CONCERNING THE MECHANISM OF THE OXIDATIVE DECOMPOSITION OF CYCLOBUTADIENEIRON TRICARBONYL

> Thesis for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY ROGER ALLEN GREY 1973

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## ABSTRACT

## CONCERNING THE MECHANISM OF THE OXIDATIVE DECOMPOSITION OF CYCLOBUTADIENEIRON TRICARBONYL

### By

## Roger Allen Grey

The oxidative decomposition of cyclobutadieneiron tricarbonyl in the presence of dienophiles was studied in order to obtain a definite answer to the question of whether or not "free" cyclobutadiene is an intermediate in this reaction.

An optically active cyclobutadieneiron tricarbonyl §2, of known optical purity was prepared. Decomposition in the presence of a variety of dienophiles with ceric ammonium nitrate gave totally racemic product. It was concluded from this result that significant reaction does not occur from an intermediate where the dienophile and cyclobutadiene are coordinated to the iron and that "free" cyclobutadiene is indeed an intermediate in this reaction.

## CONCERNING THE MECHANISM OF THE OXIDATIVE DECOMPOSITION OF CYCLOBUTADIENEIRON TRICARBONYL

By

Roger Allen Grey

#### A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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To my wife Nancy and daughter Kimberly Ann whose love and understanding during this work is greatly appreciated

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### INTRODUCTION

The preparation of cyclobutadiene  $\frac{1}{2}$  has been the

research goal of many chemists for several decades. Although now recognized to have an extremely short lifetime in the free state at room temperature,  $\frac{1}{4}$  has been found to be a suitable ligand for forming stable complexes with appropriate transition metals. In 1956 Longuet-Higgins first predicted that such complexes would be stable.<sup>1</sup> It was not until 1959 that a transition metal cyclobutadiene complex was first reported. Criegee and Schröder prepared 1,2,3,4-tetramethylcyclobutadiene nickel dichloride  $\frac{3}{4}$  by treating 1,2,3,4tetramethyl-3,4-dichlorocyclobutene  $\frac{2}{4}$  with nickel tetracarbonyl in benzene.<sup>2</sup>



The potential of cyclobutadiene transition metal complexes in synthesis, however, was not realized until the complex could be dissociated, releasing the four carbon

ligand for chemical reaction. Cyclobutadieneiron complexes have proven to be the most useful in this respect. Pettit prepared the unsubstituted complex 5 by treating 3,4dichlorocyclobutene 4 with diiron eneacarbonyl.<sup>3</sup>



Oxidative decomposition of  $\xi$  with ceric ammonium nitrate (Ce<sup>IV</sup>) yields products that would be expected from a cyclobutadiene intermediate. If no trapping agents are present, a cyclobutadiene dimer  $\xi$  is formed.<sup>4</sup>



If there are dienophiles present, such as dimethyl maleate, 5 gives products identical to those which would have arisen from a Diels-Alder reaction with 1.4



The iron complex 5 has also been shown to react with cyclopentadiene where the product 8 appears to have arisen from 1 reacting as a dienophile.



Although recently it has been reported that 1 has been observed in low temperature photolysis experiments, <sup>5,6</sup> there has been no conclusive proof of the presence of 1 as an intermediate in the oxidative decomposition of cyclobutadieneiron tricarbonyl complexes in the presence of trapping agents. Pettit and coworkers have reported most of the information concerning the mechanism of this reaction.

The first observation made about this reaction was the stereochemistry of the trapped products. Dienophiles such as dimethyl maleate and dimethyl fumarate were shown to retain their stereochemistries in the products.



This fact was used to support the argument that l was reacting from a singlet electronic state l. A triplet state reaction should give stereochemical scrambling of the products.<sup>4</sup>





In other experiments Pettit did studies on the oxidative decomposition of 1,2-diphenyl cyclobutadieneiron tricarbonyl 11 in the presence of dienophiles of varying strengths. From the examination of the products of these reactions he found that the moderately reactive dienophiles such as benzoquinone and N-phenyl maleimide gave only 12 and 13 although six isomers were possible in each case.<sup>7</sup>





Extremely reactive dienophiles such as tetracyanoethylene and 1,2-dicyanomaleimide gave two isomers 14, 15 and 16, 17respectively, of the three and six possible respectively.<sup>7</sup>



The unsymmetrical isomers  $\frac{1}{2}$  and  $\frac{1}{2}$  were in a sevenfold excess of  $\frac{1}{4}$  and  $\frac{1}{6}$  respectively.

To explain these results Pettit suggested that 1 was rectangular in nature. Therefore, 1,2-diphenyl cyclobutadiene itself would exist in two isomeric forms 18a and 18b as shown below.



He suggested that there is an equilibrium between 18a and 18b and because of the sensitivity of Diels-Alder additions to steric effects, it is expected that 18b is more reactive as a diene than 18a. With moderately reactive dienophiles, the rate of interconversion of 18a and 18b is fast compared to the Diels-Alder addition and the reaction with the dienophile proceeds via the more reactive isomer (i.e. 18b). For the extremely reactive dienophiles the rate of addition is fast compared to the interconversion rate. This equilibrium lies in favor of 18a.

One might therefore be tempted to draw the conclusion from these experiments that cyclobutadiene  $\frac{1}{4}$  is reacting from a singlet electronic state. But this conclusion is based on the assumption that  $\frac{1}{4}$  is free in this reaction and its reactivity is not at all affected by the metal. This assumption has not yet been established by experimental fact. Before valid conclusions can be drawn about the electronic state of  $\frac{1}{4}$ , one must prove that free  $\frac{1}{4}$  is indeed involved in the mechanism in the trapping step.

