroman. Analysis of the solution by glc, using durene as an internal standard, showed 20% reversion to (61) and only 8% conversion to isochroman (68). A similar run at 36 psi gave 22% reversion to (61) and 11% conversion to (68).

When, instead of being placed under carbon monoxide, the photolyzed solution of (61) was treated with a 3.5 molar excess of Ce IV, glc analysis showed only 13% reversion to (61) and 77% conversion to (68). Refluxing the Ce IV oxidized solution for several hours gave 83% conversion to (68).

Simply concentrating a photolyzed solution of (61) without further treatment with either Ce IV or carbon monoxide gave 21% reversion to (61) and 53% conversion

to (68). Concentrating in air is in effect a partial oxidation. But even so, the Ce IV oxidized run gave more isochroman and less reversion than the "untreated" run, and the carbon monoxide treated solution gave more reversion relative to the isochroman than the "untreated" solution.

These results are summarized in Table I and are consistent with the formation of intermediate (78).

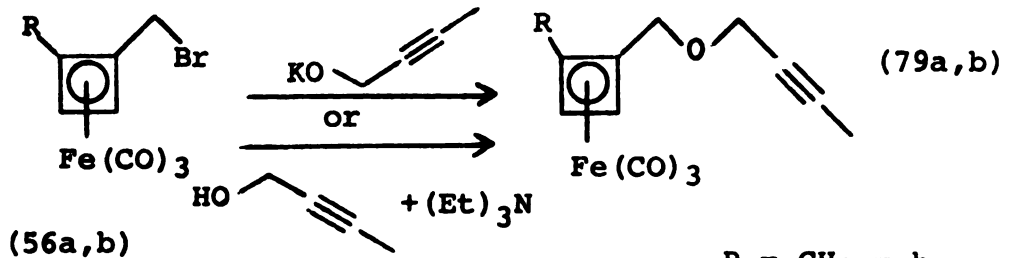
Table I. Relative Percentage of Intermediate (Proposed to be (78)) Converted to Product Versus Percentage Reverted to Starting Complex

Treatment of photolyzed solution	% reversion (complex)	% conversion (product)
44 psi CO	20	8
36 psi CO	22	11
3.5 molar excess Ce IV	13	77
Condense in air	21	53

III. Synthesis of 1-(2-Butynoxymethyl)cyclobutadienyliron Tricarbonyl (79a) and 2-Methyl-1-(2-butynoxymethyl)cyclobutadienyliron Tricarbonyl (79b)

Since decomposition of (61) gave only 5-methylisochroman, presumably *via* the unstable Dewar system (67), it was decided to try using a shorter carbon chain.

Both 2-methyl-1-(2-butynoxymethyl)cyclobutadienyliron tricarbonyl (79b) and 1-(2-butynoxymethylcyclobutadienyl-iron tricarbonyl (79a) were made using the same procedures as previously described in the synthesis of (61).



Treatment of a pentane solution of bromide (56a) prepared as before, with freshly prepared potassium-2-butyne-1-oxide gave a 90% glc yield of (79a). Distillation of the crude product gave a 64% isolated yield of air sensitive bright yellow oil (b.p. 100° at 0.5 mm).

As in the preparation of (61), this procedure gave small amounts of impurity which were difficult to separate from the product.

When the pentane solution of (56a) was treated with 2-butyne-1-ol and triethylamine, impurity free (79a) could be isolated in 47% yield.

The nmr spectrum of (79a) shows a triplet at δ 1.81 (J = 2½ Hz) for the three methyl hydrogens. The two methylene hydrogens next to the ring give a singlet at

δ 3.77. The ring hydrogen opposite the substituent gives a singlet at δ 3.98. The two equivalent ring hydrogens give a singlet at δ 4.07. The two methylene hydrogens between the oxygen and the triple bond give a quartet at δ 4.05 which is superimposed over the ring hydrogen peaks.

The methyl substituted complex (79b) was similarly prepared from the bromide (56b) which had been previously made by Grey.[35]

The ether precursor to (56b) was prepared using the original procedures developed by Grubbs and Grey (Figure 12), which were later modified for the synthesis of (55a). Treatment of (55b) in pentane with hydrobromic acid gave (56b) which was dried and used as the pentane solution.

When potassium-2-butynoxide was added to the bromide solution, the desired linkage was formed. Subsequent distillation gave (79b) in 51% yield as a bright yellow air sensitive oil (b.p. 90-97° at 0.3-0.35 mm).

The nmr spectrum of (79b) showed a singlet at δ 1.79 for the three hydrogens on the ring methyl group. Superimposed on this is a triplet at δ 1.80 (J = 2.8 Hz) from the three methyl hydrogens next to the triple bond. The two methylene hydrogens next to the ring give an AB quartet at δ 3.83 as a result of the molecule's chirality. The two ring hydrogens each give a singlet at δ 3.99 and δ 4.05 respectively. Superimposed on these singlets is a quartet

at δ 4.05 (J = 2.8) from the two methylene hydrogens between the oxygen and the triple bond.

The mass spectrum gave a parent peak at m/e 288 as well as characteristic peaks for the successive loss of three carbonyl groups and iron. Other peaks were also consistent with the assigned structure of the organic ligand.

IV. Decomposition Studies on (79a) and (79b)

With samples of both (79a) and (79b) in hand, a new series of decomposition studies was undertaken, to try to isolate stable Dewar-benzene systems. It was expected that oxidative decomposition of these complexes using Ce IV might proceed as shown below in Figure 18.

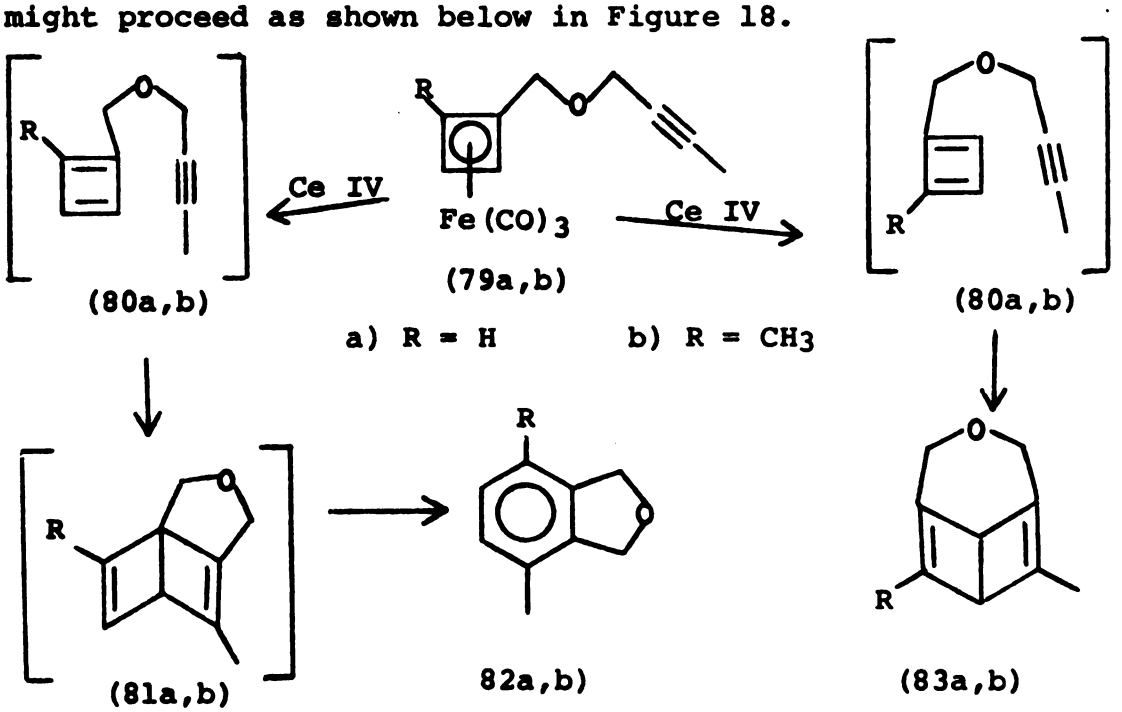
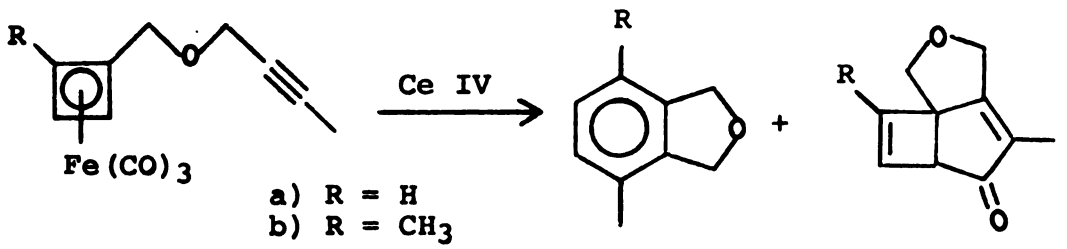


Figure 18. Expected course of oxidative decomposition of (79a) and (79b).

The two types of products could result from the two possible orientations for the Diels-Alder reaction. The phthalans (82a) and (82b) would be analogous to the isochroman (68) formed when (61) is decomposed.

When the oxidations were actually carried out, however, the results were as shown below.



79a,b 82a,b 84a,b

The complexes were decomposed by treating an acetone solution of either (79a) or (79b) with a 3.5 molar excess of crystalline Ce IV. When the bubbling ceased ether was added, and the organic solution was extracted with successive portions of saturated salt solution until no more color was removed.[35] After being dried and condensed, the sample was either injected into a gas chromatograph and the products collected, or it was put through a Florisil or silica gel column using pentane and pentane ether mixtures as eluant.

When (79a) was decomposed with Ce IV and then put through a Florisil column, 4-methylphthalan (82a) was obtained in 80% yield and 2-methyl-9-oxatricyclo[5.3.$2^{4,7}$.$0^{1,7}$]deca-1,5-dien-3-one (84a) was obtained in 15% yield.

Similar decomposition of the methyl complex (79b) with Ce IV gave the corresponding methyl substituted products. A silica gel column work-up gave 4,7-dimethylphthalan (82b) and 2,7-dimethyl-9-oxatricyclo[5,3,$2^{4,7}$, $0^{1,7}$]deca-1,5-dien-3-one (84b) in isolated yields of 53% and 16% respectively. Pure samples were also obtained by preparative glc techniques.

The assigned structures for (82a), (82b), (84a) and (84b) were arrived at only after some very confusing data had been explained, as described below.

When the initial oxidation of (79a) was carried out and the two products isolated, it was expected that they would prove to be (82a) and (83a). Such was not the case.

The nmr spectrum of the major product was consistent with its being 4-methylphthalan as expected. However, a mass spectrum of the sample showed a parent peak of m/e 148 which is 14 mass units higher than the 134 parent expected for the phthalan. The rest of the mass spectrum fit the phthalan strucrure including having a peak at m/e 134.

The nmr spectrum of the minor product had peaks corresponding to two different vinyl hydrogens, which ruled out (83a) as a possible structure. The nmr spectrum was consistent with the minor product being (81a), the postulated intermediate in the formation of the phthalan. However, it seemed unlikely that any of the intermediate (81a) should

have failed to aromatize, since Dewar-benzene systems are known to go rapidly to benzene at room temperature.

As a test of this possibility, a sample of the minor product was dissolved in deuterochloroform and heated in a sealed nmr tube. Even after 100 minutes at 90° the product failed to aromatize and the nmr spectrum remained unchanged.

A mass spectrum of the sample showed a parent peak at m/e 162. This is 28 mass units greater than the 134 expected for any simple product derived from the organic ligand.

Similar results were obtained when (79b) was oxidatively decomposed in the same manner. Pure samples of both a major product and a minor product were obtained by collecting the appropriate peaks off the glc.

The nmr spectrum of the major product indicated it was the phthalan (82b). However, the mass spectrum gave a parent peak at m/e 162, again 14 mass units over the 148 required for the phthalan. As before, the rest of the mass spectrum was consistent with (82b) being the structure, including having a peak at m/e 148.

The nmr spectrum of the minor product was similar to that obtained for the unmethylated system, except that one of the vinyl hydrogen peaks was gone, having been replaced by a second methyl peak. Just as the other spectrum fit (81a), this spectrum fit (81b) as the structure, and as

before, the nmr spectrum remained unchanged when the sample was heated.

The mass spectrum of this minor product also gave a parent peak 28 mass units greater than what would have been expected for the organic ligand alone.

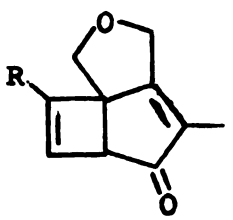
Although the too high parent peaks were misleading in the case of the major products, they provided an important clue to the structure of the minor products.

Both minor products were 28 mass units heavier than the respective organic ligands from which they derived. This difference corresponds to the mass of a carbonyl group and introduces the possibility that somehow ring closure is accompanied by carbonyl insertion.

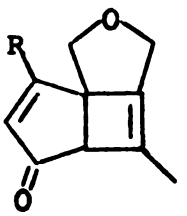
This possibility was easily tested by taking infrared spectra of the minor products. The unmethylated product had a strong absorption at 1703 cm^{-1}, characteristic of a cyclopentenone system and a broad absorption from 1025 cm^{-1} to 1105 cm^{-1} indicating an ether. There was another absorption in the carbonyl region at 1661 cm^{-1} which is probably caused by Fermi resonance.[45] The methylated product gave a similar spectrum with corresponding absorptions at 1700 cm^{-1}, 1664 cm^{-1} and from 1020 cm^{-1} to 1100 cm^{-1}.

There are two structures, (84) and (85) shown below, which fit both the nmr and mass spectral data for the minor

products. Further analysis was needed to distinguish between them.



84a,b



85a,b

a) R = H
b) R = CH_3

In order to obtain more material for analysis, an attempt was made to increase the yield of minor product by oxidizing a sample of (79b) under a carbon monoxide atmosphere. Although the focus of this experiment was the minor products, the results instead suggested a possible explanation for the mass spectral data of the major products. The focus was returned to the minor products only after the apparent inconsistencies in the data for the major products had been cleared up by the following series of experiments.

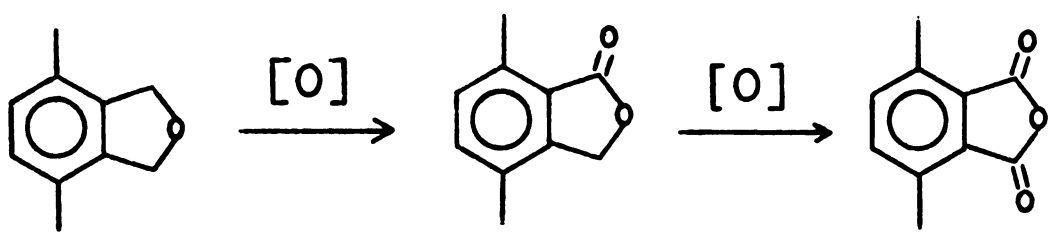
When (79b) was oxidized with Ce IV in the usual manner, but under an atmosphere of carbon monoxide instead of nitrogen, analysis of the reaction mixture by glc showed the presence of four different products.

The first two peaks were the presumed phthalan (82b) (45% glc yield) and the carbonyl insertion compound (21% glc yield) as expected. Doing the oxidation under a carbon monoxide atmosphere improved the yield of insertion product only slightly.

The fourth product (4% glc yield) of the decomposition was probably a dimer. The nmr spectrum shows only four groups of peaks. A multiplet at δ 1.9 could easily be two kinds of overlapping methyl groups (12 H). The remaining three multiplets at δ 4.2, δ 4.5 and δ 4.85 could be pairs of methylene groups or equivalent methylene hydrogens (each peak is 4H). No vinyl peaks were observed.

This is consistent with the assumption that any organic ligand otherwise unaccounted for in these decompositions probably goes to form various dimers or polymer.

The third product from the glc was the lactone (86b) (29% glc yield) which would be expected from oxidation of the phthalan (82b).



(82b) (86b) (87b)

The nmr spectrum showed two different methyl singlets and a methylene peak corresponding to only two methylene hydrogens, instead of the four methylene hydrogens observed for the phthalan. A mass spectrum of (86b) shows a large parent peak at m/e 162 but no peak at m/e 148.

It was quickly noticed that the parent peak at m/e 162 observed for the phthalan could be explained by contamination

of the phthalan sample with small amounts of the lactone. The fact that even glc collected samples of the phthalan contain this impurity indicates that the lactone must be formed after purification; for example, by air oxidation. If the phthalan were being oxidized to the lactone by air, the mass spectrum obtained would be a superposition of the lactone spectrum over the phthalan spectrum. This is in fact what is observed.

As a simple test of this explanation, a mass spectrum was run on a sample of phthalan (62a) immediately after it had been collected off of the glc and without having exposed it to the air. This spectrum showed a correct parent peak at m/e 134. When a similar sample was exposed to the air briefly, a small peak at m/e 148 appeared. Long exposure to air produced a large peak at m/e 148 and an additional peak at m/e 162, attributable to the anhydride (87a). Samples of (62b) also gave an anhydride (87b) parent peak, at m/e 176 when exposed to the air for a long time.

As a further check on the structure, several attempts were made to prepare 4-methylphthalan (62a) by independent synthesis. The reaction sequence used was similar to the ones for the isochroman systems and is shown on the following page in Figure 19.

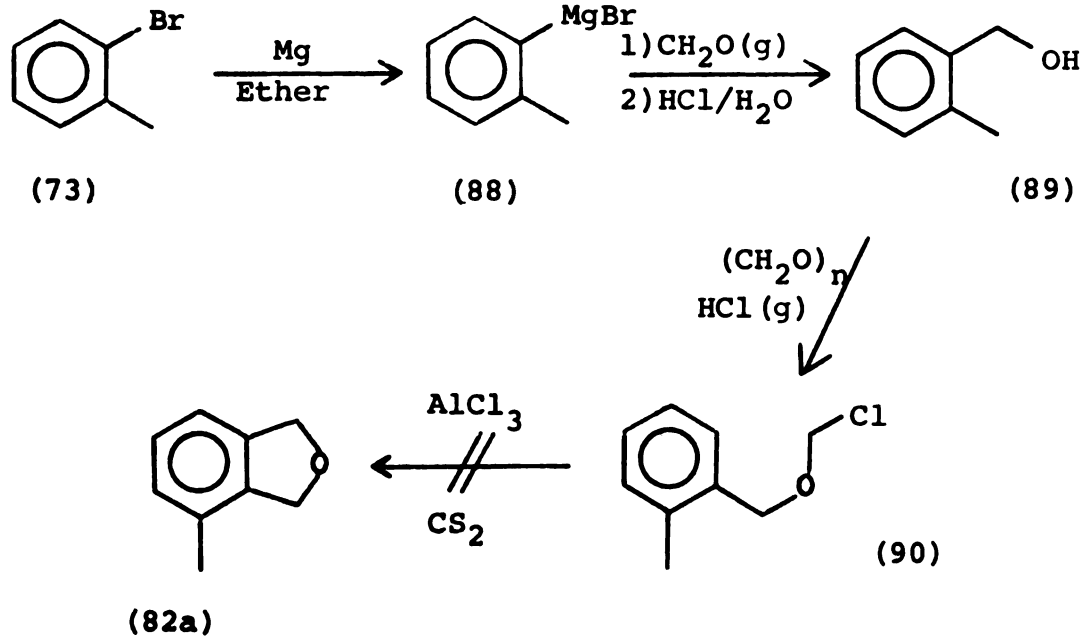


Figure 19. Reaction scheme for the unsuccessful independent synthesis of (82a).

The Grignard reagent, prepared from o-bromotoluene and magnesium metal, was used without further work-up.

The alcohol was prepared by bubbling formalin vapor through the Grignard solution and refluxing in benzene overnight. Subsequent quenching, work-up and distillation gave the product. Although this procedure did ultimately give a 41% yield of alcohol (89) as a clear solid (b.p. 44-55° at 0.05-0.25 mm) the initial results were not as satisfactory. Early runs gave up to 41% yields of a clear liquid (b.p. ~50° at 0.13 mm) which gave an nmr spectrum consistent

with its being (89) but which could not be transformed into the chloromethyl ether (90). Since the solid could be converted to (90), the mystery of the liquid was not pursued further.

The nmr spectrum of the solid showed a singlet at δ 2.27 for the three methyl hydrogens. The alcohol hydrogen gave a variable peak at δ 2.7 to δ 3.0. The two methylene hydrogens gave a singlet at δ 4.57. The four benzene hydrogens gave a multiplet at δ 7.2.

The alcohol was converted into the chloromethyl ether by bubbling hydrogen chloride gas through a benzene solution of the alcohol and formalin. After refluxing for an hour at 43° and cooling overnight the reaction was worked-up. Vacuum distillation gave a 57% yield of (90) (b.p. 60-65° at 0.45 mm).

The nmr spectrum of (90) showed a singlet at δ 2.27. The two benzylic methylene hydrogens gave a singlet at δ 4.62. The two chloromethyl hydrogens gave a singlet at δ 5.36. The four benzene hydrogens gave a multiplet at δ 7.2.

Attempts to cyclize (90) to a phthalan were unsuccessful. When aluminum trichloride was added to a carbon disulfide solution of (90) at 0° and allowed to warm to room temperature the color changed to reddish black. After quenching and work-up the organic portion was distilled.

Analysis of the fractions by nmr showed both starting material and alcohol (89) to be present, but no phthalan.

Possibly the carbonium ion (91), if it forms at all, goes on to give a benzylic cation (92) as shown in Figure 20. The benzylic ion could also form directly from (90). Hydrolysis of (92) would give the alcohol (89).

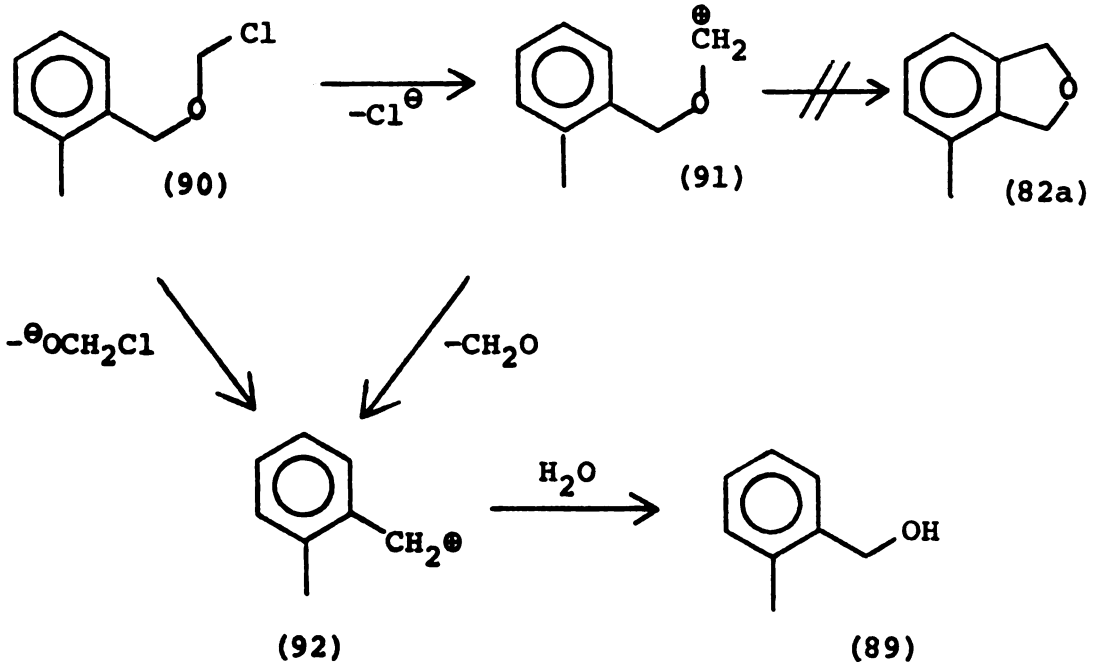


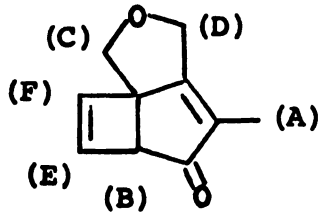
Figure 20. A possible mechanism for the decomposition of (90).

No further attempts were made to synthesize (82a) by an independent route. The major products were assigned the phthalan structures (82a) and (82b) on the basis of

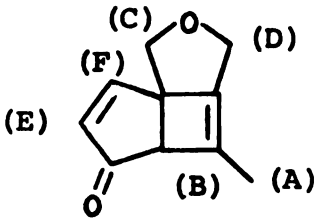
nmr and mass spectral data and by analogy to the isochroman formation observed in the decomposition of (61).

The focus now returned to assigning structures for the minor products. As a check on the polycyclic structures (84) and (85) proposed earlier, an nmr shift study was done using 2,2,6,6-tetramethyl-3,5-heptanedionate europium as the shift reagent. The europium complex was added in 2 mg portions to a deuterochloroform solution of the nonmethylated minor product in a micro nmr tube. After each addition of shift reagent nmr spectra were taken. After three additions of europium the shifts were as listed in Table II.