Pettit and coworkers realizing this, proceeded to rule out experimentally what they considered to be the four alternative pathways which would not involve a free  $\downarrow$  intermediate. First, they considered the possibility that the iron complex and dienophile reacted directly. This possibility was eliminated by mixing  $\S$  and dienophiles such as dimethyl maleate together without an oxidizing agent present. They observed no trapped product formation.<sup>8</sup>



The second possibility was that the dienophile complexed to the neutral metal complex by replacing one of the carbon monoxide ligands followed by an intramolecular addition to the cyclobutadiene still coordinated to the metal. This possibility was eliminated by photolyzing dimethyl maleate or dimethyl fumarate with  $\xi$  and isolating products 19 and 20 which contained one dienophile complexed to the neutral metal complex.<sup>8</sup>





The substitution products 19 and 20 are stable and thus undergo no further intramolecular reaction if an oxidizing agent is not present. These experiments also show that an oxidizing agent is involved in getting the desired chemical reaction.

The third possibility, they considered was that a dienophile could replace a carbon monoxide and then add to the coordinated cyclobutadiene during the oxidation.



To test this possibility, Pettit did a competition experiment with the isomeric iron substitution products 12and 20 in the presence of the opposite isomer of the dienophile as is shown on the following page.



Decomposition of an equal molar concentration of 19 and dimethyl furmarate gave a mixture of 9 and 10 in a ratio of 1:25 as shown above. Decomposition of an equal molar concentration of 20 and dimethyl maleate gave a mixture of 9 and 10 in a ratio of 1:50. Pettit reasoned that if the third possibility was the mechanism, the adduct derived from the substituted iron complex would be the major product in each case. That is, the reaction containing 19 should give predominantly 9 and the reaction containing 20 should give predominantly 10. He rules out then the third possibility noting that the major product in each case is that adduct of fumarate which is the more reactive dienophile.<sup>8</sup>

The fourth possibility considered by Pettit was that the products could arise from external attack on some oxidized form of the iron complex. Since the oxidized iron complex would be a cation or cation radical he reasoned that if  $\S$  were decomposed in the presence of an equal molar amount of 1,1-diphenyl ethylene and dimethyl maleate, the product would be predominantly that one derived from the best cation trap, i.e. from 1,1-diphenyl ethylene. When this experiment was performed and only the dimethyl maleate adduct \$ was observed, he concluded that this fourth possibility was not operating.<sup>8</sup>

After ruling out these possibilities, Pettit did an experiment which he used to illustrate that  $\frac{1}{4}$  is free during the reaction. A solution of the complex 5 in alcohol was added to a flask at 0° containing ceric ammonium nitrate in water. The gases evolved from the reaction were collected in a trap at -193°. This trap was then treated with an etheral solution of carbomethoxyacetylene. Warming to room temperature and a vpc of the ether solution showed small amounts of methyl benzoate 22.<sup>9</sup>



This experiment however has come under attack because to its nonreproduceability and it also gives no information about the possibility of competing reaction mechanisms. The question of whether  $\frac{1}{2}$  is free during the reaction still remains unanswered.

In addition to those possibilities considered by Pettit, there is an attractive alternate mechanistic possibility, related to Pettit's fourth possibility and still consistent with the experimental observations, for formation of adducts without involving free 1. This mechanism results from thinking of the reaction in terms of transition metal and coordination chemistry (for example, consider Pettit's fourth possibility in terms of the coordinating ability of the dienophiles instead of their cation trapping ability and dienophile strength). A cyclobutadieneiron tricarbonyl complex, before oxidation by ceric ions, involves an iron in the zero oxidation state and is coordinately saturated. The iron cannot therefore add anymore ligands in this oxidation state without losing one of the already coordinated ligands. However during the reaction the ceric ions oxidize the iron by removing electrons from the iron complex. The iron therefore in the oxidized state becomes coordinately unsaturated and can accept electrons in the form of ligands (previously referred to as dienophiles). In the oxidized, again coordinately saturated, form, the ligand can react with the cyclobutadiene ligand while still attached to the iron. The scheme below summarizes the new mechanistic possibility.



The experiments of Pettit do not rule out this mechanism. The experiments which ruled out the first two possibilities considered by Pettit still apply and for the same reasons as stated by Pettit. The experiment ruling out the third possibility considered by Pettit is still consistent with this new postulated mechanism since dimethyl maleate's and dimethyl fumarate's ligand coordinating ability parallel their dienophile strength. Careful examination of the product ratios reveals an actual favoring of the coordinated ligand. This can be explained by a solvent molecule occasionally entering the coordination sphere instead of the free ligand.





Products will favor ligand originally coordinated to the neutral complex The actual distribution of 2 and 12 will be a combination of the effects of the intermediates 26 and 27. The competition experiment of 5 for dimethyl maleate and 1,1-diphenyl ethylene can be easily rationalized on the basis of ligand coordinating ability. Dimethyl maleate is not only a better dienophile but also a much better ligand than 1,1-diphenyl ethylene. Therefore the results of Pettit's fourth experiment are entirely consistent with the new mechanism.

One is then left with the question of how to prove that the reaction mechanism either involves a free  $\frac{1}{6}$ , or an oxidized coordinated iron is still attached to the cyclobutadiene ligand in the trapping step. An examination of the symmetries of the two possible types of intermediates suggests an experiment which would answer the question. The two intermediates under consideration are;



If appropriate substituents X and Y were placed on the cyclobutadiene moiety in the 1 and 2 positions, one notices that intermediate  $\frac{28}{28}$  becomes chiral while intermediate  $\frac{1}{28}$  remains achiral.



An optically active iron complex being trapped as free 29will go through an achiral transition state and will give racemic trapped products. An optically active iron complex going through an intermediate type 30 in the trapping step will go through a chiral transition state and will give optically active trapped products. The scheme below outlines the two possible pathways.



The trapped adducts of the type 37, 38, 39 and 40 have the potential for optical activity since X and Y substitution and their bent structures give them chirality.

It is interesting to note that in 1972, Green and coworkers, starting with  $\xi$  and perfluoro olefins isolated  $\pi$  allyl- $\sigma$  iron compounds  $\xi_{1}^{1}$ ,  $\xi_{2}^{2}$  similar to the ones proposed as intermediates shown above.<sup>10</sup>



With this background information in mind the oxidative decomposition of cyclobutadieneiron tricarbonyl complexes in the presence of symmetrical dienophiles was investigated.

### **RESULTS AND DISCUSSION**

## Synthesis of a Chiral Iron Complex

The first goal of this thesis research was to synthesize a suitable chiral cyclobutadieneiron tricarbonyl complex, which in general can be depicted as 47 where  $R_1 \neq R_2$ . The synthesis made use of the fact that 1,2 disubstituted complexes such as 47 can be conveniently prepared by a method developed by Grubbs. Grubbs found that a useful precursor to 47 can be prepared by photolyzing 1,2 disubstituted acetylenes with vinylene carbonate 43 in acetone to give the corresponding 1,2 disubstituted, <u>cis</u>-3,4-carbonyldioxycyclobutene 44 in good yield.<sup>11</sup>



The photoadducts 44 can be converted directly to the corresponding iron complex 47 by treatment with sodium tetracarbonyl ferrate (-II).<sup>11</sup> The iron dianion can be easily made by the reduction of iron pentacarbonyl with sodium

amalgam. Therefore an iron complex with nonidentical  $R_1$  and  $R_2$  groups other than hydrogen should be available by using the appropriately substituted acetylene.

One of the ring substituents on the chiral complex should be small and inert. The other should contain the potential to be transformed into a functionality which can be used as a handle in resolutions. A methyl group seemed a likely choice for the small inert substituent. The choice of the functional substituent however was limited by the photolysis reaction. A satisfactory photolysis product, 1-methoxymethyl-2-methyl-<u>cis</u>-3,4-carbonyldioxycyclobutene  $\delta_{\lambda}$  was achieved in a 15% yield with a 40% conversion of 4.3in the following manner.



An acetone solution of 1-methoxy -2-butyne & and vinylene carbonate 43 was degassed with nitrogen and photolyzed through a Pyrex filter using a Hanovia 450 watt immersion lamp. Removal of the solvent and two careful distillations yields a bright yellow oil bp 95-105° at 0.5 mm.<sup>12</sup>

The ir spectrum (neat) showed a strong, wide absorption in the carbonyl region at  $1800 \text{ cm}^{-1}$  characteristic of the carbonate.

The nmr spectrum showed a sharp singlet at  $\delta$  3.40 for the three methoxyl protons. The three allylic methyl protons show up at  $\delta$  1.90 as a broad singlet. The two allylic methylene protons appear at  $\delta$  4.06 as a broad singlet. The two nonidentical ring protons appear at  $\delta$  = 5.3 as an AB quartet.

The mass spectrum shows no parent peak m/e 170. However a peak of m/e 126 corresponding to loss of carbon dioxide from a mass of 170 is observed. This peak and other peaks at m/e 112 and m/e 95 can be explained from known mass spectrum fragmentations of cyclobutene carbonates 44.

The reaction described below represents the successful synthesis of a chiral iron complex, 1-methoxymethy1-2methylcyclobutadieneiron tricarbony1 62 from 61 in a 12% yield.<sup>12</sup>



A tetrahydrofuran solution of sodium tetracarbonyl ferrate (-II) was added to a tetrahydrofuran solution containing the cyclobutene carbonate <u>61</u>. Flash distillation of this reaction mixture separated out the iron dianion and

other solid products. Removal of the tetrahydrofuran from the flash distillate on the rotoevaporator and distillation of the residue yielded a bright yellow oil bp 55° at 0.5 mm.

The ir spectrum (neat) showed the characteristic iron carbonyl bands with a strong sharp absorption at 2030  $cm^{-1}$  and a strong wide absorption at 1950  $cm^{-1}$ .

The nmr spectrum showed a sharp singlet at  $\delta$  1.80 for the three protons of the ring methyl. A sharp singlet at  $\delta$  3.4 appeared for the three protons of the methoxymethyl. The two ring protons had slightly different chemical shifts, appearing at  $\delta$  4.1 and  $\delta$  4.2 as sharp singlets. The two methylene protons appeared as an AB quartet at  $\delta$  3.8, nicely illustrating the chirality of 62.

The mass spectrum of 62 exhibited the correct parent peak of m/e 250. Characteristic peaks appeared at m/e 222, m/e 194, m/e 166 and m/e 110, corresponding to successive loss of three carbon monoxides and iron respectively.

The iron complex 62, typical of cyclobutadieneiron complexes is unstable to air and prolonged heating. This is true of all the other iron complexes synthesized in this research.