Table II. Data for NMR Shift Study Done on Polycyclic Product (84a)



(84a)



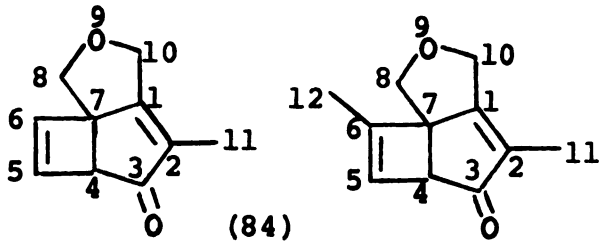
(85a)

Proton	Chemical Shift (δ) No Eu	6 mg Eu	Difference (ppm)
A	1.70	2.10	0.40
B	3.47	4.07	0.60
C	3.90	5.87	1.93
D	4.47	6.57	2.10
E	6.33	6.57	0.24
F	6.60	7.17	0.57

It has been shown,[46] that europium complexes (such as trisdipivaloylmethane europium) prefer to complex with ethers rather than carbonyl groups. It can be seen from Table II that the hydrogens nearest the ether oxygen are shifted the most as expected. Although the shift data favors (84a) slightly, it is really compatible with both structures. If (85a) were the correct structure the (A) hydrogens might be expected to show the smallest shift, being furthest away from both the major (ether) and minor (carbonyl) complexing sites. In fact the (E) hydrogen gives the smallest shift and in (84a) it is furthest from both complexing sites. One might also expect (85a) to show a slightly larger shift for the (C) hydrogens compared to the (D) hydrogens. Table II shows that the reverse is true, the (D) hydrogens shift more, again favoring (84a). The shift data are consistent in supporting (84a), but by no means conclusive.

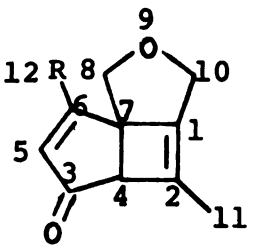
Stronger support for structures (84a) and (84b) was given by the ^{13}C nmr data shown in Table III. If (84) is correct, the four peaks for olefinic carbons can be unambiguously assigned as shown. Carbons 1 and 2 must be the peaks at 171 and 131 which show only negligible shift changes as we go from (84a) to (84b). The 40 ppm difference in their shifts indicates they are part of the double bond conjugated with the carbonyl. The shifts of carbons

Table III. C-13NMR Data for (84a) and (84b).



(84)

C#	a	b
1	171.1	171.9
2	131.6	131.3
3		201.7
4	56.4	52.8
5	136.0	126.5
6	145.3	155.3
7	62.5	63.1
8	64.6	64.4
10	69.0	67.5
11	9.45	9.3
12	----	13.6



(85)

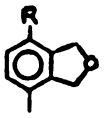
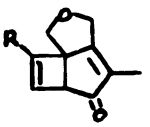
5 and 6 change in keeping with observations on cyclobutene systems made by Stothers[47] that putting a methyl group on carbon 6 should shift that peak 10 ppm away from TMS and should shift carbon 5 about 8 ppm toward TMS. If (85) were the correct structure the shifts of carbons 1 and 2 would be more nearly the same. Also carbons 5 and 6 would be farther apart, with the methylated carbon 6 coming at higher field than carbon 5.

In addition to the nmr data, the ultraviolet spectrum of the methylated minor product gave unambiguous support to the (84) structures as opposed to the (85) system. Using standard methods[48] for estimating λ_{max} values of cyclopentenone systems, theoretical values of 244 mμ and 229 mμ were calculated for (84b) and (85b) respectively. The observed value 244 mμ, was in agreement with (84b).

A summary of the results of the decomposition studies is given in Table IV. Formation of the phthalans is analogous to isochroman formation, which involves a free cyclobutadiene. The carbonyl compounds, however, cannot come from the free cyclobutadiene since carbonyl insertion must take place on the metal.

It is known that such insertion reactions require a sigma bonded carbon on the metal. This suggests the mechanistic scheme shown in Figure 21. When (61) was decomposed K_r was much greater than K_t and the only product was the isochroman. The shorter carbon chain on (79) makes trapping (K_t) competitive with release (K_r), allowing formation of (94). Green and co-workers[49] have isolated neutral complexes with similar structures to (94). Once formed, reductive elimination of (94) to (81) is inhibited by the ring strain of the product Dewar-benzene. However, carbonyl insertion to give (95) allows reductive elimination to the less strained (84) instead. Weissberger[50] has

Table IV. Summary of Product Yields for Decompositions of (79a) and (79b)

Complex	Run Number	% Yields 		Other[a]
(79a)	1[b]	55	23	22
	2[b]	60	20	20
R = H	3[b]	54	7	39
	4	75[g]	18[g]	7[h,g]
	5[c]	83	13	4
(79b)	6[d]	75[f,g]	21[g]	--[e] 4[g]
	7	53	17	18[e] 12
R = CH_3	8	58	15	25[e] 2

a) Unless otherwise noted the other products are assumed to be various dimers and polymers and were not isolated.

b) These runs were done on ~.5 g of complex each and the % yields were not as carefully determined as in subsequent runs.

c) This run used 1.3 g of complex and great care was taken to get accurate (±5%) yields.

d) This run was done under carbon monoxide instead of nitrogen atmosphere.

e) These yields are of a third, unidentified product which may come from further reaction of the phthalan (82b).

f) This includes a 29% yield of the lactone (86b) which is formed by further oxidation of 82b).

g) These are glc yields. All other yields are for isolated products unless labeled OTHER (see a).

h) This is undecomposed starting complex.

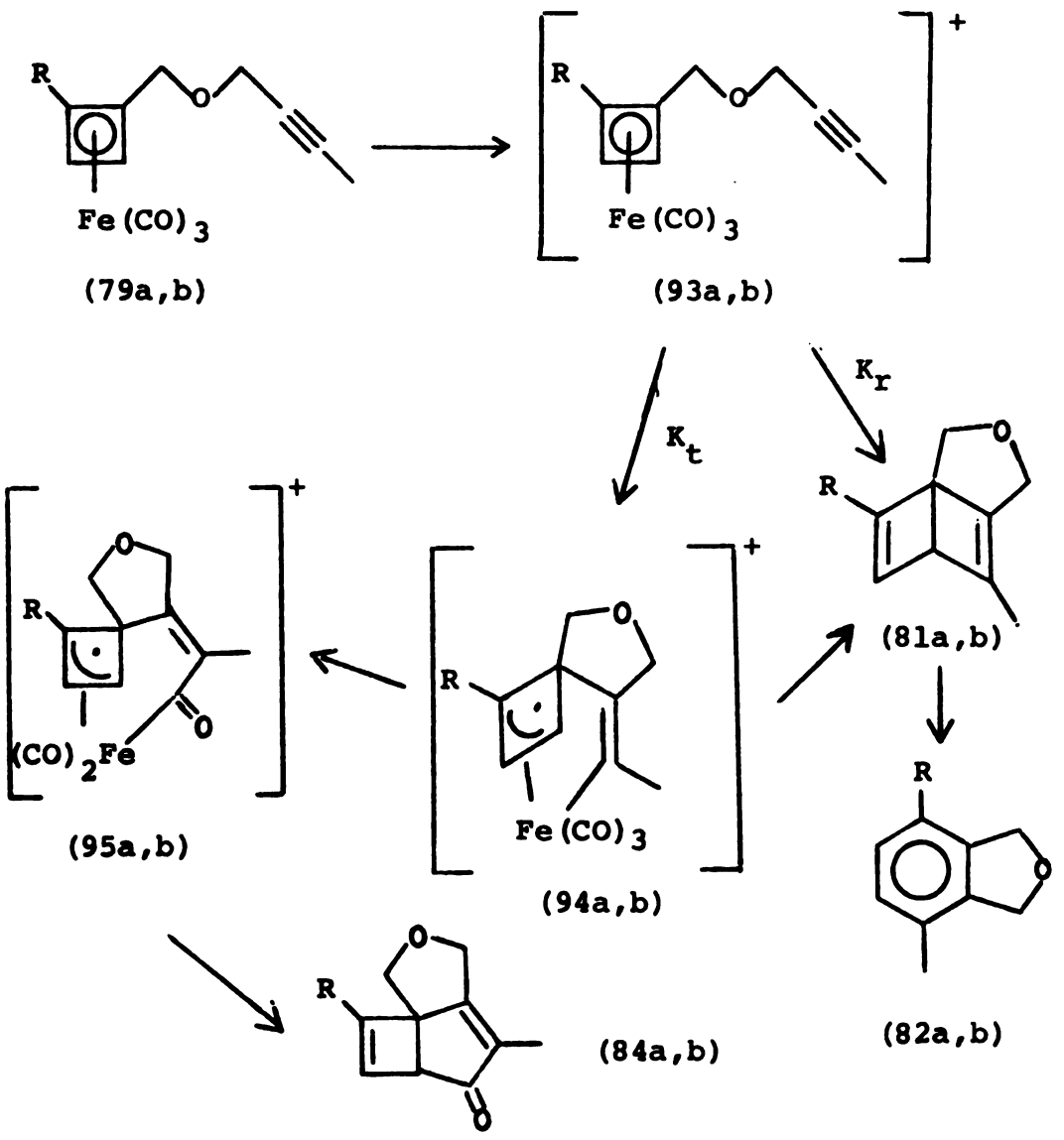


Figure 21. A possible mechanism for the formation of (84a) or (84b) from (79a) or (79b).

proposed neutral intermediates similar to (95) in the formation of carbonyl insertion products with iron pentacarbonyl catalyst.

If this mechanism is correct, it should be possible to obtain optically active (84b) from optically active (79b). Such a result would also support claims that the failure of trapping experiments to give optically active adducts from optically active complex indicates the presence of a free cyclobutadiene intermediate.

V. Alternate Routes to (55b)

The final goal of this project was to synthesize and oxidatively decompose optically active (79b) to see if optically active product (84b) results.

In order to have enough optically active complex to work with, large amounts of racemic (55b) were required. The previous synthesis not only gave poor yields of (55b), but also used large quantities of methyl-2-butynyl ether. Both the ether and the alcohol from which it is made had become much more expensive than when the synthesis was designed. In addition, it is difficult to scale up the synthesis beyond about a one gram yield of complex. Since (59), (60b) and (55b) are all air sensitive and difficult to store, it is hard to build up the large amounts needed. It was, therefore, necessary to develop a new synthesis which would give (55b) in large quantity.

It was decided to base the synthesis on a preparation of methyl hydrogen-1,2-dicarboxylate cyclobutadienyliron

tricarbonyl (101) worked out by Brian Roberts[51] and co-workers. The reaction sequence which was followed is shown in Figure 22. In almost all cases Roberts's procedures were followed with only minor changes. All reactions were done under nitrogen or argon.

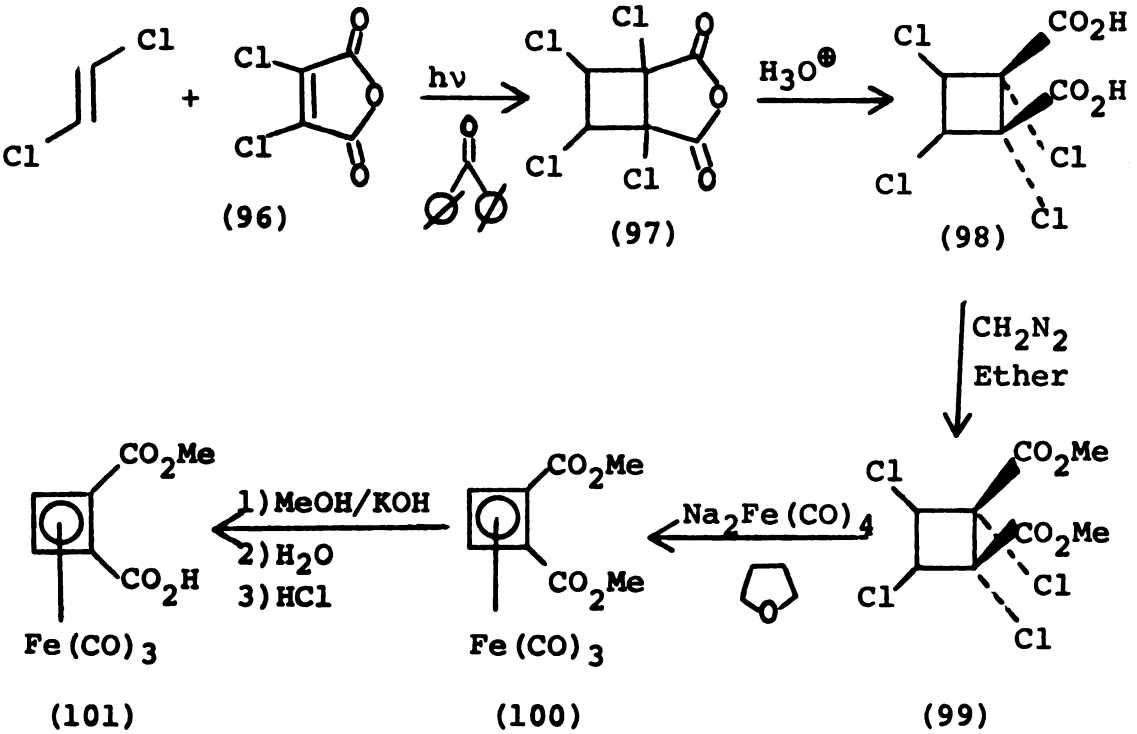


Figure 22. Reaction sequence for the preparation of (101) using Roberts's procedures.[51]

Photolysis of a dioxane solution of trans dichloroethylene and dichloromaleic anhydride (96) for 64 hr using benzophenone as a sensitizer gave (97), which was not

isolated. The reaction mixture was treated with 0.1% hydrochloric acid solution at 70° to hydrolyze the anhydride and give (98). The crude diacid was esterified with diazomethane at 0°. Recrystallization from ethanol water gave (99) as white crystals in 47% yield based on starting dichloromaleic anhydride. Compounds (96) through (99) are air and water stable and therefore are easy to store.

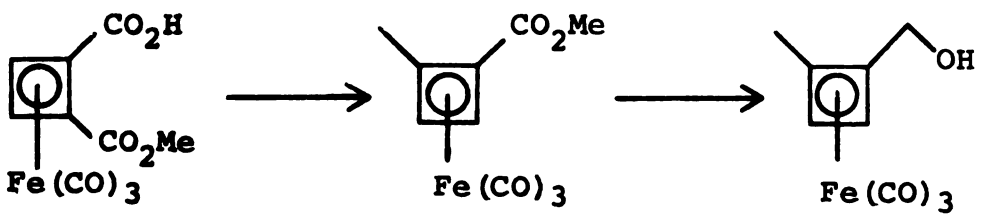
The transformation of (99) into the cyclobutadiene complex (100) was carried out using a slight modification of Roberts's procedure. Instead of dianion prepared from sodium mercury amalgam and iron pentacarbonyl, Collman reagent was used. Using Roberts's work-up gave a 37% yield of air stable yellow crystals (100) after recrystallization from hexane. The physical data agreed with those reported by Roberts.

The half hydrolysis was carried out using methanolic potassium hydroxide. Up to 95% yields of the crude half acid (101) were obtained, which could be further purified by sublimation (15% lower yields). Subsequent reactions were not improved by the sublimation, so that step was usually left out.

It should be noted that since iron carbonyls are somewhat light sensitive, the half hydrolysis and all subsequent reactions were done in a flask wrapped in aluminum foil to exclude light. All products were stored in the

dark. The half acid is air stable, making it possible to build up large amounts of it. It now remained to find a simple way to convert the half acid to the ether (55b).

The half acid was chosen as an intermediate target on the assumption that the acid could be reduced to a methyl group while leaving the ester unchanged. Subsequent hydrolysis of the ester would then allow it to be reduced to the alcohol, giving compound (103) as shown in Figure 23.

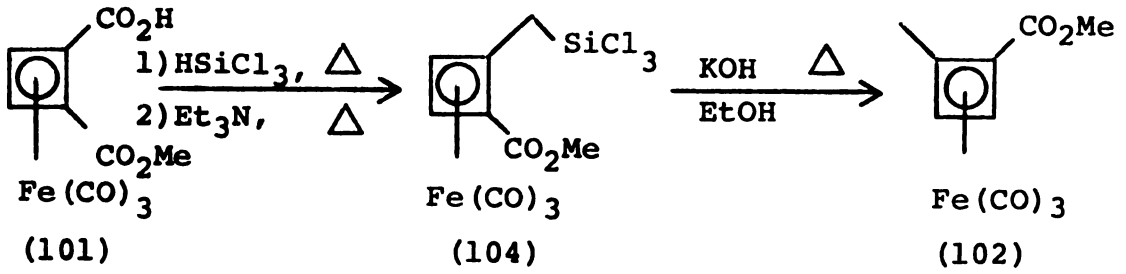


(101) (102) (103)

Figure 23. Proposed plan for making (103) from (101).

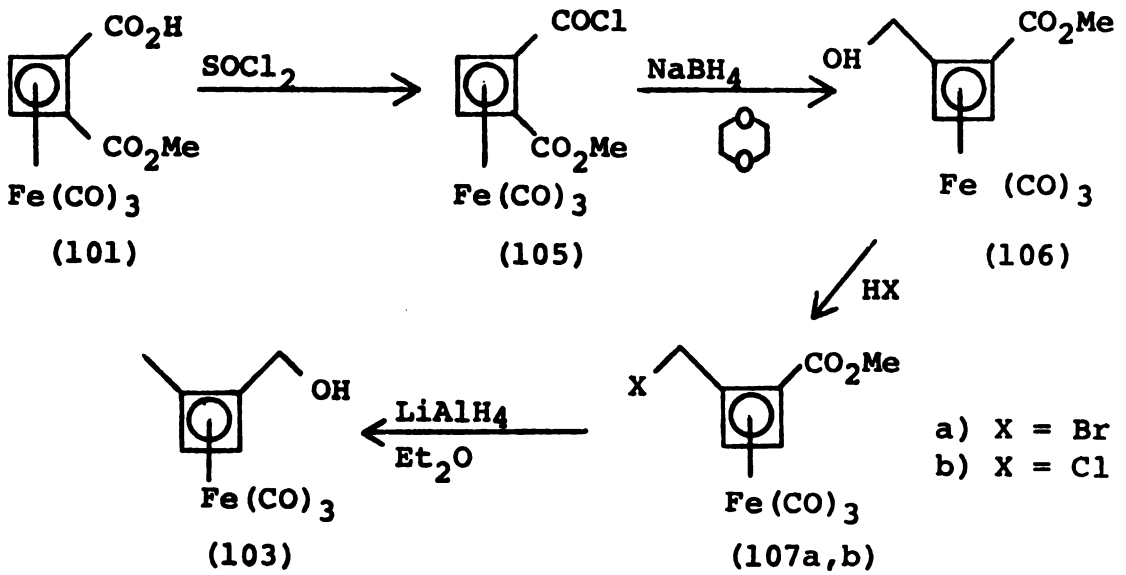
Treatment of (103) with first hydrobromic acid and then sodium methoxide was previously shown by Grey[35] to give (56b) and then (55b).

The first procedure chosen for conversion of the half acid to (102) was that of Benkeser and Ehler[52] for taking aromatic acids to toluenes as shown on the following page. The silyl compound (104) was prepared by treating the half acid first with trichlorosilane and then with triethylamine.



The crude silyl compound (104) was neither characterized nor purified, but was treated directly with ethanolic potassium hydroxide. An nmr spectrum of the worked-up product showed none of the peaks expected for the methyl compound (102), nor could any of the desired product be found.

At this point a second approach, shown below, was introduced.



The procedure for the first step had already been worked out by Roberts[51] and went in 80% yields after recrystallization. The subsequent steps appeared to be straightforward, but it was soon apparent that they were not.

Treatment of half acid (101) with thionyl chloride and pyridine gave up to 91% yields of crude (105). Recrystallization from hexanes gave up to 80% yields of air stable yellow orange crystals. Both crude and recrystallized (105) gave similar results in subsequent steps, so usually crude material was used.

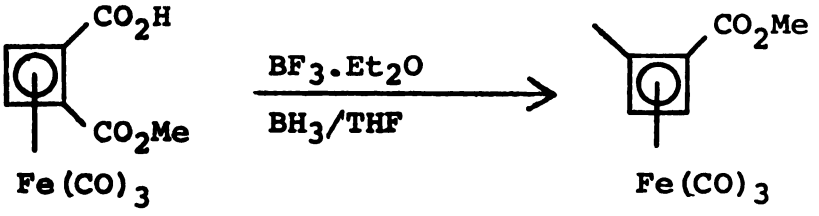
After some trial and error, the acid chloride (105) was reduced to the alcohol (106) by treatment with sodium borohydride. This gave up to 65% yields of yellow oil.

The nmr spectrum of (106) shows a peak at δ 3.60 for the methyl hydrogens. The two methylene hydrogens give a singlet at δ 4.17. The two ring hydrogens give sharp singlets at δ 4.41 and δ 4.50. The alcohol hydrogen gives a broad peak in the δ 4.6 to δ 4.8 region which disappears when deutero water is added.

The bromide (107a) was prepared by treating a benzene solution of (106) with hydrobromic acid. The crude bromide was not characterized but was dissolved in ether and added to a lithium aluminum hydride suspension. Analysis of the crude product by nmr failed to detect any of the desired alcohol (103). Further work-up by silica gel column and TLC gave the same result.

A second attempt was made using the chloride (107b) prepared by shaking a methylene chloride solution of (106) with hydrochloric acid. What was assumed to be (107b) was dissolved in ether and added to lithium aluminum hydride. As before none of the desired products could be detected.

Since none of these reductions gave satisfactory results, it was decided to return to the reaction sequence outlined in Figure 23; and try using a procedure developed by Roberts[51] for reducing the diacid to the dimethyl compound (111) to reduce the half acid (101) as shown below.



(101) (102)

The half acid (101) was dissolved in borontrifluoride etherate and treated with borane in tetrahydrofuran. An nmr spectrum of the product showed two methyl peaks, one for the ester and one for the ring methyl, indicating that reduction took place.

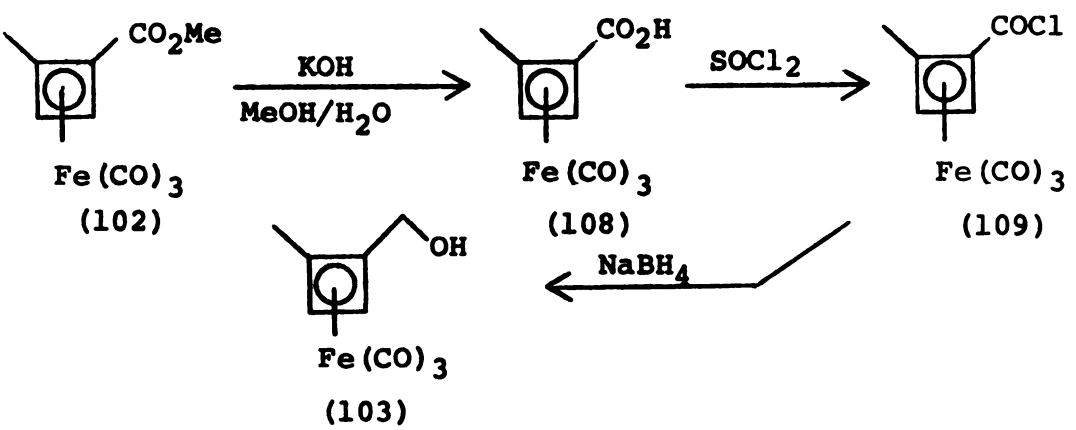
When the same procedure was used on the half acid chloride (105), reduction also took place. At first it

appeared from nmr spectra of the products that the acid and the acid chloride were being reduced to different compounds. However, when the work-up was modified to include vacuum distillation of the products prior to putting them through a column, the misleading nmr peaks disappeared. Using the best procedure both (101) and (105) gave up to 91% yields of the air sensitive yellow oil (b.p. 50-67° at 0.3 mm).

The nmr spectrum of (102) showed a singlet at δ 1.95 for the three ring methyl hydrogens. The three methyl ester hydrogens gave a singlet at δ 3.65. The two ring hydrogens gave singlets at δ 4.27 and δ 4.39 respectively.

The mass spectrum showed a parent peak at m/e 264 as well as peaks for the successive loss of three carbonyls as expected.

After reducing one ester to a methyl group, it still remained to reduce the other ester to an alcohol. It was hoped that the reaction sequence which had previously led to (106) would now give (103) as shown below.



The hydrolysis of (102) was carried out by stirring the complex in a solution of potassium hydroxide, methanol and water. Acid work-up gave up to 74% yields of (108) as yellow crystals.

The nmr spectrum of (108) showed a singlet at δ 1.97 for the three methyl hydrogens. The two ring hydrogens gave singlets at δ 4.31 and δ 4.36 respectively. The acid proton gave a broad singlet at ~δ 10.7.

The acid was converted to the acid chloride (109) using the same procedure which previously gave (105) from (101). The crude acid chloride was then reduced with sodium borohydride following the same procedure which reduced (105) to alcohol (106). The crude product was used without having been put through a silica gel column, however.

An nmr spectrum of the crude product had the expected peak for the alcohol. Unfortunately, all subsequent attempts to convert alcohol (103) prepared in this manner to the ether (56b) or the amine (115) used in the resolution (see next section) gave unsatisfactory mixtures of products.

Several attempts to prepare the ether <u>via</u> the bromide, using the previously described procedure developed for this transformation, shown in Figure 24, gave mixtures of products which included ester (102), possibly some coupling products (110), and only a small amount (less than 15%) of the ether (55b).

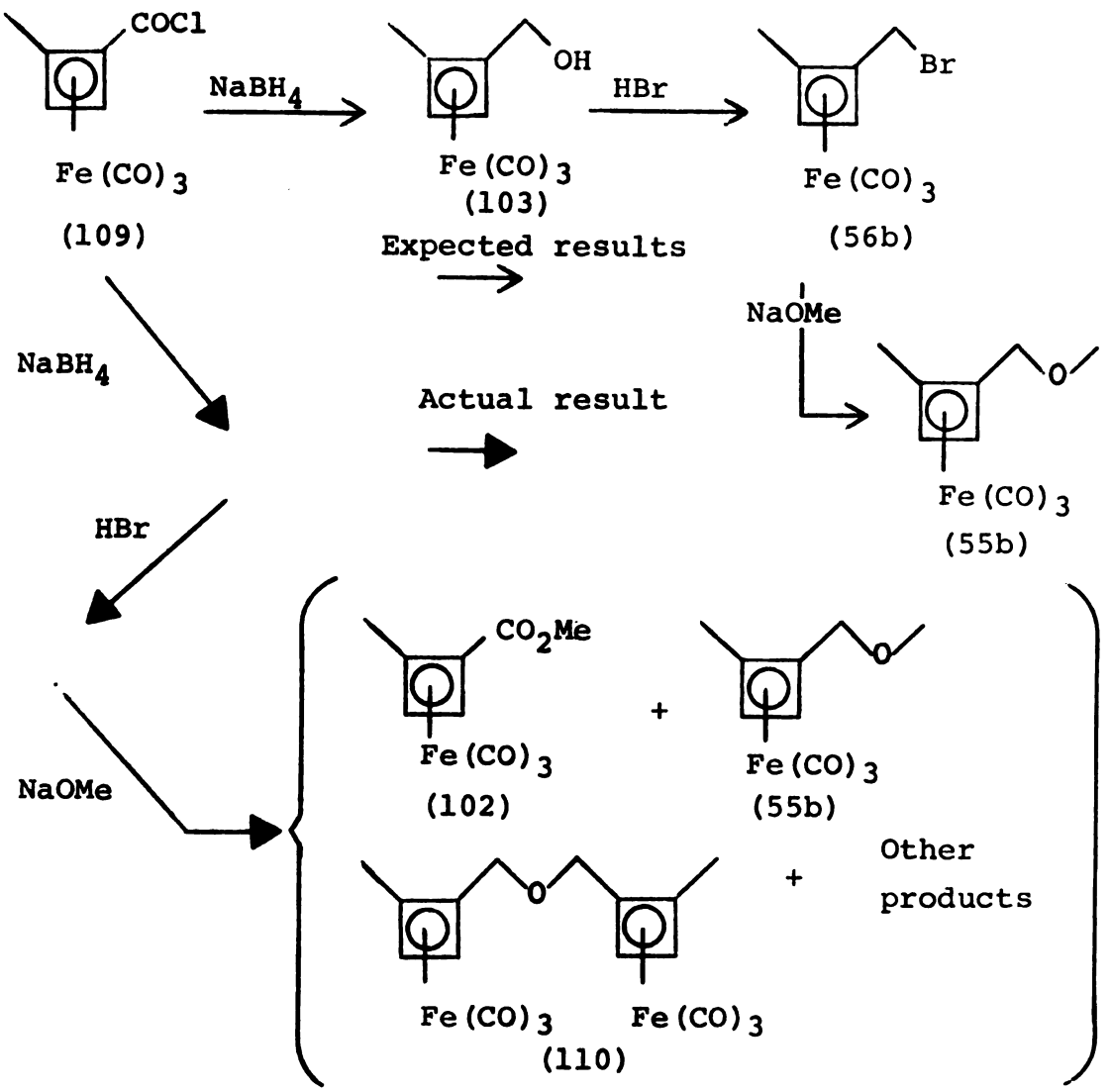


Figure 24. Proposed sequence for the preparation of (55b) from (109), and actual result.

Attempts to separate these products by distillation were unsuccessful, and since the yields of ether were very low, only a limited effort was made to continue in this line.

An attempt was also made to convert (103) to the amine (115) *via* the bromide, using a procedure developed by Grey[35] and used in the resolution (see next section). Although this procedure gives good yields of amine when used on bromide obtained from the ether (55b) it failed to give any amine when used on "bromide" made from the sodium borohydride reduction product.

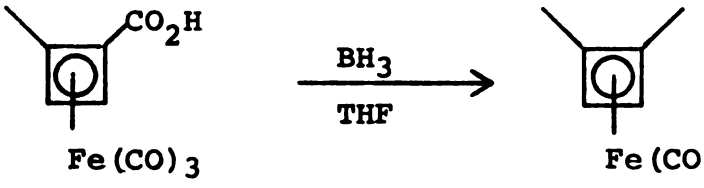
One possible explanation for this problem is that the acid chloride may be only partly reduced by the borohydride. The acid chlorides (105) and (109) are both amazingly stable to normally destructive conditions such as water. Any unreduced (109) would likely survive the various work-ups and react with the sodium methoxide to regenerate the ester (102). The acid chloride may also slowly react with the alcohol (103) to give an ester with two cyclobutadiene rings.

These and other possibilities probably result from incomplete reduction. Therefore an alternative reducing agent was again sought.

Borane is known to reduce acids to alcohols, so that was tried next. When acid (108) was treated with borane in tetrahydrofuran the isolated yellow oil gave only two nmr peaks, sharp singlets, at δ 1.70 and δ 3.79. The ratio of peak areas was 3:1 respectively, making it likely that this was the dimethyl compound (111) as shown on the following page.

On the assumption that the reaction had gone too far, the reaction was repeated with stirring for one hour at room temperature instead of overnight. The results were as before.

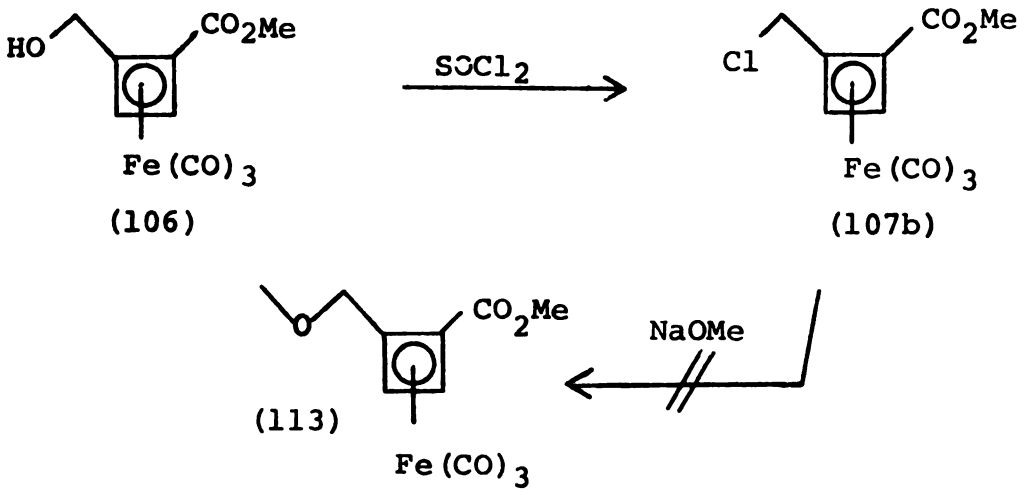
A mass spectrum of the product confirmed that it was the dimethyl complex (111), showing a parent peak at m/e 220 and the characteristic peaks for successive loss of three carbonyls.

(108) 

(111)

Apparently the electron withdrawing ester group stabilizes the alcohol in (106) and prevents it from being reduced by mild reducing reagents. When the second reduction is carried out, there is no longer any electron withdrawing group to prevent further reduction of the alcohol. Therefore, any reagent which is strong enough to reduce the acid or acid chloride in (108) or (109), will probably also reduce the alcohol in (103) and give only (111) as the product.

To get around this problem, an attempt was made to convert the alcohol in (106) to the ether (113) by first making the halide (107) and treating that with sodium methoxide as shown on the following page.

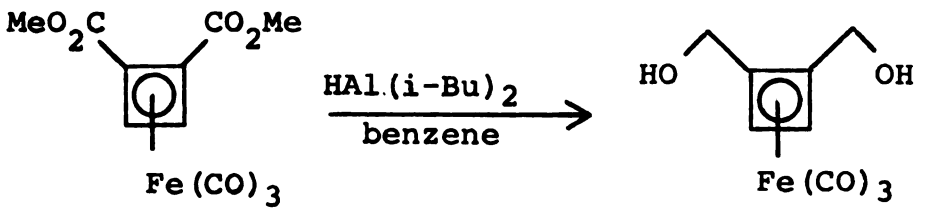


The alcohol (106) was treated with thionyl chloride at room temperature. The crude chloride was then treated with sodium methoxide and stirred overnight. After work-up, none of the desired ether (113) could be detected by nmr or otherwise identified.

Following the above attempt, attention was again directed towards reducing (102) to (103) as in Figure 23. Strong reducing agents, such as lithium aluminum hydride, had destroyed everything, while weak reagents like sodium borohydride gave only partial reductions. It was still possible that if the powerful aluminum reagent were weakened by replacing some of the hydrides with bulky alkyl groups, an intermediate strength reagent would be formed which would do the reduction.

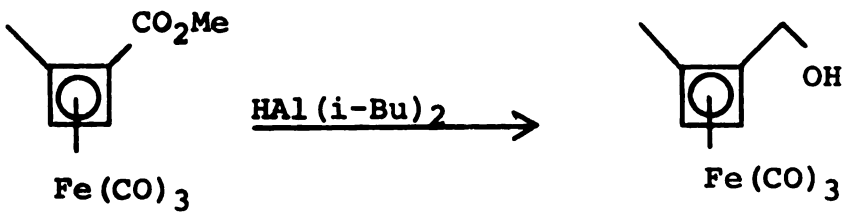
Similar difficulties with lithium aluminum hydride were reported by Roberts[51] and co-workers; however, they

were able to reduce the diester (100) to the dialcohol (114) with diisobutylaluminum hydride as shown below.



(100) (114)

It was therefore decided to try reducing (102) using Roberts's procedure as shown below.



(102) (103)

When a benzene solution of (102) was treated with diisobutylaluminum hydride in hexane at 0° and then warmed to room temperature, several products were obtained. An nmr spectrum showed the presence of starting ester (102) as well as the desired alcohol (103) and some dimethyl compound (111). When the mixture of products was treated first with hydrobromic acid and then, following the usual work-up,

with sodium methoxide, the alcohol present was converted to the desired ether (55b). This was the first time the ether had actually been made using the new route.

Unfortunately, the mixture meant that the rate of reduction of the alcohol was comparable to the rate of reduction of the ester. In order to reduce the ester without reducing the alcohol, the reaction was stirred at 0° for an hour, and then quenched without having been warmed to room temperature. This still gave some unreduced ester, but no dimethyl compound. It was also found that using hexane as the solvent instead of a benzene hexane mixture, gave a cleaner reaction and slightly higher yields.

In order to assure complete reduction of the ester, subsequent runs were allowed to stir for from four to six hours at 0° before being quenched. This gave up to 95% yields of crude alcohol (103) as an air sensitive yellow oil. Treatment of (103) with hydrobromic acid gave the bromide (56b) which could be readily converted into either the ether (55b) or the alkyne substituted complex (79b). A summary of the final reaction sequence used is given in Figure 25, on the following page.

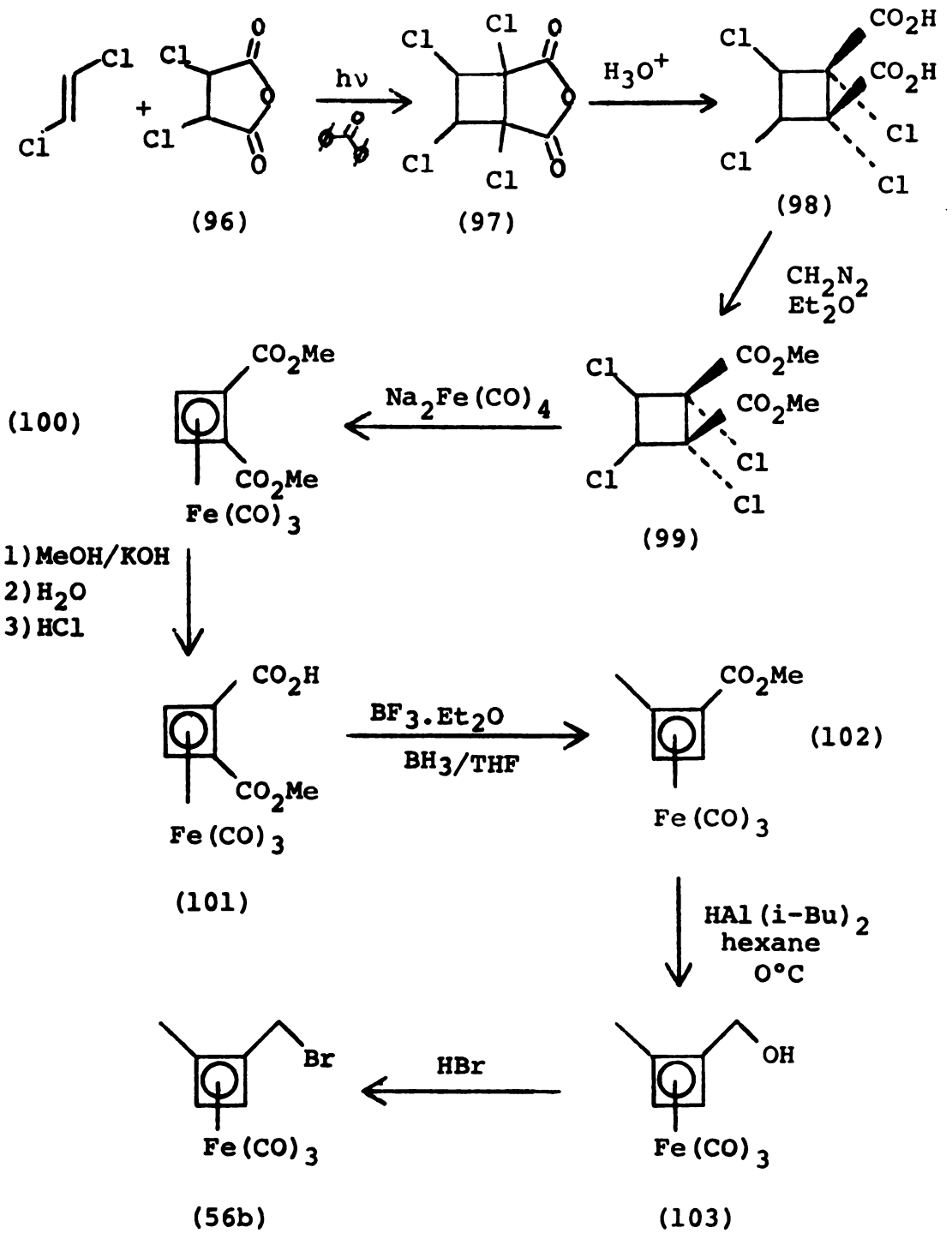


Figure 25. A summary of the total reaction sequence for the preparation of (56b) starting with dichloroethylene and (96).

VI. Synthesis of Optically Active Complex (*79b)

Using the new synthesis based on Roberts's work, it was possible to build up large amounts of the alcohol (103) for conversion to the bromide (56b). The bromide was resolved following the procedure developed by R. Grey,[35] shown in Figure 26, and then converted to (*79b).

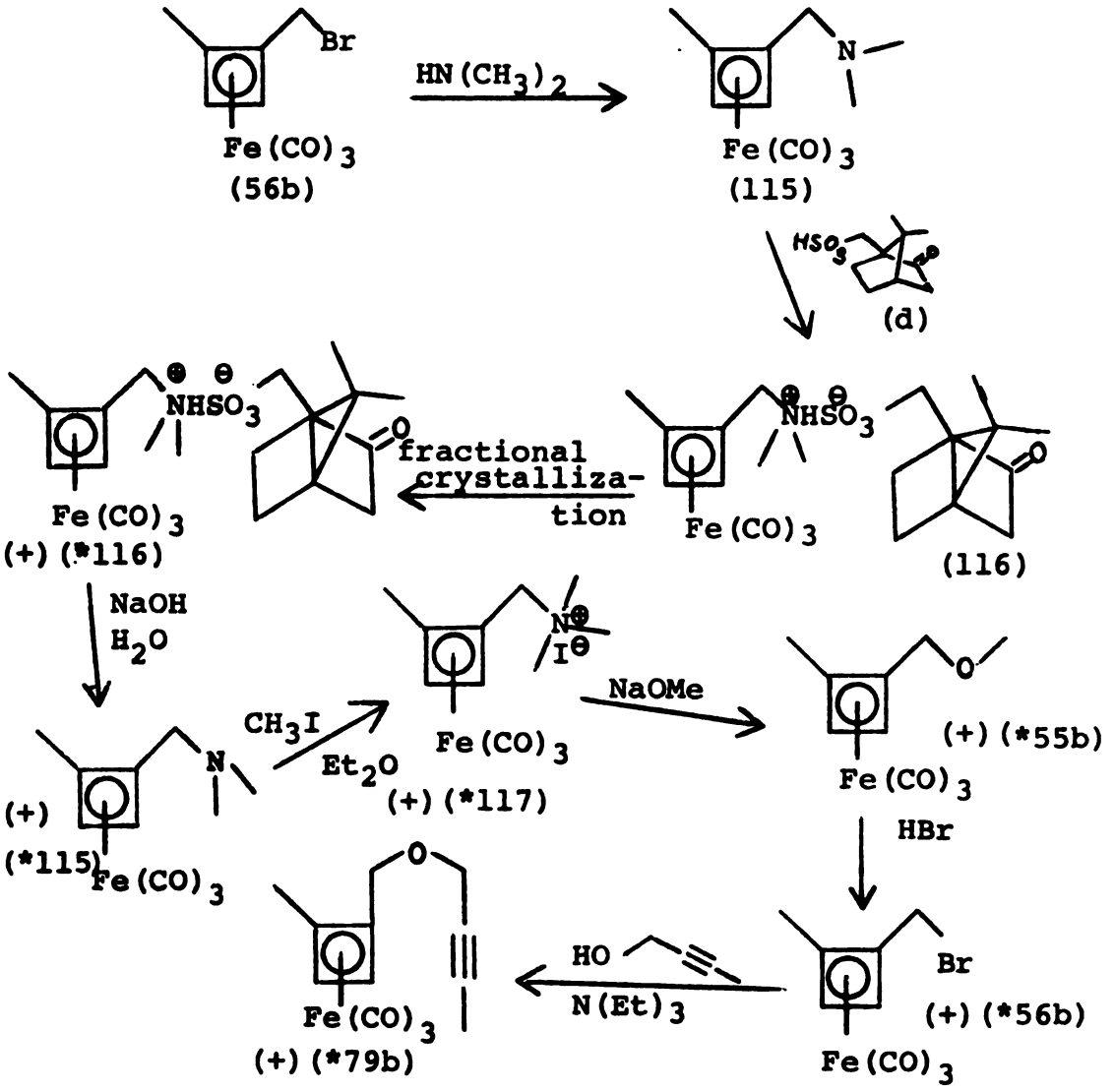


Figure 26. Summary of Grey's resolution procedure.

Treatment of the alcohol (103) with hydrobromic acid, followed by the usual work-up gave the bromide (56b) in good yield. Treatment of the bromide solution with dimethylamine gave up to 91% yields of crude amine based on starting alcohol.

The amine salt (116) was prepared by adding the crude amine to a hot solution of ethanolic d-10-camphorsulfonic acid. Crystals of the positive rotamer were driven out of solution by addition of ether followed by gradual cooling. In more dilute solutions crystals only formed after being cooled in the refrigerator. The isolated crystals were then treated with aqueous sodium hydroxide to regenerate the free amine (+) (*115). Similar treatment of the remaining solutions gave the negative amine.

In order to determine the optical purity of the samples it was necessary to convert the amine to the ether (*55b), for which a value for the specific rotation had been determined by Grey.[35] Treatment of the amine in ether with methyl iodide gave salt (*117) as a white precipitate. Addition of methanol dissolved the salt and subsequent addition of sodium methoxide allowed the methoxide to displace the amine, giving (*55b) in 95% yield overall from the amine (*115).

Optical rotations were measured using a Perkin Elmer 141 Polarimeter spectrophotometer. The observed rotations

for samples of amine and ether, along with the corresponding values calculated for their optical purity are given in Table V. Most of the rotations were done on crude (undistilled) samples. For these samples the true optical purity is higher than the calculated value given in the table.

Table V. Observed Rotations and Calculated Optical Purities for Samples of (*55b) and (*115)

Sample number	Amine Degrees Observed Rot. @ 578 nm	mg.	Ether Degrees Observed Rot. @ 578 nm	mg.	Percent optical purity[b]
1	(-) 0.153	180	(-) 0.115	260	24
2	(+) 0.088	100	(+) 0.036	53.3	36.5
3	(+) 0.045	94.6			
4	(-) 0.010	94	(-) 0.021	86.2	13.2
5	(-) 0.007	40	(-) 0.027[a]	46.6	31.3
2 & 3 & 4 combined			(+) 0.039	99.9	19.5

[a]Sample was vacuum distilled.

[b]$O.P. = \left(\frac{\text{rotation}}{.185}\right)\left(\frac{100}{\text{mg in sample}}\right)$ based on $[\alpha]^{25}_{578} = 11.2°$ for (*55b) [35]

Optically active (*79b) was prepared from the ether (*55b) as previously described for the racemic complex.

The optical purity of (*79b) was assumed to be identical to that of the (*55b) from which it was made. The optical purity calculated for sample number 5 in Table V is

much more reliable than the values based on rotations of crude samples. Both the (+) and (-) samples of (*79b) were vacuum distilled and rotations were observed. This allowed back calculation of the optical purity of the (+) sample based on the more reliable data for distilled (-) sample, rather than on the crude (+) ether data. The observed rotations and optical purity for (*79b) and (*55b) are given in Table VI. Both the (+) and (-) complex (*79b) were used about one-third optically pure to facilitate subsequent determinations of the optical purity of the decomposition products by nmr shift studies.

Table VI. Observed Rotations and Calculated Optical Purities for Samples of (*55b) and (*79b)

Sample number	(*55b) Degrees Observed Rot. @ 578 nm	mg	% O.P.	(*79b) Degrees Observed Rot. @ 578 nm	mg	% O.P.
1	(-) 0.115	260	24	(-) 0.061	98	24
2 & 3 & 4	(+) 0.039	99.9	19.5	(+) 0.051	57.6	32.2
5	(-) 0.027	46.6	31.3	(-) 0.052	60.3	31.3

VII. Decomposition Studies on Optically Active Complex (*79b)

The decomposition of optically active (*79b) was carried out three times, using Ce IV as previously described. In all cases optically active product (*84b) was obtained. The results and sample data are summarized in Table VII.

Table VII. Observed Rotations and Calculated Optical Purities from Samples of (*79b) and (*84b)

Source of (*79b)[a]	G of (*79b)	% O.P.[b] ± 5%	Mg (*84b) ± 2 mg	Rotation @ 578 nm ± 0.005°	% O.P.[c] ± 2.0%
1	0.24	(-) 24	14	(-) 0.205	----
2 & 3 & 4	0.63	(+) 32.3	52	(+) 1.105	33
5	0.54	(-) 31.3	50	(-) 0.892	30

[a]Same samples as listed in Tables V and VI.
[b]Based on optical purity of starting ether (*55b).
[c]Based on cut and weight analysis of shift study.

In order to determine the optical purity of the product, nmr shift studies were done using the chiral shift reagent tris[3-heptafluorobutyryl-d-camphorato]europium III.

First, as a standard, a racemic sample of (84b) was treated with the chiral shift reagent in 5 mg portions. It had been hoped that the methyl peaks for the two enantiomers would separate sufficiently to allow

determination of their relative amounts. However, the methyl peaks did not shift enough for separation to occur. Instead it was the methylene hydrogens responsible for the AB quartet which split into different peaks for the two enantiomers. This meant that the optical purity of the products could be determined, but only for a larger sample than would otherwise have been needed. Instead of having a single three hydrogen peak split in two, there were four peaks totaling two hydrogens, with each peak split into two. The actual peaks measured for each enantiomer corresponded to less than half a hydrogen each, instead of one and a half hydrogens each.

The first decomposition, done on 0.24 g of (-) complex, gave only 14 mg of (*84b). This was too little to obtain a meaningful number for the optical purity. The peaks for the positive rotamer were scarcely larger than the noise in the nmr spectrum. It could be seen, however, that the negative rotamer was shifted the furthest and was in excess.

In order to verify the assignment of the downfield peak to the negative rotamer, and in addition to obtain values for the optical purity of the product, two more decompositions were carried out using larger samples with both the positive and the negative rotamer in excess.