### Attempted Resolution of Chiral Iron Complexes

With the experimental details of a synthetic route to a chiral iron complex worked out, various methods of resolution were attempted. For 62 to be useful in this research, the ether function must be able to be converted into a functionality appropriate for resolutions.

It is known in the literature that cyclobutadieneiron tricarbonyl methyl alcohol 63 can be easily converted to the chloride 64 by treatment of the alcohol 63 with concentrated hydrochloric acid.<sup>13</sup>



An important feature of the chemistry of the halide 64thus formed is its high reactivity. In a solvolysis study of 64 it was found to solvolyze  $10^8$  times faster than benzyl chloride. This high reactivity is attributed to the greater stability of the  $\alpha$ -cyclobutadienyliron tricarbonyl carbonium ion.<sup>14</sup>

It was hoped therefore that mild conditions would be sufficient to cleave the methyl ether of §2. A carbon tetrachloride solution of the methyl ether complex §2 was treated with concentrated hydrochloric acid. The reaction was followed by vpc. After stirring for 20 minutes the peak for §2 completely disappeared and no other peak appeared. Decanting the organic layer gave a carbon tetrachloride solution of the chloride §5a.

An nmr spectrum of this solution is consistent with the desired chloride. A sharp singlet appeared at  $\delta$  1.82 for the three protons of the ring methyl. The two ring protons show up at  $\delta$  4.05 and  $\delta$  4.15 as two sharp singlets. An AB quartet

at  $\delta$  3.90 appears for the two methylene protons. There was no sign of an absorption for the methoxymethyl protons which was previously at  $\delta$  3.40.

The 1-chloromethyl-2-methylcyclobutadieneiron tricarbonyl 65a can be easily converted back to the methyl ether 62 in essentially quantitative yield by treatment with sodium methoxide in methanol. Again the reaction can be followed by vpc.



It was found that the above reaction could be performed just as easily with concentrated hydrobromic acid.

An nmr spectrum of the bromide 65b showed a sharp singlet at  $\delta$  1.82 for the three protons of the ring methyl. An AB quartet at  $\delta$  3.80 for the two methylene protons and two sharp singlets at  $\delta$  4.05 and  $\delta$  4.12 for the two ring protons.

Now that a chiral iron complex with a potential handle for resolution was successfully synthesized, methods of resolution had to be considered. Since an iron complex which is 100% optically pure is not essential for the trapping experiment, a kinetic resolution of  $\xi\xi$  seemed to be a possibly simple, direct approach to at least a partial resolution.
The reaction between the d and l mixture of the cyclobutadienyl halide  $\delta \xi$  and an optically pure amine would undergo a displacement reaction whose transition states between the d-cyclobutadienyl halide  $\delta \xi$  with the optically pure amine and the  $l-\delta \xi$  with the optically pure amine would be diastereomeric. Therefore the transition states would have different energies. If the difference in energies of the transition states were great enough, the differences in rate of reaction of the two enantiomers will enrich the starting d, l mixture in either the d or the l enantiomer. This type of experiment was tried using strychnine  $\delta \delta$  as the optically pure amine.





One half equivalent of strychnine 66 was stirred with 65a in benzene for 72 hours at room temperature. The solution was washed thoroughly with 10% hydrochloric acid to remove any remaining strychnine. The remaining chloride complex 65a was treated with sodium methoxide in methanol to form the methyl ether 62. After washing the organic layer with water, drying and filtering, a polarimeter was taken. The rotation was very small,  $0.009^\circ$  at 578 nm.

Several further attempts at kinetic resolutions with strychnine were made but polarimeter readings seldom exceeded  $0.01^{\circ}$  at 578 nm. Kinetic resolutions were also attempted using d- $\alpha$ (1-naphthy1) ethylamine as the resolving agent however results of these were also unsatisfactory.

Convinced now that the results from the kinetic resolution approach would not be acceptable, fractional crystallization of diastereomeric salts was the next approach used to attempt to resolve the iron complex 62. The iron complex 62 was converted to the bromide 65b and then reacted with one equivalent of strychnine 66 in benzene. It was hoped that the fractionally crystallized diastereomeric salts thus formed could then be reconverted to the ether complex 62 with sodium methoxide in methanol.



This approach however was seen to be impractical when it was found that the conversion from  $\xi / \xi$  to  $\xi / \xi$  went in a 5% yield.

Next it was decided to further functionalize the  $\alpha$ cyclobutadienyl halide  $\delta_{\lambda}$  in order to get a better handle for resolutions. The two foremost possibilities were:



The synthesis of the amine complex 62 was attempted first since the alcohol complex 62 would have to be reacted with phthalic acid before it could be reacted with a resolving agent 1-(NN-dimethyl amine)methyl-2-methylcyclobutadieneiron tricarbonyl 62 was successfully prepared by stirring the bromide complex 65b and a large excess of anhydrous dimethyl amine in pentane at 0° for 6 hr. After warming to room temperature the organic layer was washed with water, dried and filtered. Removal of the solvent and distillation of the residue yields a bright yellow oil bp 56° at 0.5 mm.<sup>12</sup>

The ir (neat) spectrum exhibited the characteristic iron carbonyl bands, a strong sharp absorption at 2030  $\text{cm}^{-1}$  and a strong wide absorption at 1950  $\text{cm}^{-1}$ .

The nmr spectrum showed a sharp singlet at  $\delta$  1.90 for the three protons of the ring methyl. A sharp singlet at  $\delta$  2.33 for the six NN-dimethyl protons. A broad singlet at  $\delta$  2.90 appeared for the two methylene protons. Two sharp singlets at  $\delta$  4.1 and 4.12 showed up for the two ring protons.