Decomposition of the 0.63 g of (+) complex gave 52 mg of isolated (*84b). Selected nmr spectra showing the

course of the chiral shift study are presented in Figure 27. The optical purity was determined by cutting out and weighing the peaks for the two enantiomers from six different spectra. The spectra used in this way were run on expanded scale with increased amplitude compared to those in Figure 27. They were selected on the basis of how well separated the enantiomeric peaks were. Sharpness and clarity of spectrum was also a criterion. The average of the six spectra gave an optical purity of 33 $\pm$ 2%. Within experimental error this is the same as the 32.3% optical purity of the starting complex, indicating complete retention of configuration in the decomposition.

Decomposition of the 0.54 g of (-) complex gave similar results. The average of five spectra gave an optical purity of 30 $\pm$ 2% for the (-) (*84b). As before, this is the same as the optical purity of the starting complex (31.3%) within experimental error. The relative sizes of the shifted peaks were reversed from the previous decomposition. A comparison of the shifted spectra for the plus, minus and racemic samples is shown in Figure 28.

The specific rotation of the product (*84b) was calculated two ways. One way was to assume the decomposition went with 100% retention and that the product therefore had the same optical purity as the starting (*79b). An average of the two large scale samples gave $[\alpha]^{25}_{578}$ = 381 $\pm$ 20°. The other calculation was based on the optical

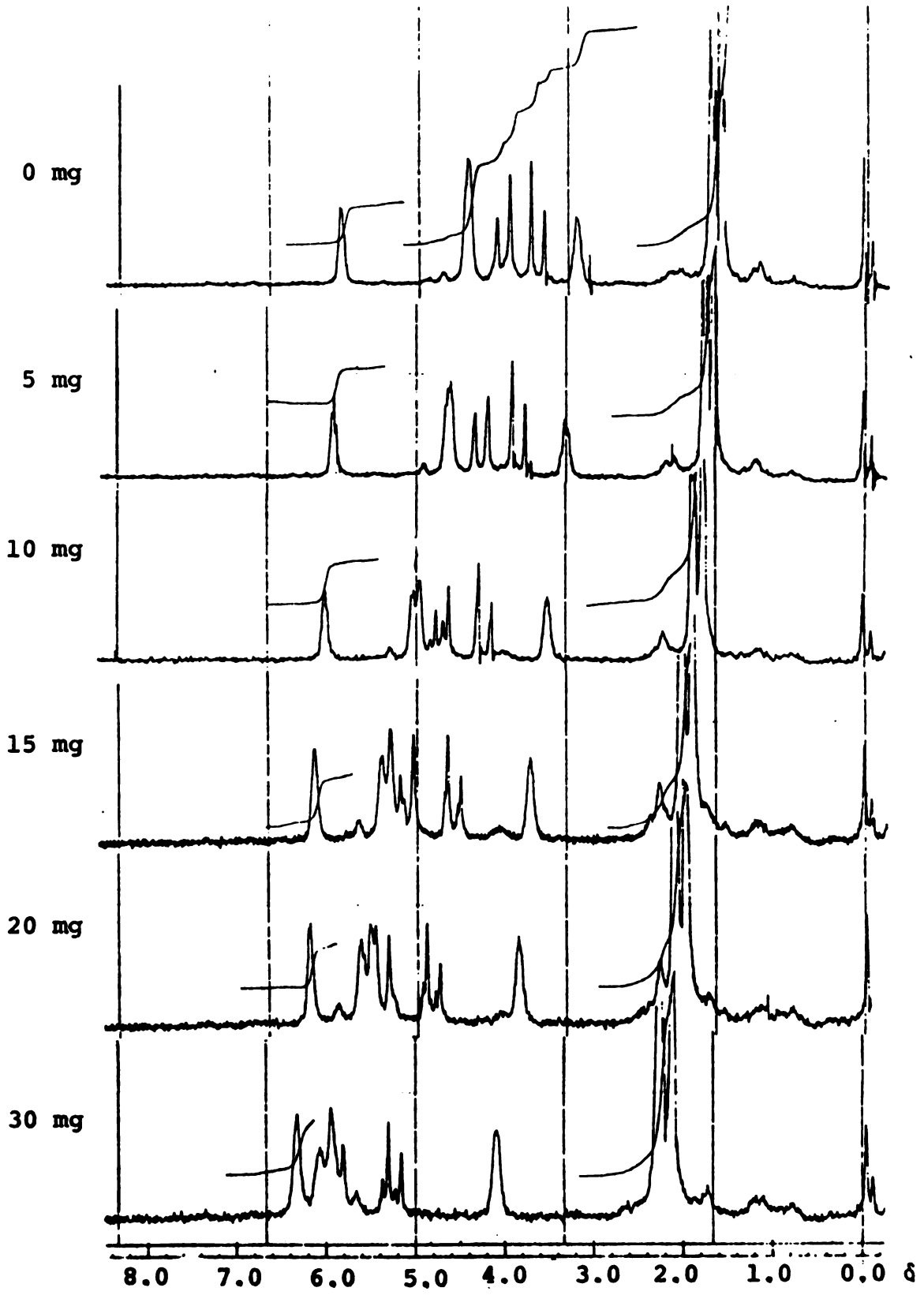


Figure 27. NMR spectra following the course of the chiral shift study as successive 5 mg portions of $Eu(hfbc)_3$ are added to (+) (*84b).

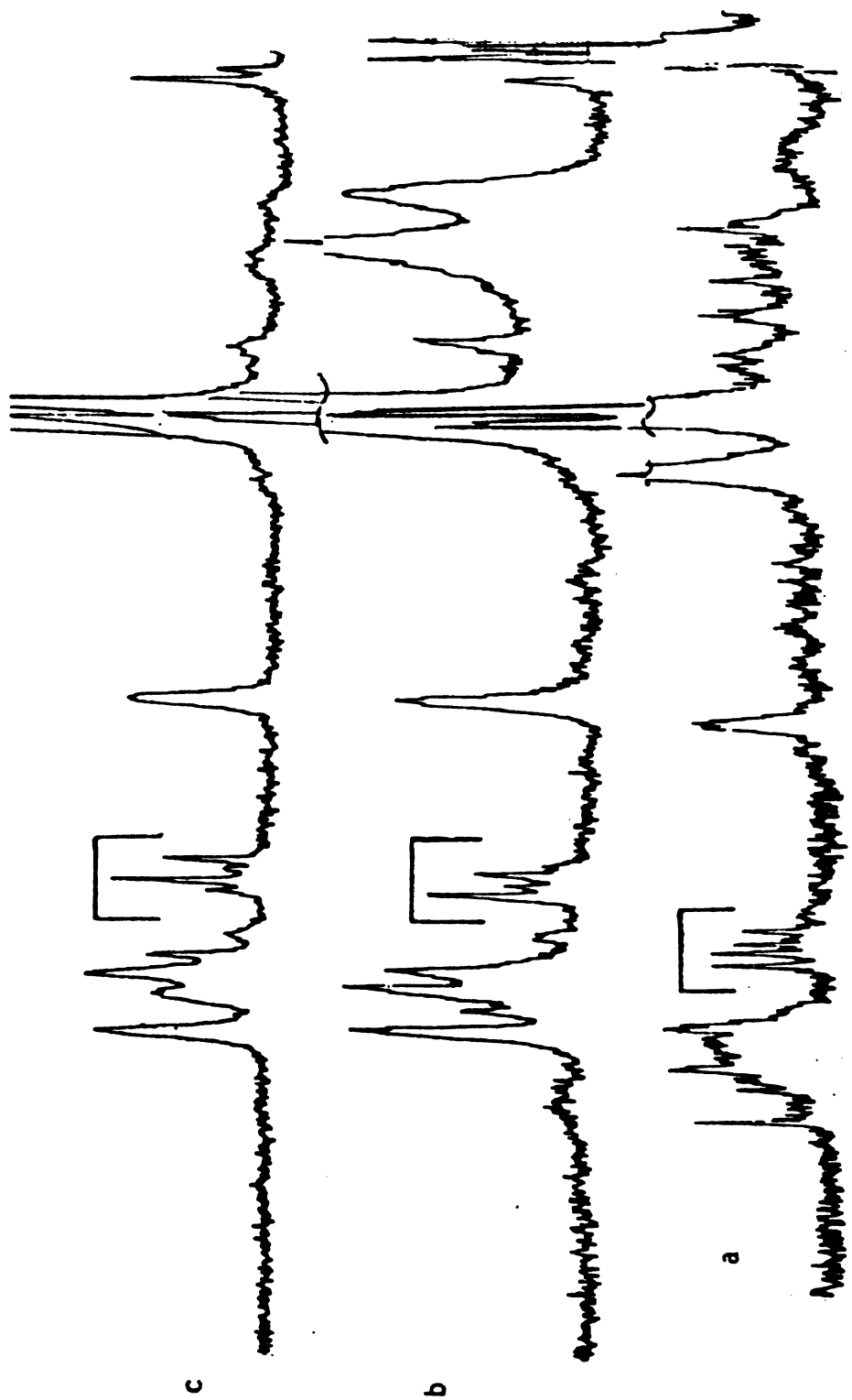


Figure 28. Optishifted spectra of (84b). The bracketed peaks indicate the relative amounts of the two enantiomers present in samples of (a) racemic (84b), (b) (-) (*84b) and (c) (+) (*84b) treated with $Eu(hfbc)_3$.

purities obtained from the shift studies and gave $[\alpha]_{578}^{25} = 384 \pm 20°$.

The finding that decomposition proceeds with retention of configuration supports the mechanistic scheme previously outlined in Figure 21. It also supports earlier findings that racemic products result from the intermediacy of free cyclobutadienes.

EXPERIMENTAL

General Procedures

All melting points, determined on a Thomas Hoover melting point apparatus, are uncorrected.

Ultraviolet spectra were recorded on a Unicam SP.800 spectrophotometer; samples were in 1 cm quartz cells. Infrared spectra were recorded on a Perkin Elmer 237B grating spectrophotometer and a Unicam SP.200 spectrophotometer. A Varian T-60 spectrometer was used to obtain Hnmr spectra. A Varian CFT-20 spectrometer was used to record C-13 nmr spectra. All Hnmr spectra are recorded as δ values in ppm downfield from an internal standard of tetramethylsilane. Mass spectra were obtained by Mrs. L. Guile on a Hitachi Perkin Elmer RMU-6 mass spectrometer.

Polarimeter measurements were obtained using a Perkin Elmer 141 Polarimeter spectrophotometer; samples were contained in 1 dm (6 ml) quartz cells.

All gas chromatographs were obtained using a Varian Aerograph Model 90-P gas chromatograph with ¼" by 6 or 8' 5% SE-30 vpc columns.

Photolyses were carried out using a Hanovia 450 watt mercury vapor lamp (quartz) unless otherwise noted.

All reactions and distillations were done under nitrogen unless otherwise noted. Reactions involving iron complexes were protected from light with aluminum foil. Ether, benzene, tetrahydrofuran and dioxane were distilled from sodium benzophenone ketyl under nitrogen before use. Hydrocarbon solvents were degassed by bubbling nitrogen through a gas dispersion tube. Boron trifluoride was distilled from calcium hydride. Thionyl chloride was distilled from triphenyl phosphite. Other reagents were used directly off the shelf unless otherwise noted.

Chloroethylene Carbonate (58)[35]

A three liter three neck round bottom flask, fitted with a mechanical stirrer, condensor and gas inlet tube, was filled with 500 g (5.7 m) of ethylene carbonate and 500 ml of carbon tetrachloride. Chlorine gas was rapidly bubbled into the stirring solution and the reaction mixture was irradiated with a Hanovia ultraviolet quartz lamp until no more ethylene carbonate remained (as determined by nmr). The reaction mixture was condensed and distilled, yielding 562 g (81%) of the clear liquid chloroethylene carbonate: b.p. 72-78°C (0.6 mm) (Lit.[39] 106-107°C (0.10 mm)); nmr in agreement with reported values.[35]

Vinylene Carbonate (59)[35]

A three liter three neck round bottom flask, fitted with a mechanical stirrer, addition funnel, and a reflux condenser with attached nitrogen line, was filled with 210 ml (2.56 m, 312 g) of chloroethylene carbonate and a new can of anhydrous ether (~500 ml). The solution was brought to reflux and 430 ml of triethylamine (distilled from barium oxide) was added dropwise over a 6 hr period. The reaction was refluxed for an additional 40 hr, during which another 100 ml of ether was added to make up for evaporation. After cooling to room temperature the reaction mixture was filtered and the brown precipitate was washed repeatedly with benzene and ether. The filtrate and washings were condensed and distilled (under nitrogen to prevent polymerization) yielding 124 g (56%) of the clear liquid vinylene carbonate: b.p. 37°C (0.5 mm) (Lit.[39] 69-72°C (30 mm)); nmr in agreement with reported values.[35]

1-Methoxymethyl-cis-3,4-dioxycarbonyl-cyclobutene (60a)[35]

A degassed solution of 50 g (0.714 m) of methyl propargyl ether and 33.5 g (0.39 m) of vinylene carbonate dissolved in 1000 ml of acetone was photolyzed for 72 hr using a Hanovia 450 watt immersion lamp. Distillation gave 19.3 g (58%) of recovered vinylene carbonate and 7.2 g (12% based on starting carbonate; 26% based on carbonate

consumed) of (60a)as a yellow oil: b.p. 95-130°C (0.5-0.6 mm); nmr ($CDCl_3$) δ 6.6 (br S, 1, vinyl), δ 5.4 (q, 2, ring), δ 4.10 (d, 2, $C\underline{H}_2O$), δ 3.43 (S, 3, methyl).

1-Methoxymethyl-2-methyl-cis-3,4-dioxy-carbonylcyclobutene (60b)[35]

A degassed solution of 45 g (0.536 m) of 2-butynylmethyl ether and 33 g (0.384 m) of vinylene carbonate in 450 ml of acetone was photolyzed for 14 hr with an immersion lamp (see (60a). Distillation gave 17 g (51%) of recovered vinylene carbonate and 7.7 g (12% based on starting carbonate; 24% based on carbonate consumed) of 60b as an orange oil: b.p. 95-150°C (1.7 mm). Redistillation of the orange oil yielded 7.1 g (11% based on starting carbonate; 23% based on carbonate consumed) of 60b as a yellow oil: b.p. 65-115°C (0.2 mm) (Lit.[35] 106-116°C (0.5 mm)); nmr in agreement with reported values.[35]

1-Methoxymethylcyclobutadienyliron Tricarbonyl (55a) from (60a) and Amalgam[35]

A solution of 2.66 g (0.114 m) of sodium metal in 14 ml (0.95 m) of mercury was treated with 150 ml of dry degassed tetrahydrofuran in a suspension funnel under nitrogen atmosphere. To this was added 6.5 ml (0.048 m) of iron pentacarbonyl in 3 ml portions over a 40 minute period. After the evolution of gas ceased, the excess mercury was removed and another 1 ml of mercury was added and stirred

for a few minutes before it too was removed. The sodium tetracarbonyl ferrate dianion so prepared was added over a 30 minute period to a solution of 5.0 g (0.032 m) of 60a in 100 ml of dry degassed tetrahydrofuran. The solution was stirred for another 5 minutes and then flash distilled at 150°C and 0.5 mm. The flash distillate was condensed and distilled yielding 1.95 g (25%) of (55a) as a yellow oil: b.p. 50-55°C (0.2 mm); nmr ($CDCl_3$) δ 4.20 (S, 2, ring), δ 4.12 (S, 1, ring), δ 3.76 (S, 2, $C\underline{H}_2O$), δ 3.40 (S, 3, methyl).

1-Methoxymethyl-2-methylcyclobutadienyl-iron Tricarbonyl (55b) from (60b) and Amalgam[35]

A tetrahydrofuran solution of tetracarbonyl ferrate dianion was prepared as before (see (55a) prep.) using 2.66 g (0.114 m) of sodium metal, 14 ml (0.95 m) of mercury and 6.5 ml (0.048 m) of iron pentacarbonyl. The dianion solution was added to a solution of 5.0 g (0.0296 m) of 60b in 100 ml of dry degassed tetrahydrofuran over a 40 minute period. The solution was flash distilled at 150°C (0.5 mm). The flash distillate was condensed and distilled yielding 0.686 g (9.2%) of (55b) as a yellow oil: b.p. 53-60°C (0.3-0.4 mm) (Lit.[35] 55°C (0.5 mm)); nmr in agreement with reported values.[35]

Disodium Tetracarbonyl Ferrate (Collman Reagent)

NB: Collman reagent is pyrophoric in air.

Nitrogen or argon from a tank was passed through BASF catalyst (removes oxygen), molecular sieve (removes water) and a solution of benzophenone ketyl (removes oxygen and water) before entering the reaction flask.

A three liter three neck round bottom flask, fitted with a mechanical stirrer, an addition funnel and a reflux condenser attached to an inert gas line, was filled with 18.2 g (0.1 m) of benzophenone and 23.1 g (1.0 m) of sodium metal in 1250 ml of dry degassed dioxane. The solution was stirred and refluxed for 15 minutes past the initial appearance of the blue ketyl color. During the next hour 65 ml (1.0 m) of iron pentacarbonyl (dried over molecular seive) was added dropwise to the refluxing solution to form a white precipitate. The reaction was refluxed for another hour after addition was complete and then allowed to cool overnight. The solvent was removed by forcing it through a gas dispersion tube under pressure. The solid Collman reagent was rinsed twice with 500 ml of petroleum ether (stored over molecular sieve and degassed) and then pumped on under vacuum until no more solvent collected in the traps. The yield was 170 g (79%) of white solid which was stored in a dessicator in a dry box.

1-Methoxymethylcyclobutadienyliron Tricarbonyl (55a) from (60a) and Collman Reagent

A solution of 5.0 g (0.032 m) of (60a) in 100 ml of dried degassed tetrahydrofuran was cooled to -78° (dry ice ethanol) and added to a solution of 11.4 g (0.033 m) of Collman reagent in 50 ml of dry degassed tetrahydrofuran, also at -78° and under nitrogen. To this cold solution was added 11.3 g (0.048 m) of mercurous chloride. The cold solution was then flash distilled at 200-210°C under vacuum. The flash distillate was condensed and distilled yielding 0.5 g (10%) of (60a) (b.p. 82-110°C (0.12 mm)) and 1.88 g (25% based on starting 60a) of 55a as a yellow oil: b.p. 40-50°C (0.12 mm).

1-Bromomethylcyclobutadienyliron Tricarbonyl (56a) from (55a)

To a solution of 1.0 g (0.0042 m) of (55a) in 8 ml of degassed pentane, was added 18 ml of concentrated hydrobromic acid under nitrogen. The solution was stirred until no more starting complex (55a) could be detected by glc (~20 minutes) and then 35 ml of degassed pentane was added to the solution. The layers were separated and the organic portion was washed with 10 ml of saturated salt solution. The combined aqueous portions were extracted with 2 x 10 ml of pentane. The combined pentane solutions were dried and filtered through magnesium sulphate. The flask and filter

funnel were rinsed with additional pentane giving a near quantitative yield of (56a). The pentane solution was used directly in subsequent reactions.

1-Bromomethyl-2-methylcyclobutadienyliron Tricarbonyl (56b) from (55b)[35]

To a solution of 1.0 g (0.0040 m) of(55b) in 7 ml of degassed pentane was added 19 ml of concentrated hydrobromic acid under nitrogen. The solution was stirred until no more starting complex (55b) could be detected by glc (~20 minutes) and then 20 ml of degassed pentane was added to the solution. The organic portion was washed with saturated salt solution and dried with magnesium sulphate (also filtered through it) giving a near quantitative yield of (56b). The pentane solution was used directly in subsequent reactions.

1-(3-Pentynoxymethyl)cyclobutadienyliron Tricarbonyl (61) from Potassium Oxide

To a solution of 1.0 ml (0.0112 m) of 3-pentyn-1-ol in 5 ml of tetrahydrofuran was added 0.56 g (0.012 M0 of potassium metal. The reaction was heated with a heat gun until most of the potassium was consumed and a precipitate had formed. The salt solution was added to a pentane solution of (56a) prepared as described above from 1.6 g (0.0067 m) of (55a) and using 100 µl of decalin as an internal standard. After 10 hr of stirring, analysis by glc showed two products accounting for all of the starting complex. The reaction

mixture was filtered, condensed and passed through a silica gel column using pentane with increasing amounts of ether as eluent. This gave 1.4 g (71%) of (61) as an air sensitive yellow oil: b.p. 85-90°C (0.1 mm); nmr ($CDCl_3$) δ 4.07 (S, 2, ring), δ 4.00 (S, 1, ring), δ 3.74 (S, 2, $C\underline{H}_2O$), δ 3.48 (t, 2, $OC\underline{H}_2CH_2$, J = 6.7 Hz), δ 2.34 (m, 2, $CH_2C\underline{H}_2C\equiv C$, J = 2.2 Hz, J = 6.7 Hz), δ 1.73 (t, 3, methyl, J = 2.2 Hz); mass spectrum m/e 232 [P-$(CO)_2$], 204 [P-$(CO)_3$], 148 [P-$Fe(CO)_2$]. The byproduct was not identified.

1-(2-Butynoxymethyl)cyclobutadienyliron Tricarbonyl (79a) from Potassium Oxide

To a solution of 0.59 ml (0.0089 m) of 2-butyn-1-ol in 5 ml of dry degassed tetrahydrofuran was added 0.35 g (0.009 m) of potassium metal. The reaction was refluxed until most of the potassium was consumed. The salt solution was added to a pentane solution of (56a) prepared as described above, from 1.3 g (0.0055 m) of (55a) and using 100 µl of decalin as an internal standard. After 4 hr of stirring, analysis by glc showed a product peak corresponding to a 90% yield and a small impurity peak as well. The reaction mixture was filtered, condensed and distilled giving 0.97 g (64%) of (79a) as an air sensitive yellow oil: b.p. 100°C (0.5 mm); nmr ($CDCl_3$) δ 4.07 (S, 2, ring), δ 4.05 (q, 2, $C\underline{H}_2C\equiv C$, J = 2½ Hz) δ 3.98 (S, 1, ring), δ 3.77 (S, 2, $C\underline{H}_2O$), δ 1.81 (t, 3, methyl, J = 2½ Hz).

2-Methyl-1-(2-butynoxymethyl)cyclobutadienyl-iron Tricarbonyl (79b) from Potassium Oxide

To a solution of 0.45 ml (0.006 m, 0.42 g) of 2-butyn-1-ol in 5 ml of dried degassed tetrahydrofuran was added 0.270 g (0.0069 m) of potassium metal. The reaction was refluxed until most of the potassium was consumed. The salt solution was added to a pentane solution of (56b) prepared as described above from 1.0 g (0.0040 m) of (55b). The reaction was stirred overnight, filtered, condensed and distilled, giving 0.587 g (51%) of (79b) as an air sensitive yellow oil: b.p. 90-97°C (0.30-0.35 mm); nmr ($CDCl_3$) δ 4.05 (q, 2, $CH_2C{\equiv}C$, J = 2.8 Hz), δ 4.05 (S, 1, ring), δ 3.99 (S, 1, ring), δ 3.83 (ABq, 2, CH_2O, J = 2 Hz, J = 0.5 Hz), δ 1.80 (t, 3, methyl, J = 2.8 Hz), δ 1.79 (S, 3, ring methyl); mass spectrum m/e 288 (parent), 260 (P-CO), 232 [P-$(CO)_2$], 204 [P-$(CO)_3$], 148 [P-$Fe(CO)_3$].

1-(3-Pentynoxymethyl)cyclobutadienyliron Tricarbonyl (61) from Alcohol

A pentane solution of (56a) was prepared as described above, from 0.45 g (0.002 m) of (55a). To this was added 0.18 ml (0.002 m, 0.168 g) of 3-pentyn-1-ol and 0.28 ml (0.002 m, 0.202 g) of triethylamine, and the solution was stirred overnight. Analysis by glc showed none of the second byproduct found when the alkoxide preparation was used. The solution was dried with sodium sulphate condensed and distilled, giving 0.095 g (17%) of 61.

1-(2-Butynoxymethyl)cyclobutadienyliron Tricarbonyl (79a) from Alcohol

A pentane solution of (56a) was prepared as described above, from 1.43 g (0.006 m) of (55a). To this was added 0.4 ml (0.006 m, 0.423 g) of 2-butyn-1-ol and 0.84 ml (0.006 m, 0.610 g) of triethylamine, and the reaction was stirred overnight. Analysis by glc showed none of the unwanted second product formed in the alkoxide procedure. The solution was dried with sodium sulphate, filtered, condensed and distilled, giving 0.776 g (47%) of (79a) as a yellow oil: b.p. 85-95°C (0.45 mm).

2-Methyl-1-(2-butynoxymethyl)cyclobutadienyl-iron Tricarbonyl (79b) from Alcohol

A pentane solution of (56b) was prepared as described above, from 1.7 g (0.0072 m) of crude (103). To this was added 0.54 ml (0.0072 m) of 2-butyn-1-ol and 0.97 ml (0.007 m) of triethylamine. The reaction was stirred overnight, then filtered through sodium sulphate and condensed, giving 1.3 g of crude product. Distillation gave 0.652 g (31%) of (79b): b.p. 84-92°C (0.05-0.07 mm).

cis,trans,trans-1,2,3,4-Tetrachlorocyclo-butane-1,2-dicarboxylic Acid (98)[51]

A degassed solution of 137 ml (1.794 m, 174 g) of trans dichloroethylene, 100 g (0.60 m) of dichloromaleic anhydride (96) and 18.3 g (0.10 m) of benzophenone in 752 ml of oxygen and water free dioxane was photolyzed for 64 hr using a

Hanovia 450 watt immersion lamp. The solution was condensed and the resulting viscous oil was poured into 750 ml of 0.1% hydrochloric acid solution at 70°C. After stirring for 2 hr the solution was allowed to cool overnight. The supernatent aqueous layer was decanted off of the tarry oil which had separated out, washed with 250 ml of benzene, saturated with sodium chloride and extracted with 3 x 250 ml of ether. The combined organic portions were dried with magnesium sulphate filtered and condensed, giving 163 g of crude diacid (98) as an air stable viscous oil. The crude diacid was used directly without further purification.

Dimethyl-cis,trans,trans-1,2,3,4-tetrachlorocyclobutane-1,2-dicarboxylate (99)[51]

Diazomethane was generated using EXR 101 commercial precursor (30% N,N-dinitroso-N,N-dimethyl-p-phthalamide by weight). In a 1 liter size diazomethane apparatus was placed 120 ml of 30% sodium hydroxide solution, 90 ml of diethyleneglycolmonoethylether and 500 ml of ether. The solution was cooled to 0° and 36 g (gives 0.1-0.15 m) of precursor was added. The ice bath was replaced with a heating mantel and the diazomethane was distilled over into a solution of 28 g (~0.1 m) of the crude diacid (98) in 100 ml of ether at 0°. Excess diazomethane was destroyed by adding more diacid to the solution, usually 5 to 10 g. The ethereal diester solutions from five such runs as

described above were combined, dried with potassium carbonate and filtered. The solution was heated with Norit, filtered, condensed and redissolved in hot ethanol. Water was added to the hot solution until crystals appeared (along with an oil) at which point more ethanol was added. Upon cooling, crystals formed (used an ice bath). The crystals were filtered and dried under vacuum, giving 87 g (49% based on starting (96)) of (99). The crystals soon became yellow however, requiring another treatment with Norit and recrystallization. This gave 69 g (38% based on (96)) of (99) as air stable colorless crystals which remained unchanged: m.p. 90-91°C (Lit.[51] 92-93°C); nmr in agreement with reported values.[51]

Dimethyl-1,2-dicarboxylate Cyclobutadienyl-iron Tricarbonyl (101)[51]

To a solution of 10.23 g (0.033 m) of diester (99) in 100 ml of dry, oxygen free tetrahydrofuran was added a solution of 23.54 g (0.068 m) of Collman reagent in 300 ml of dry, oxygen free tetrahydrofuran. The solution was stirred for 6 hr and then filtered twice. The filtrate was condensed and extracted repeatedly with ether. The solid residue from the filtrations and extractions was put in a continuous extracter and extracted with ether for 4 days. The combined ether extracts were put through a 12" by 1" column of alumina and then condensed. The crude product

was recrystallized from hexane (cooled in the refrigerator giving 3.7 g (37%) of diester (100) as yellow crystals: m.p. 102-103°C (Lit.[51] 105-106°C); nmr in agreement with reported values.[51]

Methyl Hydrogen-1,2-dicarboxylate Cyclobutadienyliron Tricarbonyl (101)[51]

To 48.6 ml of a 0.4 M solution of potassium hydroxide (85% pellets) in methanol was added 6.0 g (0.0195 m) of diester (100). The reaction was stirred for 19 hr, condensed to one fourth of its original volume and then diluted up to 150 ml with distilled water. The solution was extracted with 20 ml of methylene chloride which was then dried with magnesium sulphate and condensed, giving 0.732 g of recovered diester (100). The aqueous solution was acidified to pH 3 by dropwise addition of concentrated hydrochloric acid and then extracted with 5 x 25 ml of ether. The combined extracts were washed with 25 ml of saturated salt solution, dried with magnesium sulphate, filtered and condensed, giving 4.786 g (95% based on (100)) consumed) of crude half acid (101). Sublimation (120-130°C (0.2 mm)) gave 4.23 g (83% based on (100) consumed) of pure (101) as yellow crystals. The crude and the sublimed half acid gave similar results in subsequent reactions, so the sublimation was usually not done: m.p. 129-133°C (Lit.[51] 130-137°C); nmr in agreement with reported values.[51]

1-Methylcarboxylate-2-methylcyclobutadienyliron Tricarbonyl (102) from (101)[51]

A solution of 2.0 g (0.0068 m) of half acid (101) in 9.4 ml of borontrifluoride etherate was treated with dropwise addition of 16 ml (0.0195 m) of 1.22 m borane in tetrahydrofuran solution. The reaction was refluxed for 1.5 for and then poured over cracked ice. The solution was extracted with 40 ml and 3 x 20 ml of ether. The combined extracts were dried with magnesium sulphate, condensed and distilled, giving two fractions of crude product at 35-65°C and 0.2 mm. Each fraction was put through a 20 cc column of alumina eluted with chloroform. Samples were dissolved in several ml of chloroform with 1 ml of ether added when loaded on the column. The final yield was 1.52 g (85%) of (102) as an air sensitive yellow oil: b.p. 50-67°C (0.3 mm); nmr ($CDCl_3$) δ 4.39 (S, 1, ring), δ 4.27 (S, 1, ring), δ 3.65 (S, 3, $OC\underline{H}_3$), δ 1.95 (S, 3, methyl); mass spectrum m/e 264 (parent), 236 (P-CO), 208 [P-$(CO)_2$], 180 [P-$(CO)_3$].

Methylchloro-1,2-dicarboxylate Cyclobutadienyliron Tricarbonyl (105)[51]

A 100 ml three neck round bottom flask was filled with 4.766 g (0.0162 m) of crude half acid (101) and 16.8 ml (0.236 m) of thionyl chloride (distilled). To this solution was added 1.2 ml of pyridine (dried over molecular seive) dropwise using a syringe. Excess thionyl chloride was removed using an aspirator and a warm water bath.

The remaining solid was heated with 20 ml of benzene, cooled with an ice bath, and the orange supernatant benzene solution was removed with a syringe. This extraction process was repeated with 8 x 10 ml of benzene, until additional benzene failed to take up color. The benzene portions were combined and condensed. The crude acid chloride was recrystallized from hexane in the refrigerator, giving 4.61 g (91%) of (105) as orange crystals (two crops); nmr in agreement with reported values.[51]

1-Methylcarboxylate-2-methylcyclobutadienyl-iron Tricarbonyl (102) from (105)

A solution of 1.47 g (0.0047 m) of half acid chloride (105) in 8 ml of borontrifluoride etherate (distilled from calcium hydride) was treated with dropwise addition of 14 ml of 1.22 M borane in tetrahydrofuran solution. The reaction was refluxed for 3.5 hr and then poured over cracked ice. The solution was extracted with 2 x 40 and 2 x 20 ml of ether. The combined extracts were dried with magnesium sulphate, condensed and distilled, giving two fractions at 40-50°C and 0.1 mm and totalling 1.214 g (98%) of crude (102). The early fraction (0.356 g) was put through a 15 cc silica gel column and the later fraction (0.858 g) was put through a 20 cc silica gel column giving 1.10 g (89%) of (102).

1-Hydroxymethyl-2-methylcyclobutadienyl-iron Tricarbonyl (103)[50]

To a solution of 2.0 g (0.0076 m) of (102) in 8 ml of hexane at 0°C (ice bath) was added 11 ml of a 1.56 M solution of diisobutylaluminum hydride in hexane (0.0172 m) slowly. The reaction stirred for 4 hr at 0°C. To destroy the excess hydride, a solution of 4 ml of methanol in 12 ml of benzene was slowly added to the cold reaction, followed by a solution of 2 ml of water in 8 ml of methanol. The resulting suspension was stirred for 20 minutes and then filtered. The solid residue was washed with 12 ml of benzene, 12 ml of ether and 12 ml of methanol in that order. The solids were then placed in a 100 ml round bottom flask along with 30 ml of methanol and 30 ml of ether and left to stir overnight. The organic portions were combined, filtered through sodium sulphate and condensed, giving 1.7 g (95%) of crude (103) as an air sensitive yellow oil: nmr ($CDCl_3$) δ 4.07 (S, 1, ring), δ 3.97 (S, 1, ring), δ 3.97 (S, 2, $C\underline{H}_2$), δ 2.4-2.0 variable (broad, 1, alcohol), δ 1.78 (S, 3, methyl).

1-Bromomethyl-2-methylcyclobutadienyliron Tricarbonyl (56b) from (103)

To a solution of 1.7 g (0.0072 m) of crude (103) in 12 ml of degassed pentane, was added 30 ml of concentrated hydrobromic acid. After 30 minutes of stirring, 40 ml of degassed pentane was added to the reaction and the layers

were separated. The aqueous acid layer was washed with 20 ml of degassed pentane and the combined organic portions were washed with 10 ml of almost saturated salt solution. The combined acid and salt solutions were extracted with another 20 ml of degassed pentane. The combined organic portions were filtered through sodium sulphate giving a near quantitative yield of (56b). The solution was used directly in subsequent reactions.

1-Methylcarboxylate-2-methylcyclobutadienyl-iron Tricarbonyl (102) via 1-Methylcarboxylate-2-(trichlorosilyl)methylcyclobutadienyliron Tricarbonyl (104) Attempted Synthesis[51]

To a solution of 2.0 g (0.068 m) of half acid (101) in 5 ml of acetonitrile was added 4 ml (0.0418 m) of trichlorosilane. The reaction was stirred at reflux for 1 hr and then cooled to 0°C. The cold solution was treated with 2.7 ml (0.0209 m) of triethylamine (rapidly) and then refluxed for 17 hr. When the reflux stopped, 62.5 ml of ether was added to the reaction and it was stored in the refrigerator. The crude (104) was filtered and condensed prior to use, but was not otherwise isolated or characterized.

The crude silyl compound (104) prepared above was dissolved in 27 ml of ethanol and refluxed for 1 hr. To this was added a solution of 0.484 g (7.26 mm) of potassium hydroxide in 11 ml of ethanol over a 10 minute period. The procedure being followed[51] called for addition of 0.9 g of

base to make the solution basic to hydrion pH paper. However, the solution was already basic so no additional base was added. The reaction refluxed for an additional 0.5 hr after addition. The solution was decanted and filtered, and the filtrate was washed with 15 ml of ethanol. The solution was then diluted with 350 ml of water and extracted with 6 x 30 ml of ether (following addition of 40 ml of ether). The solution was dried with magnesium sulphate and condensed, but no evidence for the presence of (102) could be found (nmr). Further treatment of the aqueous portions yielded nothing.

1-Methylcarboxylate-2-hydroxymethylcyclobutadienyliron Tricarbonyl (106)

To a suspension of 0.4736 g (0.0128 m) of sodium borohydride in 20 ml of dry dioxane, cooled to 0°C, was added 2.0 g (0.0064 m) of crude half acid chloride (105). The reaction was heated on a steam bath for 4 hr at almost reflux, and then cooled to 0°C. Distilled water was slowly added to the cold solution to hydrolize the borate salts. The solution was then acidified with hydrochloric acid, diluted with salt (sodium chloride) solution, and extracted with 6 x 20 ml of ether. The combined extracts were dried with magnesium sulphate and condensed. The crude product was put through a 20 cc column of silica gel using ether as the eluent. An nmr spectrum indicated the presence still

of some dioxane. This was removed by diluting the sample with ether and condensing it on the rotovap again, giving 1.5 g (85%) of (106) as a yellow oil: nmr ($CDCl_3$) δ 4.5-4.8 variable (broad, 1, alcohol), δ 4.51 (S, 1, ring), δ 4.41 (S, 1, ring), δ 4.18 (S, 2, $C\underline{H}_2$), δ 3.62 (S, 3, methyl).

1-Hydroxymethyl-2-methylcyclobutadienyliron Tricarbonyl (103) via 1-Methylcarboxylate-2-bromomethylcyclobutadienyliron Tricarbonyl (107a) Attempted Synthesis

To a solution of 1.0 g (0.0035 m) of alcohol (106) in 6 ml of degassed benzene was added 17 ml of concentrated hydrobromic acid with stirring. When the glc peak for the alcohol (106) disappeared, the bromide (197a) was assumed to have formed. The solution was then diluted with 20 ml of benzene and the aqueous layer was removed. The aqueous layer was extracted with benzene and the combined benzene portions were then washed with saturated salt solution. The organic portion was dried with sodium sulphate, condensed and redissolved in 10 ml of ether. This was assumed to be 0.0035 moles of (107a) in ether.

A suspension of 0.266 g (0.0070 m) of lithium aluminum hydride in 20 ml of ether was stirred at reflux for 15 minutes. The bromide solution (197a) was slowly added to the hydride suspension, and the reaction was allowed to stir for 1 hr. The reaction was then cooled to 0°C and

10% sodium hydroxide solution (aqueous) was added to destroy excess hydride. The solution was then treated with sodium chloride and filtered. The ether layer was separated out, dried with sodium sulphate and condensed. The resulting 0.54 g of material was an unidentifiable yellow oil. The product was put through two silica gel columns in succession giving several fractions, none of which was the desired alcohol (103). Most of the complex simply decomposed.

1-Hydroxymethyl-2-methylcyclobutadienyliron Tricarbonyl (103) via 1-Methylcarboxylate-2-chloromethylcyclobutadienyliron Tricarbonyl (107b) Attempted Synthesis

To a solution of 1.23 g (0.0042 m) of alcohol (106) in 14 ml of methylene chloride was added 14 ml of concentrated hydrochloric acid. After 3-5 minutes of shaking the acid was removed and a second portion of fresh acid (14 ml) was added and shaken. The organic layer was removed and dried with sodium sulphate. The solution was filtered, condensed and redissolved in 15 ml of ether giving what was assumed to be 0.0042 moles of (107b) in ether.

The ether solution of (197b) was slowly added to a suspension of 0.327 g (0.0086 m) of lithium aluminum hydride in 24 ml of ether. (Originally only 0.266 g (0.0070 m) of hydride was used, but part way through the addition of the chloride (107b) the solution ceased to fizz when chloride was added. It was assumed that all of the

hydride had reacted so more was added.) The solution was stirred for 1 hr after addition was complete and then cooled to 0°C. Water was slowly added to the reaction mixture, followed by more ether. The solution was filtered and the organic portion was separated out and condensed. The resultant oil contained none of the desired alcohol (103). A subsequent attempt to convert this material to 1-chloromethyl-2-methylcyclobutadienyliron tricarbonyl by dissolving it in 12 ml of methylene chloride and shaking it with 2 x 14 ml of hydrochloric acid gave nothing also. It was subsequently reported by other workers[51] that lithium aluminum hydride reductions on similar cyclobutadienyliron tricarbonyl complexes do not give the desired products but give largely decomposition. That is what we observed also.

1-Hydrogencarboxylate-2-methylcyclobutadienyliron Tricarbonyl (108)

A stock solution was made up using 19.8 g of potassium hydroxide, 20 ml of water and 300 ml of methanol.

A solution of 1.0 g (0.0040 m) of (102) in 10 ml of the potassium hydroxide stock solution was stirred for 3 hr. The solution was then condensed, diluted with 30 ml of water and acidified by dropwise addition of concentrated hydrochloric acid. The solution was extracted with ether, dried with magnesium sulphate and condensed, giving 0.738 g (74%)

of crude acid (108) as yellow crystals: nmr ($CDCl_3$) δ 10.7 (broad, 1, $CO_2\underline{H}$), δ 4.36 (S, 1, ring), δ 4.31 (S, 1, ring) δ 1.97 (S, 3, methyl). Addition of D_2O causes the peak at δ 10.7 to disappear.

1-Chlorocarboxylate-2-methylcyclobutadienyliron Tricarbonyl (109)

In a 50 ml three neck round bottom flask was placed 1.0 g (0.004 m) of acid (108) and 5 ml of thionyl chloride. To this was added 0.3 ml of dry pyridine (stored over barium oxide) dropwise using a syringe. The solution was allowed to stir for 5.5 hr following which the excess thionyl chloride was removed using a steam bath and aspirator. The residue was dissolved in 5 ml of benzene, heated to reflux and cooled with an ice bath. The benzene was removed with a syringe. This extraction process was repeated nine times. The combined benzene portions were condensed and the resultant crude (109) was used directly in subsequent reactions.

1-Methoxymethyl-2-methylcyclobutadienyliron Tricarbonyl (55b) from (109) via (102) and (56b)

A suspension of 0.3 g (0.008 m) of sodium borohydride in 10 ml of dioxane was cooled using an ice bath. A solution of the crude chloride (109) (assumed 0.0032 m from 1.0 g of starting acid) in 5 ml of dioxane was added to the cold hydride suspension and stirred for 5 hr. The reaction

was carefully hydrolyzed by slow addition of 15 ml of water and then acidified with concentrated hydrochloric acid. The solution was treated with sodium chloride and then extracted with 4 x 20 ml of ether. The combined ether portions were dried with magnesium sulphate and condensed giving at least some of the alcohol (103).

To a solution of the crude alcohol (103) (assumed 0.003 m) in 10 ml of pentane was added 10 ml of concentrated hydrobromic acid. The solution was diluted with 10 ml more of pentane and the acid layer was removed with a syringe. The organic portion was washed with 15 ml of almost saturated salt solution and dried with sodium sulphate. The bromide (56b) solution was used directly.

To the above bromide solution was added 0.27 g (0.005 m) of sodium methoxide and the reaction was allowed to stir for 2 days. The solution was filtered through sodium sulphate and distilled, giving a yellow oil (b.p. 60°C at 0.25 mm). The nmr spectrum indicated the presence of both the desired ether (55b) and the ester (102). The yield of (55b) was less than 15%. A mass spectrum taken of a second fraction of the distillation, which did not contain any (55b) (by nmr) showed the possible presence of the following compounds: (102), (108), (103).

1,2-Dimethylcyclobutadienyliron Tricarbonyl (111)

To a solution of 0.87 g (0.0035 m) of complex [75% (108), 25% (102)] in 12 ml of tetrahydrofuran at 0°C was added 2.5 ml (0.00365 m) of borane in tetrahydrofuran solution (1.22 M) slowly. The reaction was stirred for 0.5 hr at 0°C and an additional hour at room temperature. The solution was hydrolized with 3 ml of water and then treated with potassium carbonate. The layers were separated and the aqueous portion was extracted with ether. The combined organic portions were dried with magnesium sulphate and condensed, giving (111) as a yellow oil (along with the unchanged (102)): nmr ($CDCl_3$) δ 3.83 (S, 2, ring), δ 2.70 (S, 6, methyl); mass spectrum m/e 220 (parent), 192 (P-CO), 164 [P-$(CO)_2$], 136 [P-$(CO)_3$].

1-Methylcarboxylate-2-methoxymethylcyclobutadienyliron Tricarbonyl (113) via (107b) Attempted Synthesis

A solution of 0.84 g (0.003 m) of (106) in 4 ml of thionyl chloride was stirred at room temperature for 6 hr. The excess thionyl chloride was evaporated off under reduced pressure (aspirator and water bath). The crude (197b) was dissolved in 80 ml of ether and filtered through sodium sulphate. To the solution of (197b) was added 0.54 g (0.01 m) of sodium methoxide and the reaction was allowed to stir overnight. The reaction mixture was filtered through

sodium sulphate and condensed to a yellow oil. An nmr spectrum of the oil showed nothing. The oil was put through a 25 cc column of alumina, using ether as the eluent. An nmr spectrum of the condensed product indicated the presence of some starting material and some unidentified decomposition products.

1-(N,N-Dimethylamine)methyl-2-methylcyclobutadienyliron Tricarbonyl (115) from (56b)[35]

To a solution of ~0.014 m of bromide (56b), prepared from 2.6 g (0.015 m) of alcohol (103) as previously described, in 100 ml of pentane at 0°C was added 35 ml of dimethylamine. The reaction was stirred for 6 hr and then warmed to room temperature. The solution was washed with 3 x 90 ml of water and the aqueous portions were extracted with 60 ml of pentane. The organic portions were separately dried with sodium sulphate and condensed giving a total yield of 3.65 g (92% based on starting alcohol) of amine (115) as an air sensitive yellow oil: nmr in agreement with reported values.[35]

Resolution of (115)[35]

The amine (115) was converted to the salt (116) as follows. A sample of 3.72 g (0.016 m) of d-10-camphorsulfonic acid was placed in a 50 ml centrifuge tube with 10 ml of ethanol. The tube was sealed with a serum cap (under nitrogen) and heated to dissolve the acid. To the

hot solution was added 4.07 g (0.0154 m) of amine (115) and the solution was boiled (heat gun) while passing nitrogen over it, until the volume was reduced to 13.5 ml. Subsequent cooling, even in the refrigerator, gave no crystallization. Addition of 3 ml of ether produced some crystals. The solution was reheated and the volume reduced as before to 10.6 ml. Subsequent cooling still gave no crystallization. Addition of 5 ml of ether gave crystals again but they would not go back into solution. Another 2 ml of ethanol was added and the ether was boiled off. Then 4 ml of ether was added to the warm (not hot) solution to give a total volume of 16 ml after a final brief heating. Upon cooling, crystals formed within an hour. After 2 hr the centrifuge tube was placed in the refrigerator overnight. The crystals were broken up and the mixture was centrifuged (5 minutes at 55). The liquid was decanted and saved leaving 7 ml of white crystals. The crystals were then washed with 9 ml of a 50/50 ether/ethanol solution, centrifuged and the liquid decanted as before. The washing centrifugation and decanting procedure was repeated with 3 x 8 ml of solution leaving 5 ml of crystals, and then with 2 x 7 ml of solution giving a final volume of 4 ml of crystals of salt (*116).

All of the washings and decanted solutions were recombined and subjected to the recrystallization procedure again for a second crop of crystals.

The free amine (*115) was regenerated by dissolving 4.0 ml of crystals (*116) in 11.5 ml of hot methanol and adding 9 pellets (0.948 g) of sodium hydroxide and 23 ml of water to the solution. After stirring for 35 minutes 23 ml of ether was added and the layers were separated. The organic portion was dried with sodium sulphate (stir for 20 minutes) and condensed, giving 1.24 g of crude (+) rotamer of amine (*115) (O.P. $\approx$ 30%). Similar treatment of the remaining solutions gave (-) amine.

1-Methoxymethyl-2-methylcyclobutadienyliron Tricarbonyl (*55b) from (*115) via 1-(N,N,N-Trimethylammonium iodide) methyl-2-methylcyclobutadienyliron Tricarbonyl (*116)[35]

To a solution of 1.8 g (0.0068 m) of crude (-) amine (*115) in 130 ml of ether was added 5.1 g (2.2 ml = 0.0359 m) of methyliodide, and the reaction was stirred overnight. The white precipitate (*116) which formed was dissolved by adding 125 ml of methanol. To this solution was added 2.0 g (0.0370 m) of sodium methoxide, which fizzed when added, as though water were present. Two more 2 g portions of sodium methoxide were subsequently added, which also fizzed. It had been expected that 2.0 g of methoxide would be sufficient but either the sample or the methoxide was probably wet. After stirring for three days the reaction was diluted with 150 ml of ether and enough water (~ 100 ml)

to separate the layers and dissolve any salts. The organic portion was washed with 2 x 30 ml of water and the aqueous portions were extracted with 75 ml of ether, which portion was in turn washed with 2 x 10 ml of water. The combined organics were dried twice with sodium sulphate and then with sodium carbonate. The condensed solution gave 2.0 g of crude (-) ether (*55b) which the nmr showed contained considerable impurities, mostly hydrocarbon. Distillation gave 1.14 g (67% yield based on starting amine (*115)) of (-) (*55b) as a yellow oil: b.p. 49-73°C (0.5 mm).

2-Methyl-1-(2-butynoxymethyl)cyclobutadienyl-iron Tricarbonyl (*79b) from Alcohol (Sample No. 5 in Table VI)

A pentane solution of (*56b) was prepared as described above, from 1.14g (0.00456 m) of (*55b) with an addition to the procedure. When the aqueous acid layer was separated from the pentane portion it was treated with more pentane and stirred for several days. The initial pentane solution of (56b) was condensed and dissolved in 3.0 ml (0.042 m) of 2-butyn-1-ol. To this was added 0.75 ml of triethylamine. The reaction was stirred for 56 hr and then added to 42 ml of water. After addition of another 125 ml of pentane the layers were separated and the aqueous layer was extracted with 45 ml of pentane. The pentane layers were dried with magnesium sulphate and condensed giving 0.90 g of crude product. The pentane which had stirred with the

aqueous acid for several days was brought up to a total pentane volume of 50 ml, separated from the aqueous portion and washed with 5 ml of almost saturated salt solution. The solution was then dried with magnesium sulphate and condensed giving 0.22 g of crude (*56b). To this was added 1.0 ml (0.014 m) of 2-butyn-1-ol and 0.25 ml of triethylamine, and the reaction was stirred overnight. At the same time the water portions from the various preparations above were distilled (to remove the water) and the residues were combined and dissolved in 4.0 ml (0.056 m) of 2-butyn-1-ol and 1 ml of triethylamine. This was also stirred overnight. The two overnight reaction solutions were combined and diluted with 40 ml of water and 125 ml of pentane. The pentane portion was separated, dried with magnesium sulphate and condensed giving 0.535 g of crude product. The two samples of crude (*79b) were distilled at 88-95°C (0.2 mm) giving 0.539 g (41%) of (*79b).