The mass spectrum of & showed the correct parent peak of m/e 263. Peaks characteristic for iron carbonyls appeared at m/e 235, m/e 207, m/e 179 and m/e 123 corresponding to successive loss of three carbon monoxides and iron respectively.

Attempts were then made to resolve the amine complex 69 with  $\alpha$ -tartaric acid 70 in methanol.



Upon sitting for two days at room temperature, no crystals fell out of solution. Reduction of the temperature or the amount of solvent also did not induce crystallization. Removal of all of the solvent revealed no crystals, but instead a gel was formed. Another optically active acid was then sought as a resolving agent.

D-10 camphor sulfonic acid  $\chi_Q$  was the next acid reacted with the amine complex  $\xi_Q^{12}$ . Dissolution of  $\xi_Q^Q$  and  $\chi_Z^Q$  in hot ethanol and cooling the reaction mixture to room



temperature yielded white crystals 73 after 48 hrs. Cooling this mixture at 0° caused further crystallization. After doubling the volume with diethyl ether, the reaction mixture was centrifuged and the liquid decanted from the crystals 73. The crystals were then washed several times with a 50/50 v/v ethanol, diethyl ether solution. The salt 73 was treated with aqueous sodium hydroxide and the free amine 69 was extracted into diethyl ether. The ether layer was dried, filtered and evaporated down to 6 ml. A polarimeter reading of this solution exhibited a rotation of (+)0.238° at 578 nm. The decantate of 73 was treated in a similar manner and revealed a polarimeter reading of (-)0.215° at 578 nm. The magnitudes of these rotations were judged satisfactory enough to pursue this approach to optically active iron complexes.

The amine functionality of  $\xi 2$  however is unstable toward the oxidative decomposition conditions. The dimethyl amine was thus converted to the quaternary salt 74 by stirring  $\xi 2$ with methyl iodide in ether for 24 hr.



The quaternary salt 74 was then treated in situ with sodium methoxide in methanol at room temperature for 16 hr. Washing the ether layer with two portions of water, drying, filtering and removal of the solvent gave crude 62 in essentially a quantitative yield (as determined by vpc). Three micro-distillations of this crude 62 afforded pure 62.<sup>12</sup>

The previously mentioned amine complex 62 which exhibited the (+)0.238° rotation at 578 nm, when subjected to the above reaction conditions gave crude 62 which showed a rotation of (+)0.347° at 578 nm. After three micro-distillations, 180 mg of 62 gave the following polarimeter readings in tetrahydrofuran, (+)0.266° at 578 nm, (+)0.322° at 546 nm, and (+)0.838° at 436 nm.

A question yet to be determined about this resolution is how effectively does the fractional crystallization separate the enantiomers. A method for determining the optical purity of the iron complex was then sought. Treatment of 62 with a chiral europium shift reagent, tris[3-(heptafluorobutyryl)-d-camphorato]-europium(III) [Eu(hfbc)<sub>3</sub>] did not split out any nmr absorptions. The complex seemed to be chemically unstable in prolonged contact or in an excess of the shift reagent.

The method found to determine the optical purity of  $\xi \xi$ involved the conversion of the ether complex  $\xi \xi$  to the bromide  $\xi \xi \xi$  and subsequent reaction of  $\xi \xi \xi$  with the potassium salt of (+)a-methoxy-a-trifluoromethyl-a-phenylacetic acid  $\zeta \xi$  in tetrahydrofuran for 5 hr.<sup>12</sup>



The tetrahydrofuran solution was washed with salt water, dried, filtered and the solvent removed giving the crude diastereomeric esters  $\chi_{0}^{\epsilon}$ . An nmr spectrum was taken of the crude  $\chi_{0}^{\epsilon}$  and after several  $\mu$ -distillations yielding purer  $\chi_{0}^{\epsilon}$ .

The nmr spectrum revealed that only two sets of the protons showed up as diastereotopic protons. The three protons of the ring methyl appeared as two sharp singlets centered at  $\delta$  1.73 with each absorption integrating to 1.5 protons. One of the ring protons showed up as two sharp singlets centered at  $\delta$  4.08 each integrating to 0.5 proton. The other ring proton appeared at  $\delta$  4.18 as a sharp singlet. The three protons of the methoxymethyl appeared at  $\delta$  3.58 as a broad singlet. The five phenyl protons showed up at  $\delta$  7.47 as a broad singlet. An AB quartet appeared at  $\delta$  4.73 for the two methylene protons. The fluorine nmr spectrum showed a broad singlet for the three fluorines of the the fluoromethyl.

The ir spectrum (neat) shows the characteristic iron carbonyl bands with a strong sharp absorption at 2140 cm<sup>-1</sup> and a strong wide absorption at 1970 cm<sup>-1</sup>. Another strong carbonyl absorption appears at 1750 cm<sup>-1</sup>.

The mass spectrum of 76 exhibited the correct parent peak of m/e 452. Characteristic peaks appeared at m/e 424, m/e 396, m/e 348, and m/e 292, corresponding to successive loss of three carbon monoxides and iron respectively.

A 40 mg sample of  $\xi \chi$ ; rotation = (-)0.037° at 578 nm, (-)0.047° at 546 nm and (-)0.151° at 436 nm, was converted into the diastereomeric ester  $\zeta \xi$  in the above manner. An optical purity of 50% was calculated for the starting complex  $\xi \chi$  by measuring the difference in area of the diastereotopic ring methyls. The specific rotation of  $\xi \chi$  was calculated to be 11.2° ± 3% at 578 nm. By comparison with this experiment, all further resolutions produced optical purities for the positive rotamers from 39 to 79%. The negative rotamers varied from 23 to 50% in optical purity.