2-Methyl-1-(2-butynoxymethyl)cyclobutadienyliron Tricarbonyl (*79b) from Alcohol (Samples 2 & 3 & 4 combined in Table VI)

A pentane solution of (*56b) was prepared as described above from ~1.5 g (~0.0072 m) of crude (not distilled) (*55b) and then condensed. The bromide was dissolved in 4 ml (0.056 m) of 2-butyn-1-ol and 1 ml of triethylamine and allowed to stir overnight. The reaction mixture was then added to 50 ml of water and 150 ml of pentane.

The layers were separated and the organic portion dried with magnesium sulphate and condensed giving 1.04 g of crude product. The aqueous layer was extracted with 100 ml of pentane, dried and condensed giving 0.20 g of crude product. The crude products were combined and distilled giving 0.64 g (31%) of (*79b): b.p. 98-114°C (0.27 mm).

Decomposition of 1-(3-pentynoxymethyl)-cyclobutadienyliron Tricarbonyl (61)

Using Ce IV[35]

To a solution of ~100-150 mg (0.00035-0.00051 m) of (61) in 20 ml of 95% ethanol was added 1.0 g (0.0019 m) of ceric ammonium nitrate (Ce IV) in 2 ml of water. Ether and salt water were then added to the reaction and the layers were separated. The aqueous portion was extracted several times with ether and the combined ether portions were dried with magnesium sulphate and condensed. Analysis by nmr disclosed no peaks assignable to either Dewar-benzene systems, isochromans or starting complex. Adding the ethanolic complex to the aqueous Ce IV gave the same results. Subsequent attempts to work-up the "product" using a small silica gel column were equally unsuccessful. Apparently intractable tars and polymers are the result of direct Ce IV oxidation of (61).

Using Light

A solution of 0.5 g (0.0017 m) of (61) in 100 ml of pentane was photolyzed for 1 hr, by which time no more

starting material peak showed in glc analysis. The reaction mixture was condensed and put through a 6 cc column of silica gel. Analysis of the column fractions by nmr showed both starting complex (61) and an isochroman (68), identified by comparison to an authentic sample, to be present.

Using Light Followed by Ce IV or CO

A solution of 0.278 g (0.00096 m) of (61) and 0.129 g (0.00096 m) of durene as an internal standard in 150 ml of pentane was photolyzed for 12.5 hr, until glc analysis showed that no more of the starting (61) was present. Subsequent studies were done using portions of this solution.

A 25 ml portion of the photolyzed solution was placed in a pressure jar under 44 psi of carbon monoxide atmosphere for 22 hr. Analysis by glc showed 20% starting (61) and 8% isochroman (68).

A 25 ml portion of the photolyzed solution was placed in a pressure jar under 36 psi of carbon monoxide atmosphere for 68 hr. Analysis by glc showed 22% starting (61) and 11% isochroman (68).

A 25 ml portion of the photolyzed solution (should contain 0.00016 m of complex) was condensed and redissolved in acetone. To this solution was added 0.308 g (0.00056 m) of crystalline Ce IV. The solution was stirred until two

minutes after bubbling ceased, and then 40 ml of ether and 25 ml of saturated salt solution was added. The layers were separated and the organic portion was washed with 4 x 20 ml of salt solution until no more orange color (from the cerium) was removed. The organic portion was dried with magnesium sulphate and condensed. The crude product was redissolved in benzene and refluxed for several hours. Analysis by glc showed 83% isochroman (68).

A second solution of 0.42 g (0.00146 m) of (61) and 0.0205 g (0.000153 m) of durene in 300 ml of pentane was photolyzed for 3.25 hr as before.

A 50 ml portion of the second photolyzed solution (0.00024 m) was redissolved in acetone and treated with 0.399 g (0.00089 m) of Ce IV as previously described. The crude product was not boiled in benzene but was directly analyzed by glc. Analysis showed 13% starting (61) and 77% isochroman (68).

A 100 ml portion of the second photolyzed solution was condensed directly without any additional treatment. Analysis by glc showed 21% starting (61) and 53% isochroman (68). This is essentially air oxidation.

A summary of yields is given in Table I.

Decomposition of 1-(2-butynoxymethyl)-cyclobutadienyliron (79a)

To a solution of 1.3 g (0.00477 m) of (79a) in 135 ml of acetone was added 9.167 g (0.0167 m) of crystalline Ce IV

slowly. When the bubbling ceased 140 ml of ether was added, and the solution was then washed with successive 20 ml portions of almost saturated salt solution until no more color was removed. The solution was dried with magnesium sulphate and condensed. The crude product mixture was put through a Florisil column (1 by 25 cm) eluting first with pentane and then with a 10:1 mixture of pentane and ether. The condensed pentane fractions gave ~0.53 g (83% yield) of phthalan (82a) and the condensed pentane/ether fractions gave ~0.1 g (13%) of polycycle (84a).

A summary of yields is given in Table IV.

4-Methylphthalan (82a) Physical Data

Hnmr ($CDCl_3$) δ 7.15 (S, 3, ring) δ 5.18 (S, 4, $C\underline{H}_2$), δ 2.28 (S, 3, methyl); mass spectrum m/e 134 (parent), 119 (P-CH_3), 105 (13), 91, 77.

2-Methyl-9-oxatricyclo[5.3.2.^{4,7}O^{1,7}]deca-1,5-dien-3-one (84a) physical data[54]

Hnmr ($CDCl_3$) δ 6.60 (d, 1, vinyl, J = 2.7 Hz), δ 6.33 (d of d, 1, vinyl, J = 2.7 Hz, J = 1.5 Hz), δ 4.47 (m, 2, allylic $C\underline{H}_2$), δ 4.12 (d, 1, one of $C\underline{H}_2$, J = 9 Hz), δ 3.72 (d, 1, other of $C\underline{H}_2$, J = 9 Hz), δ 3.47 (d, 1, $C\underline{H}$, J = 1.5 Hz), δ 1.70 (t, 3, methyl, J = 1.5 Hz); C-13 nmr 191.7 (1)[53], 171.1 (3), 145.3 (7), 136.0 (8), 131.6 (2), 69.0 (4), 64.6 (5), 62.5 (6), 56.4 (9), 9.45 (10); mass spectrum m/e 162 (parent), 148, 132, 119, 105, 91, 84, 74, 59 (B); ir ($CHCl_3$) (cm^{-1}) 1750 (shoulder, alkene), 1703 (strong, C=O), 1661 (Fermi resonance[45]), 1025-1105 (broad, ether).

Decomposition of 2-Methyl-1-(2-butynoxymethyl)-cyclobutadienyliron Tricarbonyl (79b)[35]

The procedure for decomposition of (79b) was identical to the procedure for the decomposition of (79a). A sample of 0.63 g (0.00219 m) of (+) (*79b) in 63 ml of acetone was treated with 4.158 g of crystalline Ce IV. Using a 25 cc column of silica gel as the final work-up gave 0.171 g (53% yield of phthalan (82b) and 0.060g (16% yield) of polycycle (84b).

A sample of 0.5 g (0.00174 m) of (79b) in 50 ml of acetone was decomposed as described previously with 3.330 g (0.0061 m) of Ce IV, but under a carbon monoxide atmosphere instead of nitrogen. The crude product mixture was put through a Florisil column as the final work-up. Analysis by glc showed four products. The relative yields were phthalan (82b) (45%), polycycle (84b) (21%), lactone (86b) (29%) and dimer (?) (4%).

A summary of yields is given in Table IV.

4,7-Dimethylphthalan (82b) Physical Data

Hnmr ($CDCl_3$) δ 7.03 (S, 2, ring), δ 5.17 (S, 4, $C\underline{H}_2$), δ 2.21 (S, 6, methyl); mass spectrum m/e 148 (parent), 133 (B), 119, 105, 91, 77.

2,7-Dimethyl-9-oxatricyclo[5.3.2.$^{4,7}O^{1,7}$]-deca-1,5-dien-3-one (84b) Physical Data

Hnmr ($CDCl_3$) δ 5.93 (m, 1, vinyl), δ 4.47 (m, 2, allylic $C\underline{H}_2$), δ 4.12 (d, 1, one of $C\underline{H}_2$, J = 9 Hz), δ 3.72 (d, 1, other of $C\underline{H}_2$, J = 9 Hz), δ 3.27 (m, 1, $C\underline{H}$), δ 1.80

(m, 3, methyl), δ 1.70 (t, 3, methyl by CO, J = 1.5 Hz); C-13 nmr 201.7 (1), 171.9 (3), 155.3 (7), 131.3 (2), 126.5 (8), 67.5 (4), 64.4 (5), 63.1 (6), 52.8 (9), 13.6 (11), 9.3 (10); mass spectrum m/e 176 (parent), 162, 148, 133 (B), 105, 91, 77; ir ($CHCl_3$) (cm^{-1}) 1750 (alkene), 1700 (strong, C=O), 1664 (Fermi resonance[45]), 1020-1100 (broad, ether); UV (95% ethanol) λ_{max} 244 mμ; $[\alpha]^{25}_{578}$ = 280 ± 20°C (0.015 g in ether).

4,7-Dimethylphthalide (86b) Physical Data

Hnmr ($CDCl_3$) δ 7.39 (d, 1, ring, J = 10.3 Hz), δ 7.26 (d, 1, ring, J = 10.3 Hz), δ 5.24 (S, 2, CH_2), δ 2.68 (S, 3, methyl), δ 2.33 (S, 3, methyl); mass spectrum m/e 162 (parent), 147, 133 (B), 115, 105, 91, 77, 63.

NMR Shift Studies

A sample of 23 mg (0.000142 m) of polycycle (84a) was dissolved in deuterochloroform and placed in a micro nmr tube and 2,2,6,6,-tetramethyl-3,5-heptanedionate Europium was added in 2 mg portions until a total of 6 mg had been added. After each addition nmr spectra were taken. (See Table IV for shift data.)

A sample of 47 mg (0.000267 m) of (+) polycycle (*84b) was dissolved in deuterochloroform and placed in a micro nmr tube. To this was added tris-[3-heptafluorobutyryl-d-camphorato] Europium III (Eu(hfbc)) in 5 mg portions

until a total of 30 mg had been added, the last 10 mg all at once. After each addition nmr spectra were taken.

A similar procedure was used on the ~50 mg (0.000285 m) of (-) polycycle (*84b).

4-Methylphenyl Lithium (70)[42]

To a suspension of 0.808 g (0.1164 m) of lithium ribbon, cut in pieces, in 46 ml of ether was added a solution of 7.2 ml (0.0585 m) of 4-bromotoluene in 12 ml of ether slowly using an addition funnel. The reaction was stirred (mechanical stirrer) for 30 minutes after addition was complete and used directly without further work-up.

4-(β-Hydroxyethyl)toluene (71)[43]

To the ether solution of (70) prepared above and cooled to 0°C was slowly added a cold (0°C) solution of 2.94 ml (0.0582 m) of ethylene oxide in 50 ml of ether. After stirring for several hours the solution was allowed to warm to room temperature. Benzene was then added to the solution and the ether was evaporated on a rotary evaporator. The reaction was quenched with 10% hydrochloric acid and the layers were separated. The aqueous layer was extracted with benzene. The organic layers were combined and distilled giving 5.674 g (71% yield) of alcohol (71) as a clear liquid; nmr ($CDCl_3$) δ 7.13 (S, 4, ring), δ 3.83 (t, 2, $C\underline{H}_2OH$, J = 6.3 Hz), δ 2.81 (t, 2, $C\underline{H}_2CH_2$, J = 6.3 Hz), δ 2.31

(S, 3, methyl), δ 1.64 (S, 1, alcohol); addition of deutero water removes the alcohol peak.

4-(β-Chloromethoxyethyl)toluene (72)[44]

To a flask containing 5.64 g (0.0415 m) of alcohol (71) was added 1.387 g of paraformaldehyde. Hydrochloric acid was slowly bubbled through the solution at room temperature for an hour (the procedure calls for 2.77 g of dry gas but I had no way to measure accurately and used an excess). The reaction mixture was refluxed for an hour and then dried with magnesium sulphate. The crude yield was 2.135 g (27.5%) of (72) as a clear liquid: nmr (neat) δ 6.6-7.3 (m, 4, ring), δ 4.7 (S, 2, $C\underline{H}_2Cl$), δ 3.9 (m, 2, $C\underline{H}_2O$), δ 2.8 (m, 2, $C\underline{H}_2CH_2$), δ 2.4 (S, 3, methyl).

7-Methylisochroman (66)[44]

The following procedure uses twice as much catalyst and solvent as necessary.

To a cold (0°C) solution of 1.86 g (0.014 m) of aluminum trichloride in 16.5 ml of carbon disulfide was added 2.135 g (0.011 m) of the chloromethyl ether (72) dropwise. When addition was complete the solution was allowed to warm to room temperature. The solution was slowly hydrolyzed with distilled water and the layers were separated. The aqueous layer was extracted with ether and the organic portions were then combined and distilled giving 0.749 g (47% yield) of (66) as a clear liquid:

nmr ($CDCl_3$) 6.7-7.1 (m, 3, ring), δ 4.73 (S, 2, $C\underline{H}_2O$), δ 3.93 (t, 2, $CH_2C\underline{H}_2O$, J = 5.8 Hz), δ 2.77 (t, 2, $C\underline{H}_2CH_2O$, J = 5.8 Hz), δ 2.29 (S, 3, methyl).

2-Methylphenyl Lithium (74)[42]

To a suspension of 0.808 g (0.1164 m) of lithium ribbon, cut in pieces, in 46 ml of ether was added a solution of 7.1 ml (0.0585 m) of 2-bromotoluene (73) in 12 ml of ether slowly. The reaction was stirred for 30 minutes after addition was complete, and was used directly without further work-up.

2-(β-Hydroxyethyl)toluene (75)[43]

To the ether solution of (74) prepared above and cooled to 0°C was added a cold (0°C) solution of 3 ml (0.0593 m) of ethylene oxide in 50 ml of ether using a cooled addition funnel. After stirring for several hours at 0°C, the reaction was allowed to warm to room temperature overnight. The reaction was diluted with 35 ml of benzene and the ether was evaporated off using a rotary evaporator. The reaction was quenched with 10% hydrochloric acid and the layers were separated. The aqueous layer was extracted twice with benzene. The organic layers were combined and distilled giving 2.56 g of starting bromide (73) and 5.255 g (65.8% yield) of (75) as a clear liquid: nmr (neat) δ 7.15 (S, 4, ring), δ 5.0 (S, 1, alcohol), δ 3.83 (t, 2, $C\underline{H}_2OH$,

J = 7.5 Hz), δ 2.91 (t, 2, $C\underline{H}_2CH_2$, J = 7.5 Hz), δ 2.81 (S, 3, methyl).

2-(β-Chloromethoxyethyl)toluene (76)[44]

To a flask containing 5.255 g (0.0383 m) of alcohol (75) was added 1.295 g (0.0431 m) of paraformaldehyde. Hydrochloric acid was slowly bubbled through the solution at room temperature for an hour (as before an excess was used). The reaction was refluxed slowly (~40°C) for an hour and then dried with magnesium sulphate and condensed. Analysis of the crude product by nmr indicated that both the desired product (76) and some starting alcohol (75) were present. Another 0.5 g of paraformaldehyde was added and the reaction was refluxed for another hour. When the work-up had been repeated additional nmr spectra looked the same as before. The yield of impure (76) was 2.987 g (42.3%), which was used without further work-up.

5-Methylisochroman (68)[44]

To a cold (0°C) solution of 1.12 g (0.0085 m) of aluminum trichloride in 9.9 ml of carbon disulfide was added 2.987 g (0.0162 m) of impure chloromethyl ether (76) dropwise. When addition was complete the solution was allowed to warm to room temperature. The solution was slowly hydrolyzed with distilled water, and the layers were separated. The aqueous portion was extracted with ether.

The combined organic portions were distilled giving 1.87 g (78% yield) of (68) as a clear liquid: b.p. 75°C (0.8 mm), nmr (neat) δ 7.15 (S, 3, ring), δ 4.83 (S, 2, $C\underline{H}_2O$), δ 4.03 (t, 2, $CH_2C\underline{H}_2O$, J = 5.8 Hz), δ 2.63 (t, 2, $C\underline{H}_2CH_2O$, J = 5.8 Hz), δ 2.29 (S, 3, methyl), mass spectrum m/e 148 (parent), 133, 118 (B), 105, 91, 77, 65.

2-Methylphenylmagnesiumbromide (88)

To a suspension of 2.0 g (0.0824 m) of magnesium turnings in 16 ml of ether was added 10.0 g (~7.03 ml = 0.0585 m) of 2-bromotoluene dropwise from an addition funnel. A heat gun was used to heat the reaction until it could maintain its own reflux. The Grignard reagent (88) was used directly without further work-up.

2-Hydroxymethyltoluene (89)

A flask containing 2.0 g (0.0666 m) of formalin was heated so that the vapor was bubbled through the Grignard (88) solution prepared above. During addition of the formalin the reaction mixture was stirred and occasionally heated with a heat gun. After addition was complete 40 ml of benzene was added and the reaction was refluxed overnight. The reaction was quenched by slowly adding 50 ml of 10% hydrochloric acid to it. The layers were separated and the aqueous portion was extracted with 3 x 10 ml of benzene, 2 x 10 ml of ether and then 10 ml more of benzene.

The organic portions were combined, condensed and filtered through magnesium sulphate. Distillation gave 3.033 g (41% yield) of (89) as a clear solid: b.p. 44-55°C (0.05-0.25 mm); nmr ($CDCl_3$) δ 7.2 (m, 4, ring), δ 4.57 (S, 2, $C\underline{H}_2$), δ 2.7-3.0 variable (S, 1, alcohol), δ 2.27 (S, 3, methyl).

2-(Chloromethoxymethyl)toluene (90)[44]

Dry hydrochloric acid was bubbled through a solution of 3.858 g (0.0316 m) of alcohol (89) and 1.2 g (0.04 m) of formalin in 10 ml of benzene for an hour at room temperature (an excess of hydrochloric acid). The solution was refluxed for an hour at 43°C and then filtered through magnesium sulphate (wash with more benzene) and condensed. Distillation gave 3.026 g (57% yield) of (90) as a clear liquid: b.p. 60-65°C (0.45 mm); nmr ($CDCl_3$) δ 7.2 (m, 4, ring), δ 5.36 (S, 2, $C\underline{H}_2Cl$) δ 4.62 (S, 2, $C\underline{H}_2O$), δ 2.27 (S, 3, methyl).

4-Methylphthalan (82a) from (90) Attempted

To a solution of 3.026 g (0.0178 m) of chloromethyl-ether (90) in 112 ml of carbon disulfide at 0°C was added 1.10 g (0.0083 m) of aluminum trichloride catalyst. The solution was allowed to warm slowly to room temperature while stirring. Distilled water was slowly added to destroy excess catalyst and salt solution was added to enhance

separation of the layers. The aqueous portion was extracted several times with ether and the organic portions were then combined and condensed. Distillation gave 0.873 g (40% yield) of alcohol (89) (b.p. 29-35°C (0.2 mm)), 0.307 g (10% yield) of starting chloromethylether (90) (b.p. 50-55°C (0.2 mm)) and 0.637 g of unidentified product mixture which includes some more (90) but none of the desired phthalan (82a).

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APPENDIX

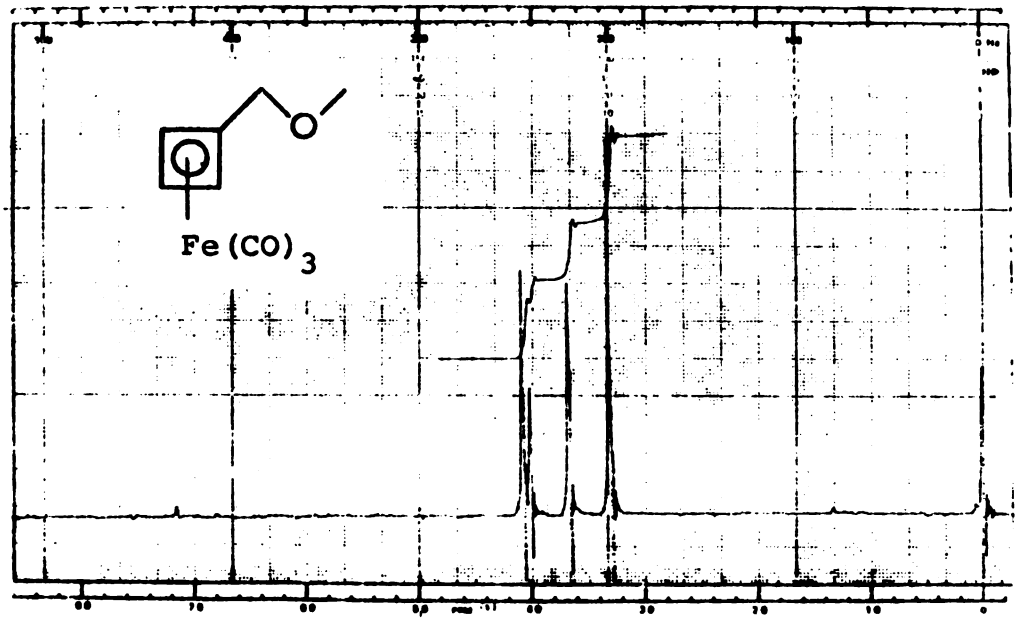

Figure 29. NMR spectrum of 1-methoxymethylcyclobutadienyliron tricarbonyl (55a) ($CDCl_3$)

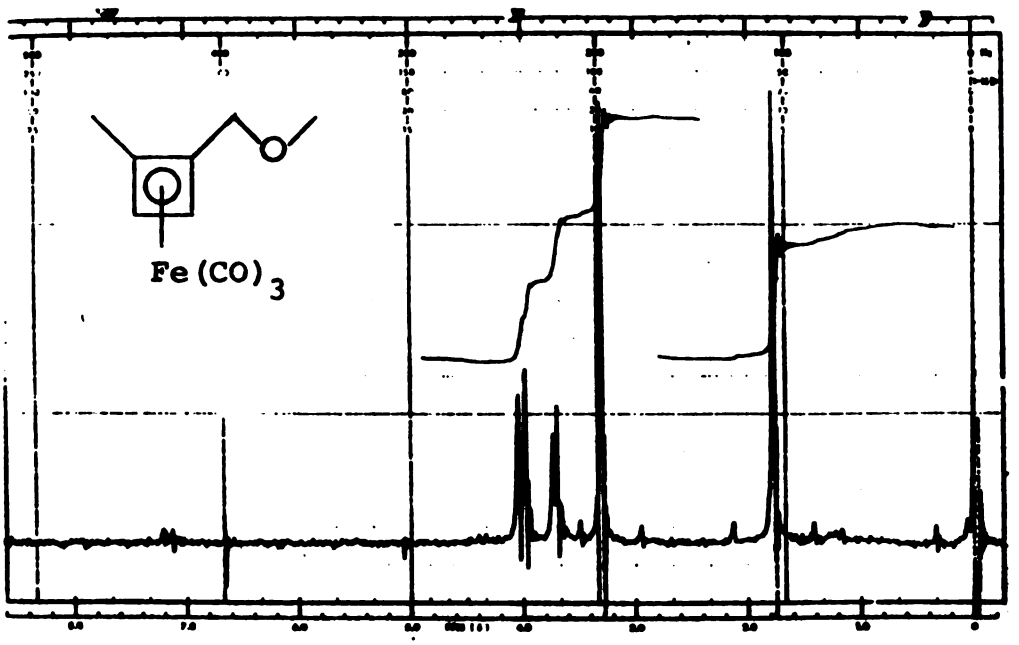

Figure 30. NMR spectrum of 1-methoxymethyl-2-methylcyclobutadienyliron tricarbonyl (55b) ($CDCl_3$)

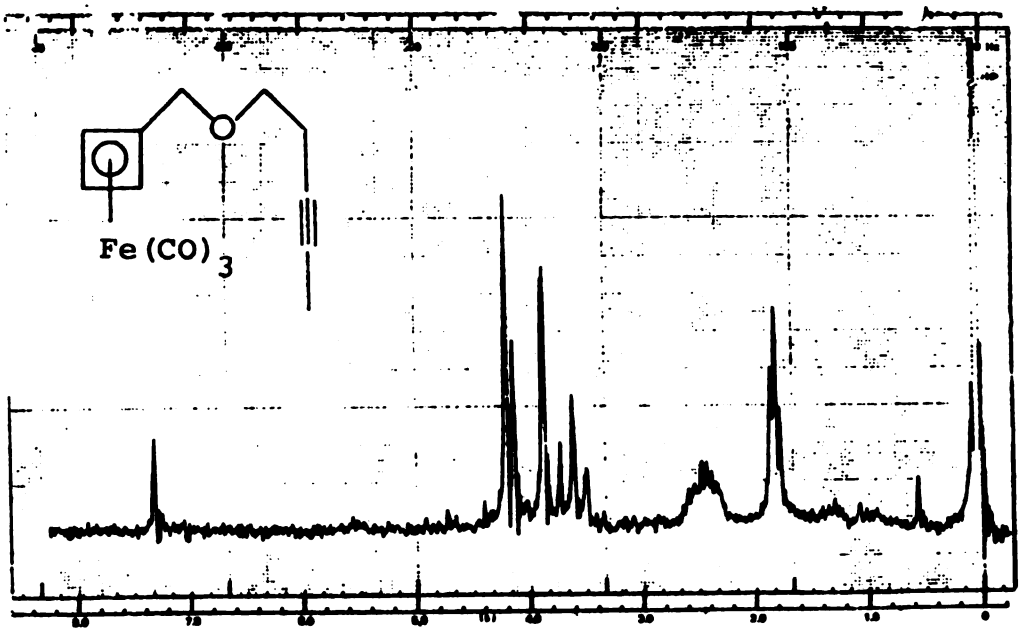

Figure 31. NMR spectrum of 1-(3-pentynoxymethyl)cyclobutadienyliron tricarbonyl (61) ($CDCl_3$).