An interesting property of the resolved complex §2 is that upon heating at 120° in xylene for 48 hr. less than 5% racemization of §2 is observed. This should be compared to a related butadieneiron complex, (+)tricarbonyl(methyl-5formylpenta-2,4-dienoate)iron ZZ which racemizes with  $t_{1/2} =$ 46.5 hr. at 119.4°.

Since electron-withdrawing groups normally stabilize metal-olefin complexes and racemization requires decomplexation of at least one of the double bonds of the diene, the predicted half-life of racemization of a butadiene complex analogous to the cyclobutadiene complex §2 should be less than 46.5 hr. at 119.4°. The much slower racemization rate of the cyclobutadiene complex §2 must be due to the requirement that the cyclobutadiene ligand must become completely detached from the metal in order for racemization to occur, whereas, the butadiene complex requires the

decomplexation of only one bond in the racemization process as shown below.  $^{12}$ 



With a route to an optically active ether complex  $\xi_{k}^{2}$  of known optical purity available, the decomposition in the presence of dienophiles could be attempted.

## The Decomposition of the Chiral Iron Complex

Optically active §2 was decomposed with ceric ammonium nitrate in the presence of three dienophiles; either tetracyanoethylene 78, or N-phenylmaleimide 83, or benzoquinone 88. The general procedure for decomposition is described below.

The ether complex & was stirred with an equal molar amount of the dienophile in acetone (the tetracyanoethylene Z& reaction was done in tetrahydrofuran). The ceric ammonium nitrate was added as a powder over a 3.5 minute period. The reaction mixture was allowed to react until the carbon monoxide bubbles ceased. Diethyl ether was added and the reaction mixture was washed with portions of salt water until the aqueous layer remained colorless. The organic layer was dried, filtered and the solvent removed leaving the adducts in essentially a quantitative yield. When optically active ether complex  $\xi_{\mathcal{X}}^2$  was used, the solvent was reduced to 6 ml and a polarimeter reading taken before the solvent was completely removed.



The ir spectrum (neat) of the mixture  $\chi_2$ ,  $\chi_2$ ,  $\chi_1$  and  $\chi_2$  showed a weak sharp absorption at 2240 cm<sup>-1</sup> for the cyano groups.

The nmr spectrum of the mixture of  $\chi_2$ ,  $\chi_2$ ,  $\chi_1$  and  $\chi_2$  showed that  $\chi_2$  was the major isomer formed comprising about 50% of the mixture. Three sharp singlets appeared at 6 3.43, 6 3.40 and 6 3.33 for the methoxyl protons. Three broad absorptions at 6 4.20, 6 4.03 and 6 3.80 account for the methylene and ring protons. A vinyl absorption appears at 6 5.5 for isomer  $\chi_2$  and two vinyl absorptions of equal intensity appear at  $\delta$  6.36 and  $\delta$  6.46 which were assigned to isomers  $\delta Q$  and  $\delta 1$ . The other methyl absorptions show up at  $\delta$  2.08,  $\delta$  1.73 and  $\delta$  1.9.

Isomer 79 could be isolated from 80, 81 and 82 by tituration of the oily mixture with diethyl ether and washing the precipitate with cool chloroform. Pure  $\chi_2$  is a white solid with a melting point of 124-125°. The nmr spectrum of 79 showed no absorptions in the vinyl region. A broad singlet at  $\delta$  2.08 appeared for the three protons of the allylic methyl. A sharp singlet appeared at  $\delta$  3.45 for the three methoxyl protons. One ring proton showed up at  $\delta$  4.0 and the other at  $\delta$  4.1, both as broad singlets. The allylic methylene appeared at  $\delta$  4.22 as a broad singlet.

The mass spectrum of 72 and the mixture 72, 80, 81 and  $\underline{\&2}$  showed the correct parent peak of m/e 238.

The mixture of 72, 80, 81 and 82 showed a uv absorption from 345 to 200 nm with a slight shoulder at 270 nm.

 $\underline{Ce}^{IV}$ 



82

62





87

The ir spectrum (neat) of the mixture of &4, &5, &6 and &7 exhibited strong wide absorptions at 1690 cm<sup>-1</sup> for the carbonyl bands, and a strong wide absorption at 2900 cm<sup>-1</sup> for the aromatic region.

The nmr spectrum of the mixture of adducts §4, §5, §6 and §7 showed that by far §4 was the major isomer comprising about 75% of the mixture. The isomer §4 showed a broad singlet at  $\delta$  1.83 for the allylic methyl, a sharp singlet at  $\delta$  3.33 for the methoxyl, a multiplet at  $\delta$  3.57 for the four ring protons, a broad singlet for the allylic methylene at  $\delta$  3.93 and a complex multiplet at  $\delta$  7.5 for the aromatic protons. Separate absorptions appearing for the other isomers were; vinyl absorptions of equal intensity at  $\delta$  6.03 and  $\delta$  6.17 assigned to isomers §5 and §6, a vinyl absorption at  $\delta$  5.53 assigned to isomer §7, one other methoxyl absorption as a sharp singlet at  $\delta$  3.4, and other methyl absorptions at  $\delta$  1.73 and  $\delta$  1.27.

The mass spectrum of the mixture §4, §5, §6 and §7 showed a correct parent peak of m/e 283.

The mixture of the adducts &4, &5, &6 and &7 absorbed in the uv from 340 to 200 nm in chloroform.



The ir spectrum (neat) of the mixture of adducts §2, 22, 21and 22 exhibited a strong carbonyl absorption at 1675 cm<sup>-1</sup>.

The nmr spectrum of the mixture of adducts showed §§ as the major isomer formed comprising about 45% of the mixture. Absorptions assigned to the methoxyl protons appeared at  $\delta$  3.3,  $\delta$  3.40 and  $\delta$  3.43 as three sharp singlets. The other methyl absorptions appeared at  $\delta$  1.5,  $\delta$  1.57,  $\delta$  1.63 and  $\delta$  1.93. A complex multiplet appeared in the region of  $\delta$  3.5-4.1 for the methylene and ring protons. The two vinyl absorptions of equal intensity appearing at  $\delta$  5.62 and  $\delta$  5.90 were assigned to isomers §Q and §1. The carbonyl vinyl absorptions appeared at  $\delta$  6.9 as a complex multiplet.

The mass spectrum of the mixture showed the correct parent peak of m/e 218.

The mixture of adducts absorbed in the uv from 400 to 200 nm with a slight shoulder at 285 nm.

When decompositions of (+) or (-) optically active ether complex 62 were performed in the presence of either 78 or 83 or 88, a polarimeter reading of the reaction mixture in diethyl ether revealed racemic adducts  $\pm$  0.003. Starting polarimeter readings of optically active 62 were on the order of 0.10° at 578 nm.

As a more sensitive probe of optical activity, circular dichroism spectra were taken of starting optically active ether complex & and the decomposition adducts. The circular dichroism spectrum of the (+) rotamer of & in pentane showed two maxima. One maximum at (+) 310 nm and the other maximum at (-) 250 nm. The circular dichroism of the (-) rotamer of & in pentane showed a maximum at (-) 310 nm and another at (+) 250 nm.

The tetracyanoethylene adducts, benzoquinone adducts and N-phenyl maleimide adducts which arose from both (+) or (-) & exhibited a circular dichroism curve identical to that of the baseline  $\pm$  0.0002° from 450 to 225 nm.

The polarimeter and circular dichroism studies indicate racemic adducts. However, because each mixture of the adducts contains four isomers, the possibility exists that some isomers may have different signs of rotation than others, the resultant magnitude of the rotation of the adducts may be very small. Also the possibility exists that the specific rotation of the adducts may be much smaller than that of the starting complex 62.

Since the diastereomeric ester complex  $\chi_{0}$  had been successful in showing the relative amounts of (+) and (-)  $\delta_{2}$ , the decomposition of  $\chi_{0}$  in the presence of a dienophile

might show diastereomeric splitting in the adducts. When  $\chi_0^{0}$  was decomposed in the presence of tetracyanoethylene  $\chi_0^{0}$ , an nmr of the adducts revealed no diastereotopic splitting of any sets of protons.

Since the adducts from the three different dienophiles all have some sort of nucleophilic functionality, it was decided to try chiral europium shift reagent experiments on the various adducts. The chiral europium shift reagent used was tris[3-(heptafluorobutyry1)-d-camphorato]europium(III) [Eu(hfbc)<sub>3</sub>].

The first adducts tried were the racemic N-phenyl maleimide adducts &4, &5, &6 and &7, since these adducts could be purified on a Florisil column and one major adduct was formed. Addition of Eu(hfbc)<sub>3</sub> to a CDCl<sub>3</sub> solution of the maleimide adducts affected the nmr spectrum mostly by line broading. However, the phenyl protons split out into two multiplets which integrated to 2:3.

methoxyls was very small  $\triangle$  0.03 ppm.

Since the tetracyanoethylene adduct 79 could be separated out as a single pure isomer from &Q, &l and &2 europium shift reagent experiments were tried on 79 in order to get a simpler clean spectrum. A chloroform solution of  $\chi_2$  from racemic  $\xi_2$  when treated with the achiral shift tris(2,2,6,6-tetramethylheptanedionate)europium reagent  $[Eu(DMP)_{7}]$  gave a simple, clean and well resolved shifted spectrum. The three methoxyl protons absorbed at  $\delta$  4.75 as a sharp singlet. The allylic methylene appeared as a multiplet at  $\delta$  5.6 integrating as two protons. The ring protons shifted out a little with one proton appearing at  $\delta$  4.1 and the other proton at  $\delta$  4.3 as broad singlets. The three protons of the allylic methyl appear at  $\delta$  2.3 as a broad singlet.

A sample of  $\chi_2^{0}$  in chloroform which came from racemic ether complex  $\xi_{\ell}^{2}$  was then treated with the chiral shift reagent Eu(hfbc)<sub>3</sub>. The shifted spectrum showed two sharp singlets at  $\delta$  4.43 and  $\delta$  4.53 which correspond to the enantiomeric methoxyls. The other proton absorptions appeared similarly as they did in the achiral europium shifted spectrum. A sample of  $\chi_2^{0}$  from 46.3% (+) optically active  $\xi_2^{2}$  and a sample of  $\chi_2^{0}$  from 38.6% (-) optically active  $\xi_2^{2}$  were treated with Eu(hfbc)<sub>3</sub>, both showed two sharp singlets for the methoxyl which integrated identical (\* 2%) to the above sample from racemic complex (See Figure 1).