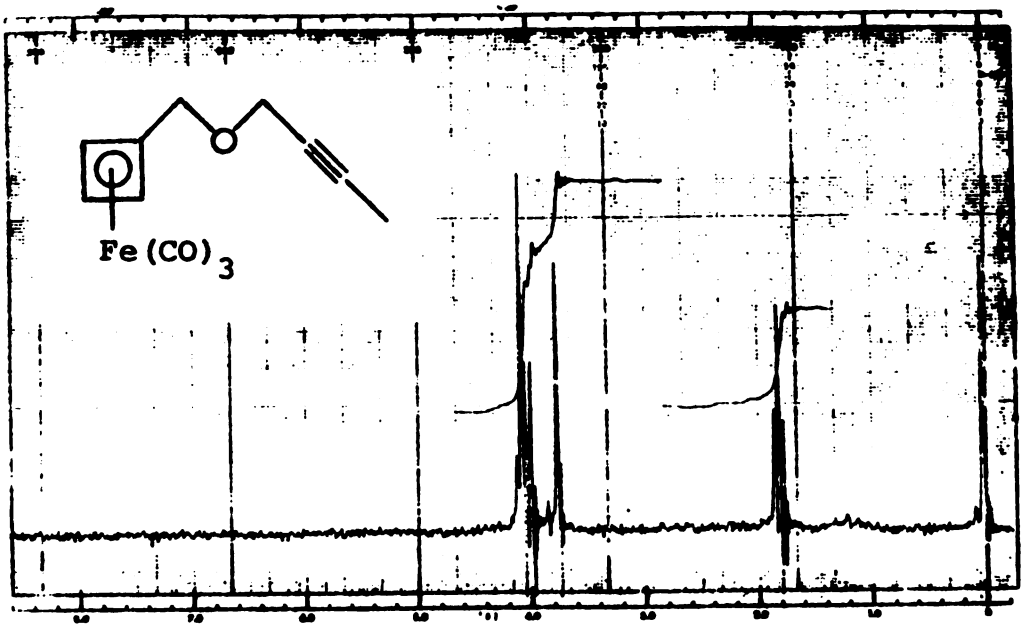

Figure 32. NMR spectrum of 1-(2-butynoxymethyl)cyclobutadienyliron tricarbonyl (79a) ($CDCl_3$).

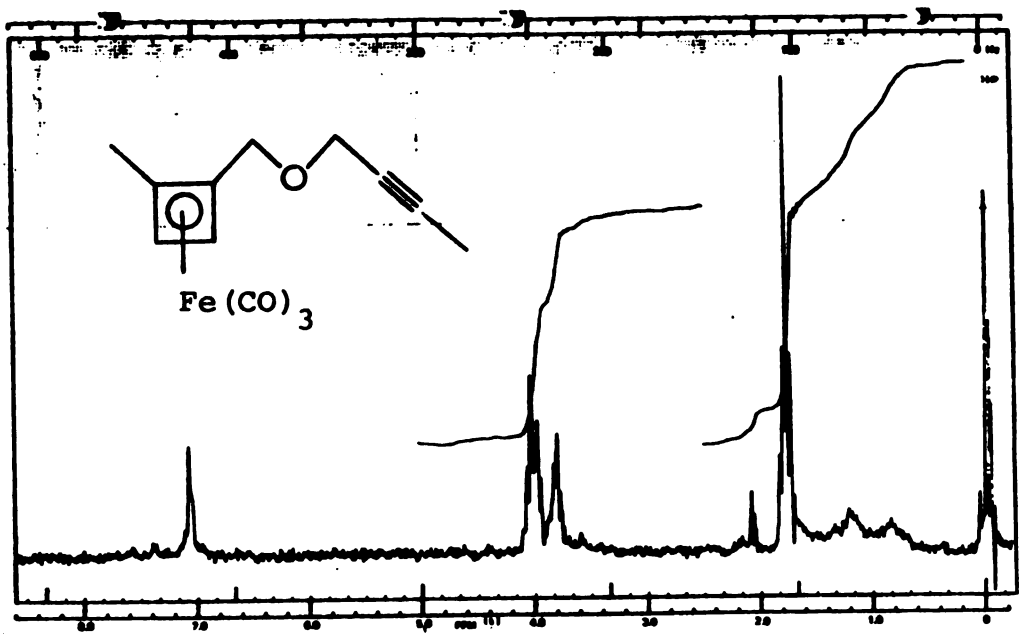

Figure 33. NMR spectrum of 2-methyl(2-butynoxymethyl)-cyclobutadienyliron tricarbonyl (79b) ($CDCl_3$).

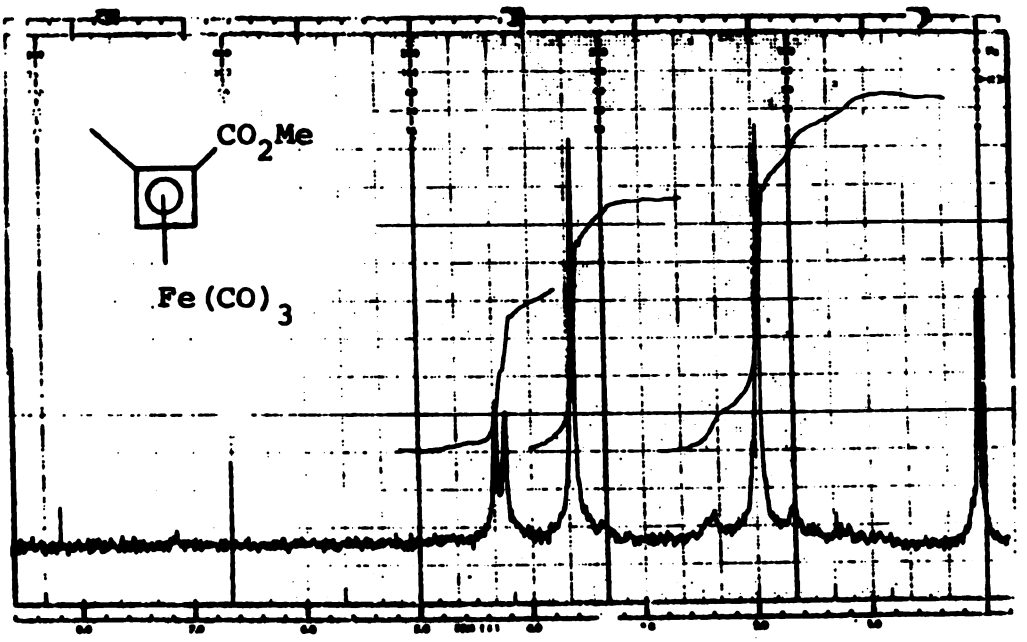

Figure 34. NMR spectrum of 1-methylcarboxylate-2-methyl-cyclobutadienyliron tricarbonyl (102) ($CDCl_3$).

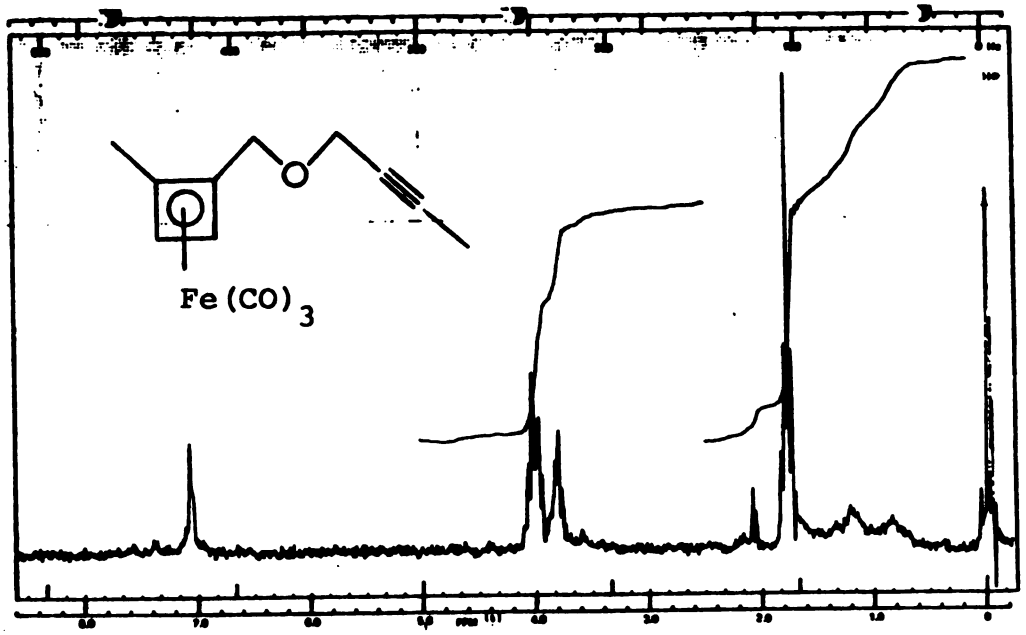

Figure 33. NMR spectrum of 2-methyl(2-butynoxymethyl)-cyclobutadienyliron tricarbonyl (79b) ($CDCl_3$).

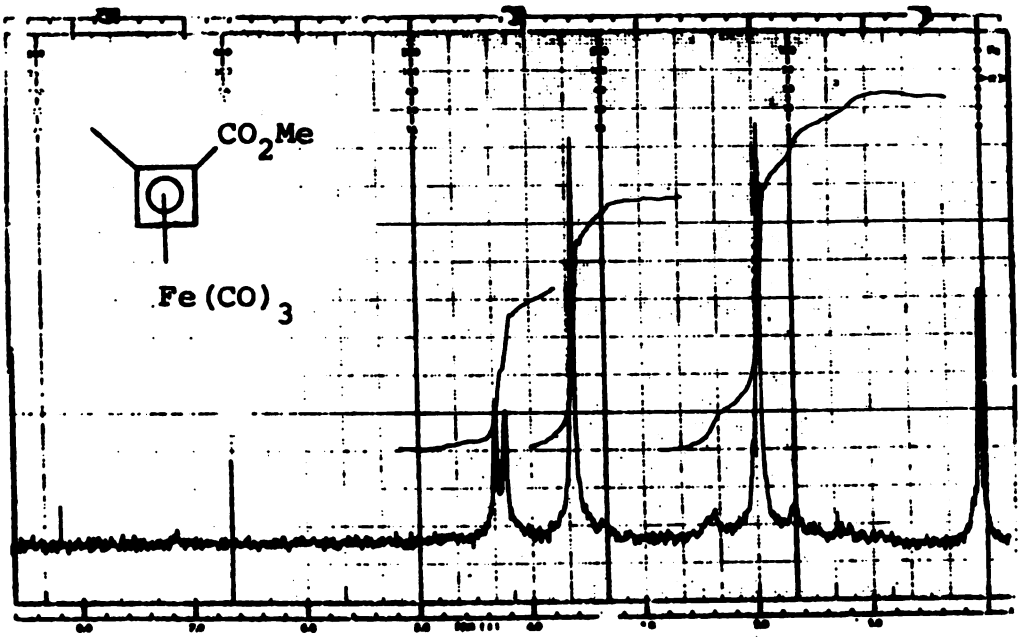

Figure 34. NMR spectrum of 1-methylcarboxylate-2-methyl-cyclobutadienyliron tricarbonyl (102) ($CDCl_3$).

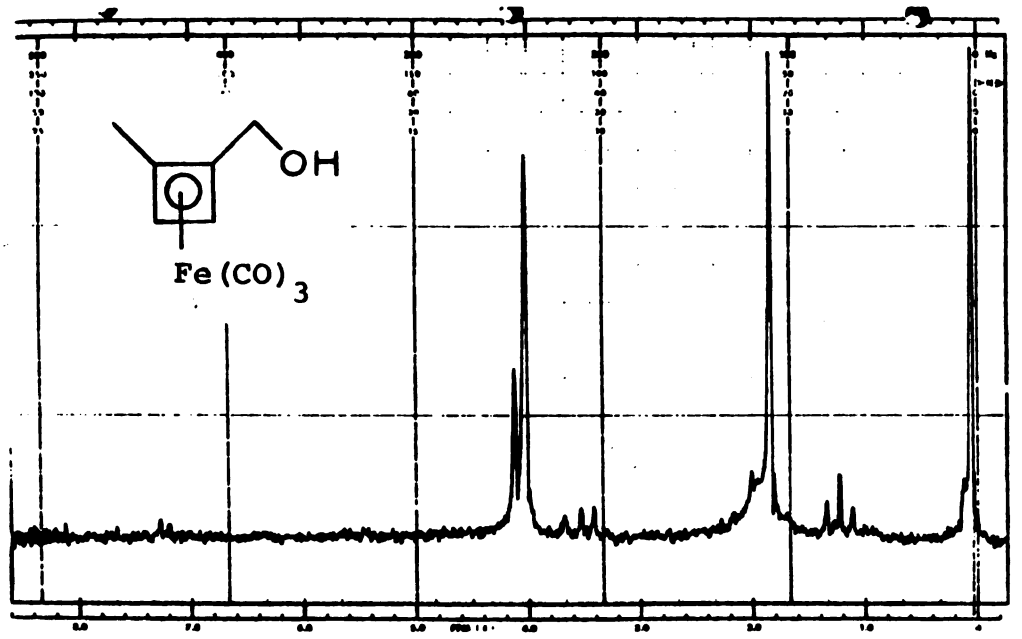

Figure 35. NMR spectrum of 1-hydroxymethyl-2-methylcyclobutadienyliron tricarbonyl (103) ($CDCl_3$).

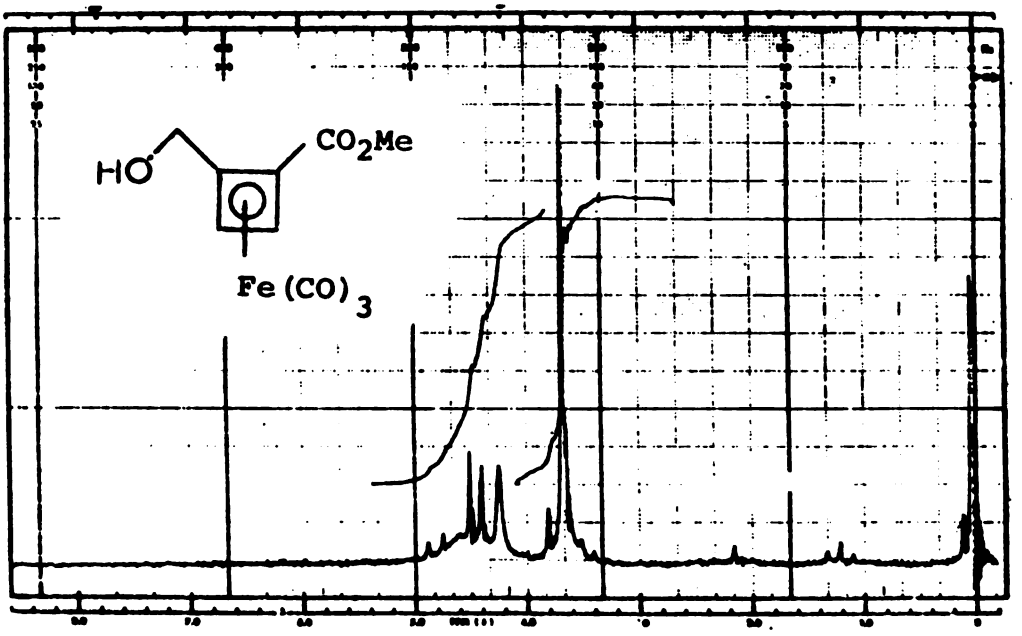

Figure 36. NMR spectrum of 1-methylcarboxylate-2-hydroxymethylcyclobutadienyliron tricarbonyl (106) ($CDCl_3$).

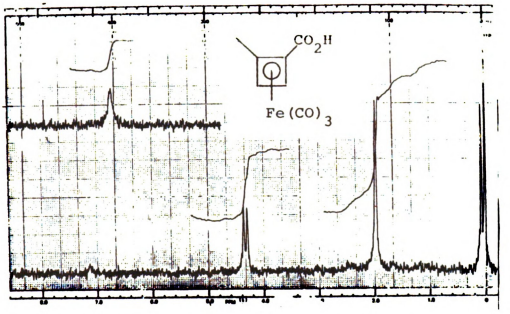

Figure 37. NMR spectrum of 1-hydrogencarboxylate-2-methylcyclobutadienyliron tricarbonyl (108) ($CDCl_3$).

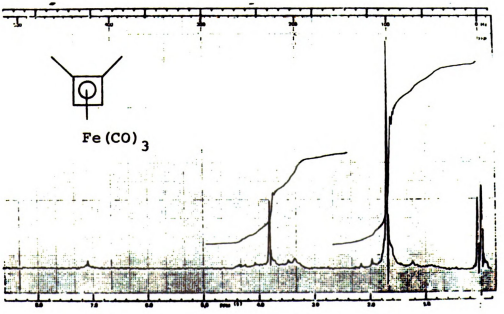

Figure 38. NMR spectrum of 1,2-dimethylcyclobutadienyliron tricarbonyl (111) ($CDCl_3$).

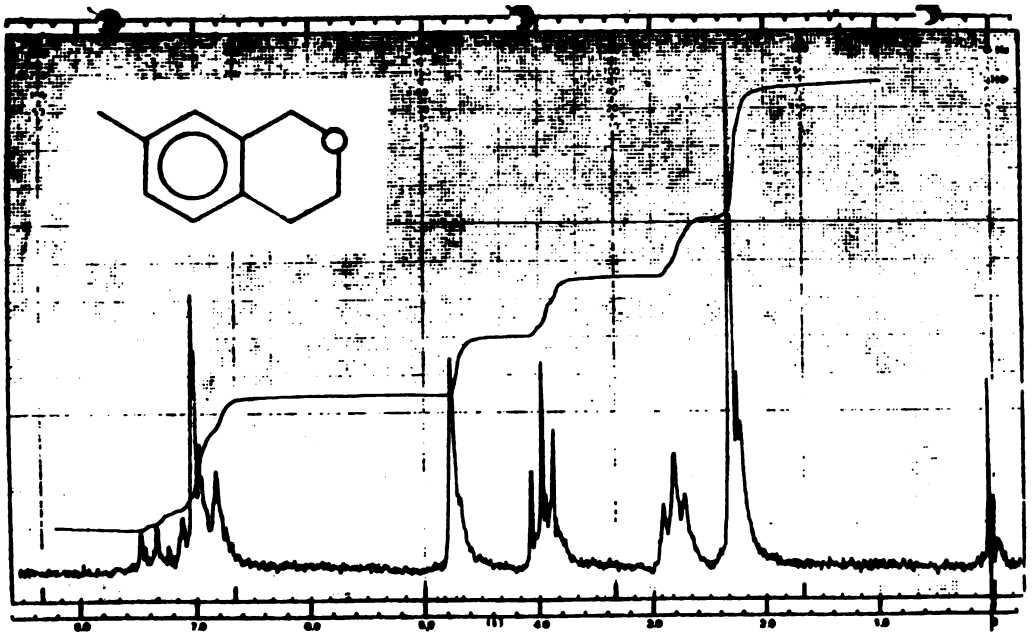

Figure 39. NMR spectrum of 7-methylisochroman (66) ($CDCl_3$).

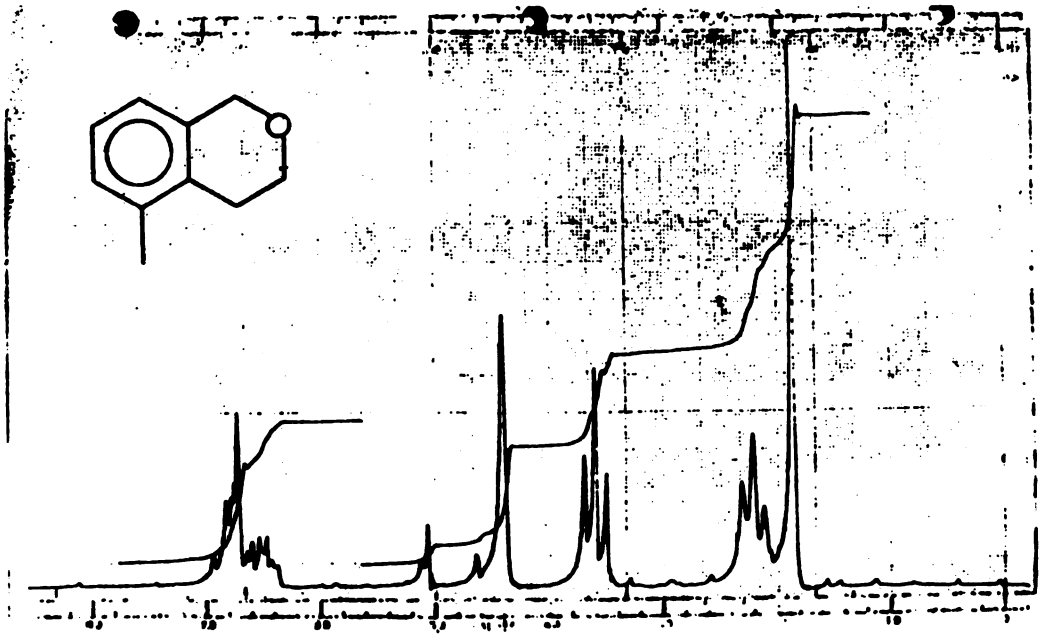

Figure 40. NMR spectrum of 5-methylisochroman (68) (neat).

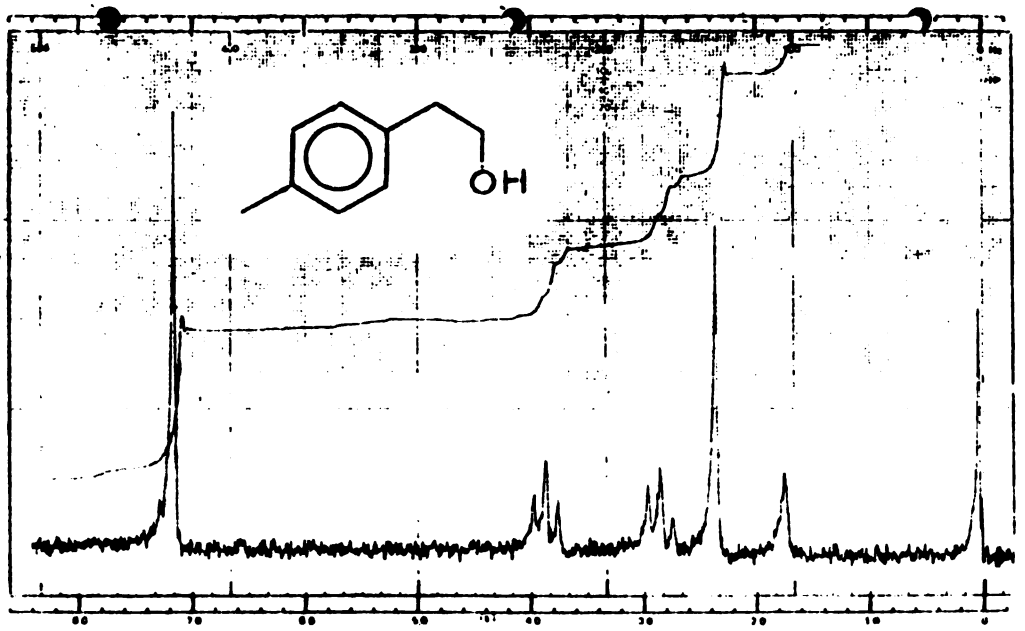

Figure 41. NMR spectrum of 4-(β-hydroxyethyl)toluene (71) ($CDCl_3$).

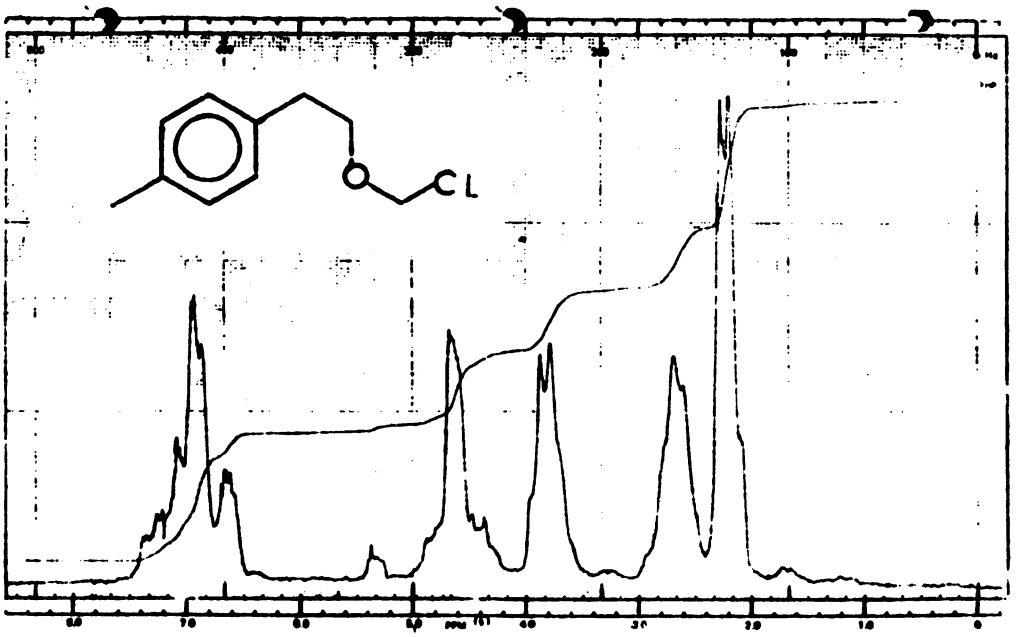

Figure 42. NMR spectrum of 4-(β-chloromethoxyethyl)toluene (72) (neat).

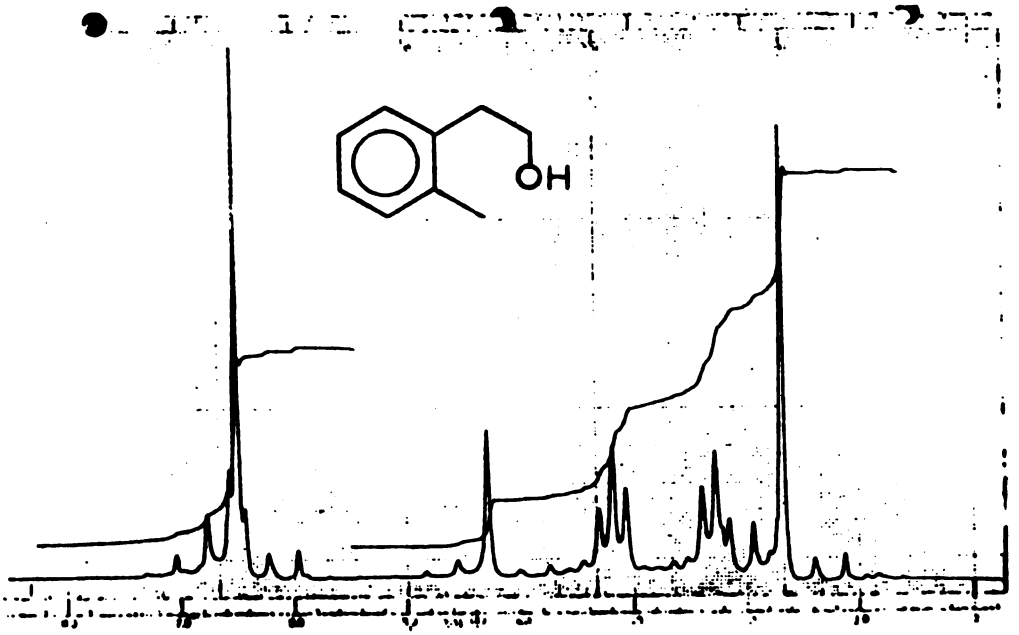

Figure 43. NMR spectrum of 2-(β-hydroxyethyl)toluene (75) (neat).

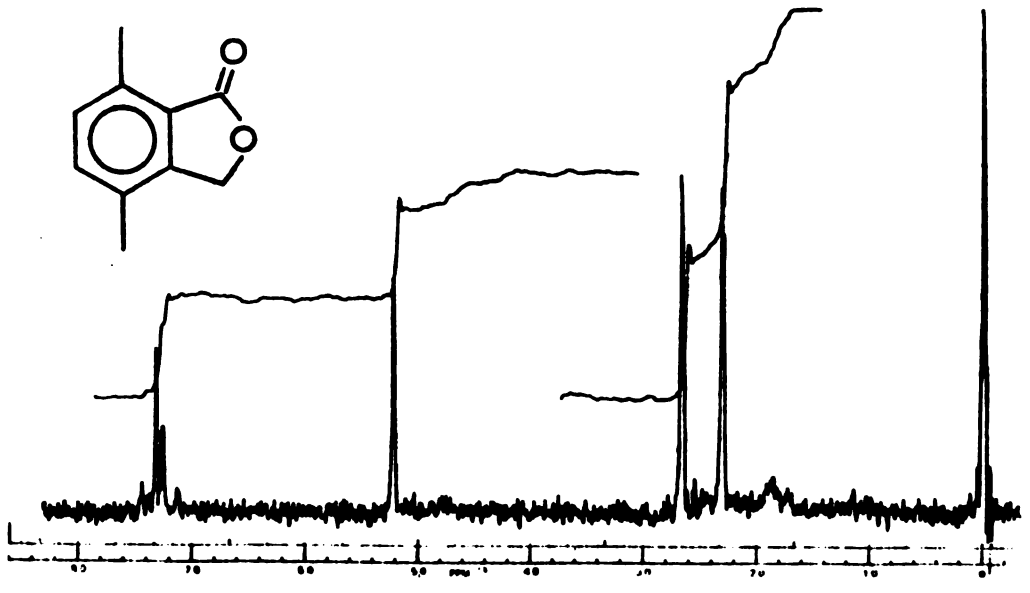

Figure 44. NMR spectrum of 4,7-dimethylphthalide (86b) ($CDCl_3$).

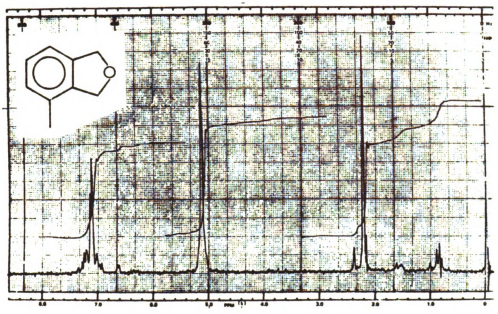

Figure 45. NMR spectrum of 4-methylphthalan (82a) ($CDCl_3$).

Figure 46. NMR spectrum of 4,7-dimethylphthalan (82b) ($CDCl_3$).

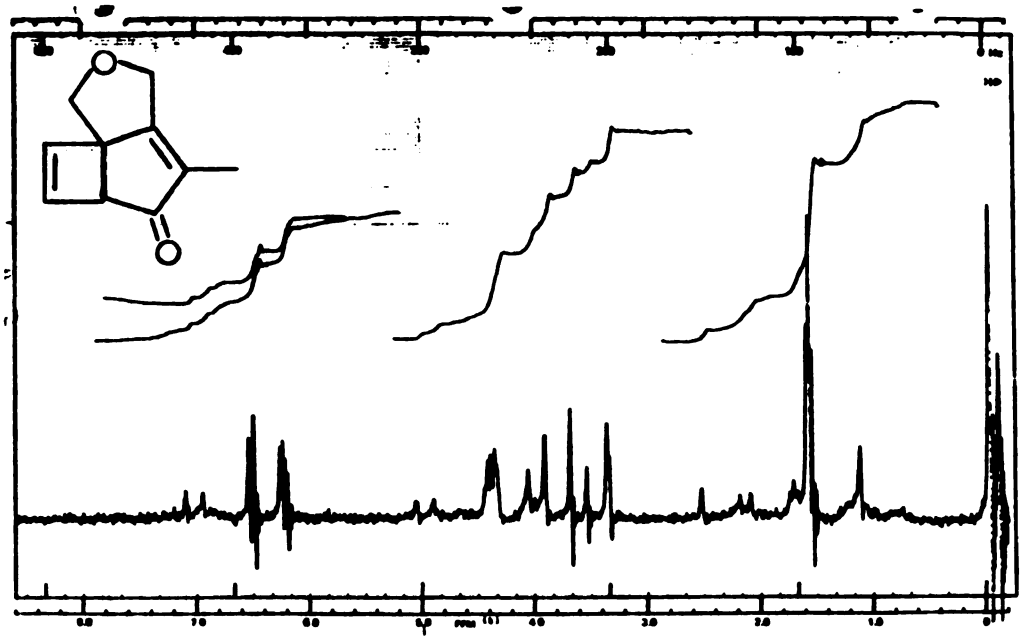

Figure 47. NMR spectrum of 2-methyl-9-oxatricyclo[5.3.2^{4,7}.O^{1,7}]deca-1,5-dien-3-one (84a) ($CDCl_3$).

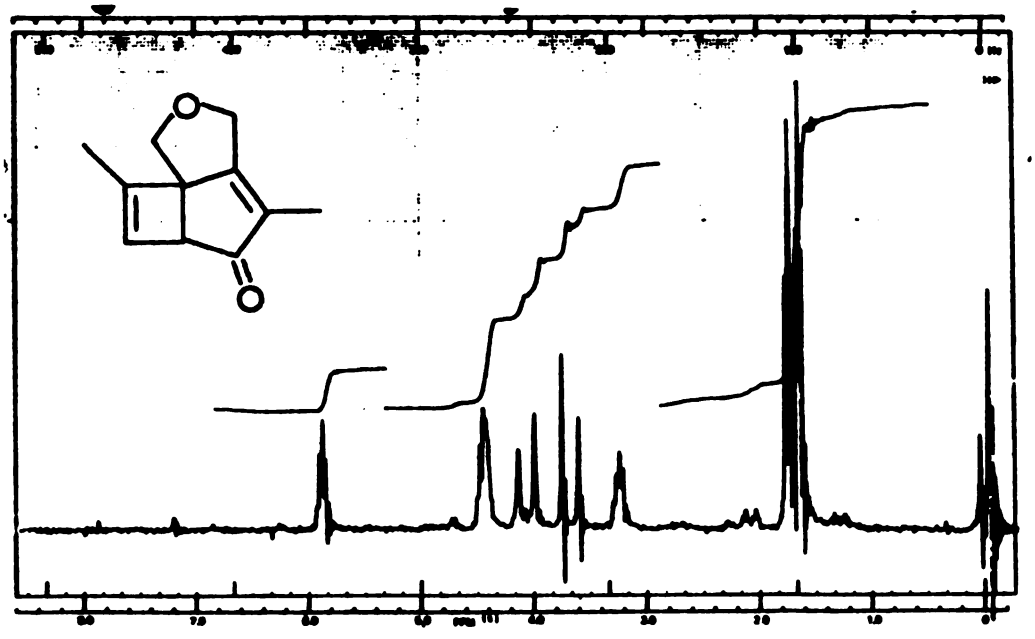

Figure 48. NMR spectrum of 2,7-dimethyl-9-oxatricyclo-[5.3.2^{4,7}.O^{1,7}]deca-1,5-dien-3-one (84b) ($CDCl_3$).

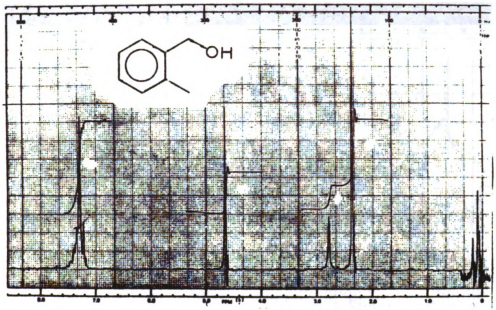

Figure 49. NMR spectrum of 2-hydroxymethyltoluene (89) ($CDCl_3$).

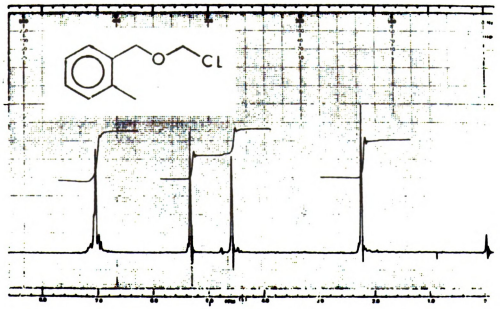

Figure 50. NMR spectrum of 2-(chloromethoxymethyl)toluene (90) ($CDCl_3$).

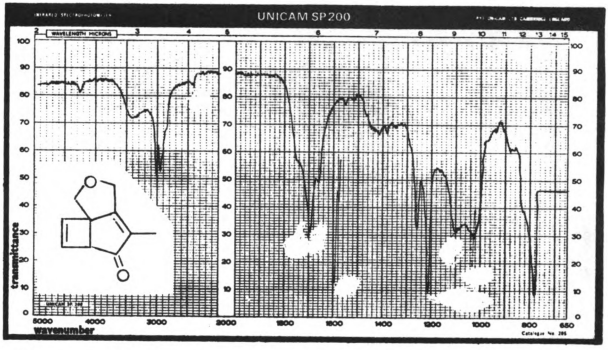

Figure 51. Infrared spectrum of 2-methyl-9-oxatricyclo-[5.3.2 ^{4,7}.0^{1,7}]deca-1,5-dien-3-one (84a) ($CHCl_3$).

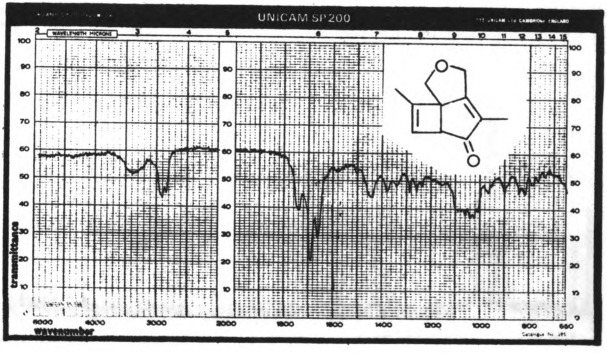

Figure 52. Infrared spectrum of 2,7-dimethyl-9-oxatricyclo-[5.3.2 ^{4,7}.0^{1,7}]deca-1,5-dien-3-one (84b) ($CDCl_3$).

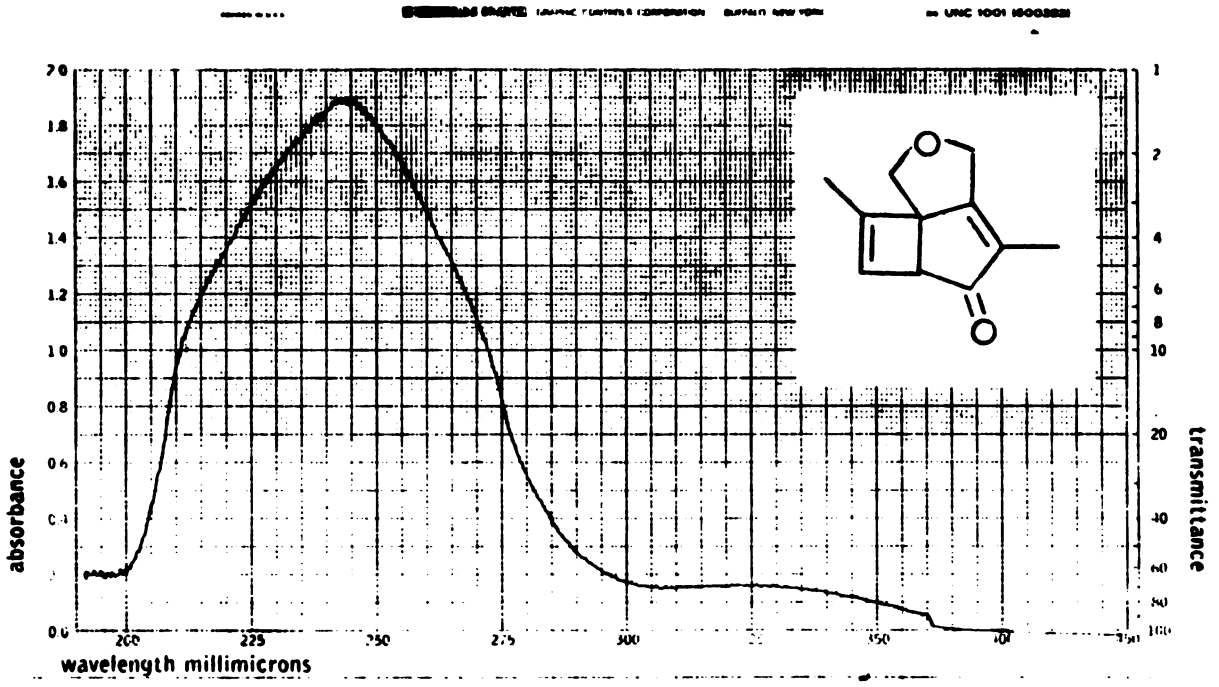

Figure 53. Ultraviolet spectrum of 2,7-dimethyl-9-oxatricyclo[5.3.$2^{4,7}$.$0^{1,7}$]deca-1,5-dien-3-one (84b) (~4.3 X 10^{-4} M in 95% ethanol).

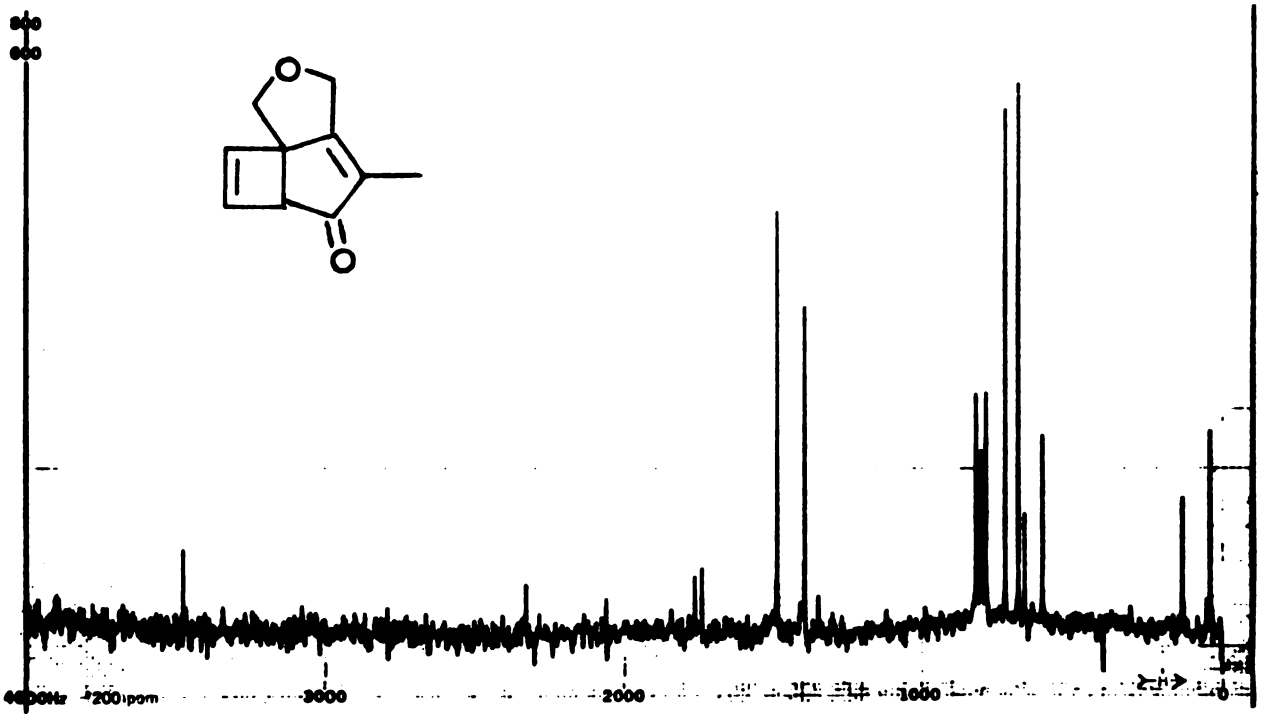

Figure 54. C-13 NMR spectrum of 2-methyl-9-oxatricyclo-[5.3.$2^{4,7}$.$0^{1,7}$]deca-1,5-dien-3-one (84a) ($CDCl_3$).

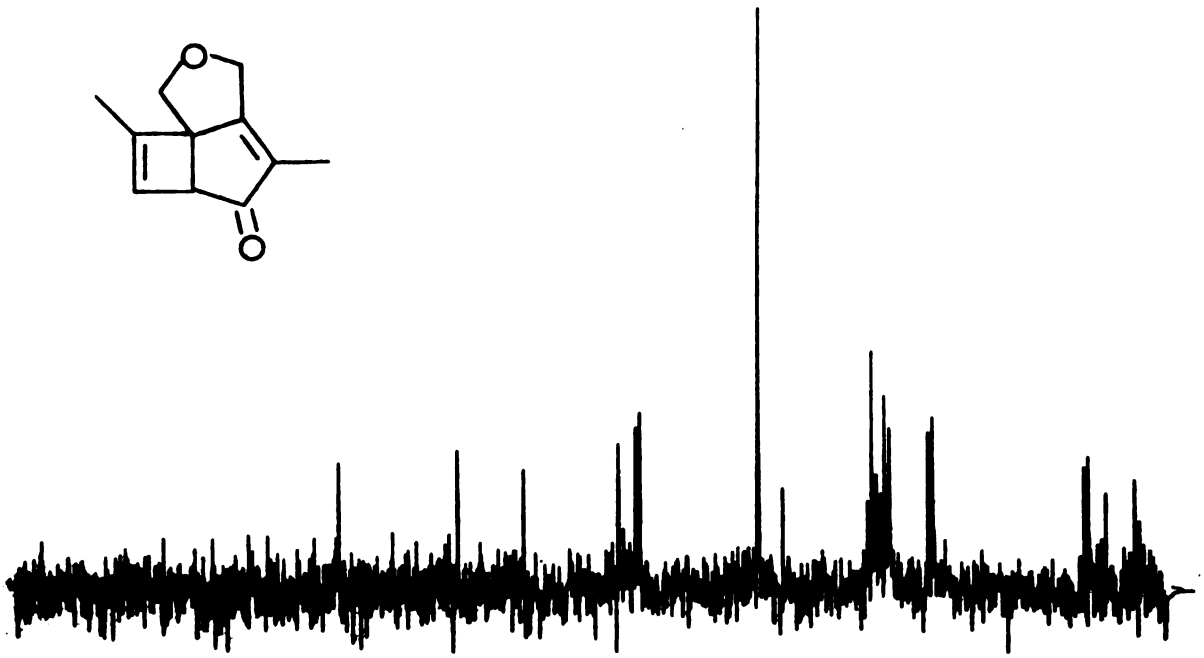

Figure 55. C-13 NMR spectrum of 2,7-dimethyl-9-oxatricyclo-[5.3.$2^{4,7}$.$O^{1,7}$]deca-1,5-dien-3-one (84b) ($CDCl_3$).

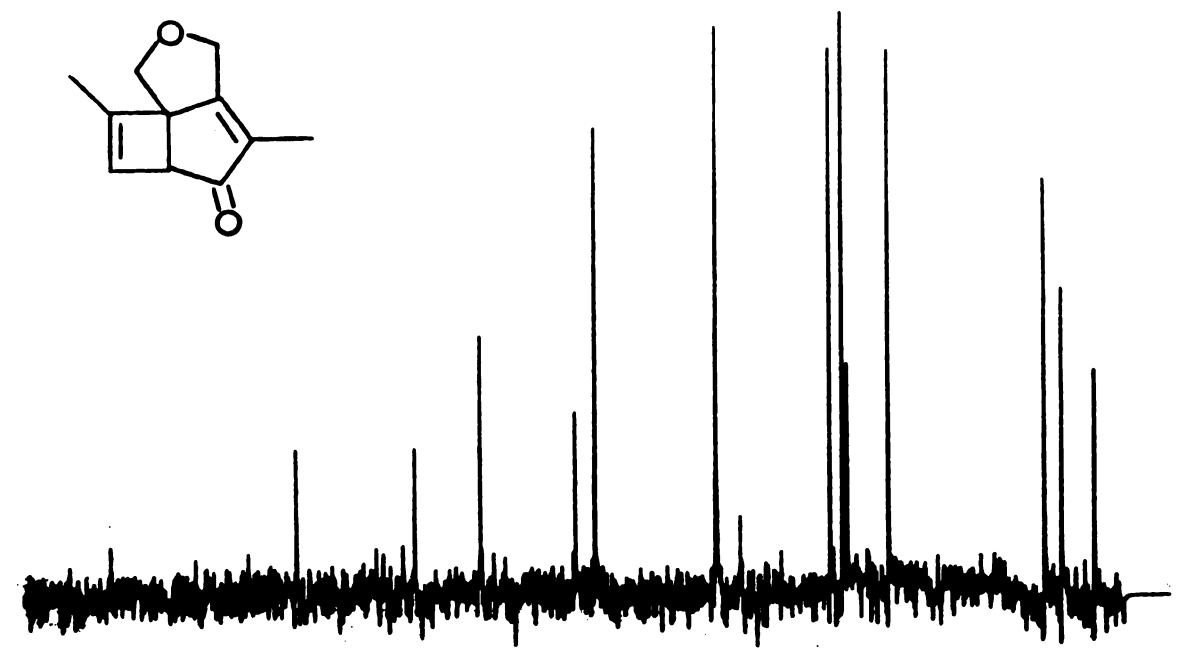

Figure 56. Decoupled C-13 NMR spectrum of 2,7-dimethyl-9-oxatricyclo[5.3.$2^{4,7}$.$O^{1,7}$]deca-1,5-dien-3-one (84b) ($CDCl_3$).