Figure 1. a) Nmr spectrum of 79 in deuterochloroform,
b) Spectrum of 79 with Eu(DPM)<sub>3</sub>, c) Spectrum of 79 from racemic 62 with Eu(hfbc)<sub>3</sub>,
d) Spectrum of 79 from 46.3% (+) 62 with Eu(hfbc)<sub>3</sub>, peaks marked X are from Eu(hfbc)<sub>3</sub>.

To insure that the starting ether complex  $\xi \chi$  was not being racemized by the oxidative decomposition conditions, the following experiment was performed. An ether complex  $\xi \chi$  of known optical purity was decomposed in the presence of 1 equivalent of tetracyanoethylene 79 by using 1/2 equivalent of ceric ammonium nitrate. A polarimeter reading of an ether solution of the reaction mixture showed 1/2 of the starting rotation. Recovery of  $\xi \chi$  from the reaction mixture by distillation yielded ether complex  $\xi \chi$  of the same optical purity as the starting  $\xi \chi$ .

### Conclusion

The results from the polarimeter measurements, circular dichroism curves and europium shift experiments show that totally racemic adducts are produced from the oxidative decomposition of optically active 62 in the presence of symmetrical dienophiles. In order for this to occur, the transition state must involve an achiral intermediate. The experimental observations from this work prove that cyclobutadiene 1 is free during this reaction . No intermediate involving cyclobutadiene 1 coordinated to the iron competes significantly under these conditions.

Further research might be done to see that if under favorable conditions, l reacting while still complexed to the iron can compete significantly with the reaction of free l during decomposition.

### **EXPERIMENTAL**

### General Procedures

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

Ultraviolet spectra were recorded on a Unicam Model SP-800B; samples were contained in 1 cm quartz cells. Infrared spectra were obtained using a Perkin Elmer Model 457 spectrophotometer. A Varian T-60 spectrometer was used to record nmr spectra. Unless otherwise indicated all spectra are recorded as  $\delta$  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 cc) quartz cells. Circular dichroism spectra were obtained with the aid of Dr. John C. Speck Jr. using a Jasco CD/ORD modified by Sproul; samples were contained in 1 cm quartz cells.

All gas chromatographs were obtained using a Varian Aerograph Model 90-P gas chromatograph with a 6' 5% SE-30 vpc column at  $130^{\circ}$ .

1-Methoxy-2-butyne &Q.

To a cooled solution of 105 g (1.25 m) of 2-butyne-1-ol 52 in 200 ml of water was added 90 g (2.25 m) of sodium hydroxide and 284 g (2.25 m) of dimethyl sulfate over a 3 hr period. The reaction mixture was refluxed for 6 hr and then allowed to stir overnight. Addition of 150 ml of water dissolved the precipitated salt. The organic layer was separated from the aqueous layer. The aqueous layer was extracted with 100, 50 and 50 ml portions of diether ether. The combined ether and organic layers were dried over potassium carbonate, filtered and distilled yielding 100 g (79%) of 60 as a clear liquid: bp 99-103°.

## Vinylene Carbonate 43.

Chlorine gas was added at a rapid rate to a stirred solution of 500 g (5.7 m) of ethylene carbonate in 600 ml of carbon tetrachloride. The reaction mixture was irradiated with a Hanovia ultraviolet quartz lamp until complete disappearance of the ethylene carbonate (as determined by nmr). Distillation yielded 460 g (65%) of the clear liquid, chloroethylene carbonate: bp 70-76° at 0.5 mm (lit. 106-107° at 10 mm).<sup>15</sup>

To a stirring refluxing solution of 312 g (2.53 m) of chloroethylene carbonate in 450 ml of anhydrous diethyl ether under a nitrogen atmosphere was added 312 g (3.08 m) of triethylamine (dried by distillation from barium oxide) over a 6 hr period. After an additional 40 hr of refluxing

(adding ether if needed) the reaction mixture was allowed to cool to room temperature and then filtered. The brown precipitate was washed four times with a benzene-ether solution. Distillation yielded 130 g (60%) of 43 as a clear liquid: bp 30-36° at 0.5 mm (lit 69-72° at 30 mm).<sup>15</sup>

1-Methoxymethy1-2-methy1-<u>cis</u>-3,4-carbonyldioxycyclobutene §1.

A degassed solution of 46 g (0.547 m) of 1-methoxy-2-butyne & and 33 g (0.39 m) of vinylene carbonate in 450 ml of acetone was photolyzed for 14 hr using a Hanovia 450 watt immersion lamp. Distillation yielded 20 g (60%) of recovered vinylene carbonate & bp 30-38° and 7 g (27%) of & as an orange oil: bp 105-145° at 0.5-1.7 mm. Redistillation of the orange oil yeilded 5.0 g (19%) of & as a yellow oil: bp 106-116° at 0.5 mm; ir (neat) 1800 (strong, wide, C=O) and 1100 cm<sup>-1</sup> (C-O-C); nmr (CDCl<sub>3</sub>) & 5.30 (q, 2, ring), &4.06 (br s, 2, CH<sub>2</sub>O), & 3.40 (s, 3, methoxy1), & 1.90 (br s, 3, methy1); mass spectrum (15 eV) no parent peak, m/e 126 (P-CO<sub>2</sub>).

1-Methoxymethy1-2-methylcyclobutadieneiron Tricarbonyl 62.

A solution of 2.62 g (0.114 m) of sodium metal in 14 ml of mercury was treated with 150 ml of dry degassed tetrahydrofuran under a nitrogen atmosphere. To this, 6.5 ml (0.0482 m) of iron pentacarbonyl was added in 2 ml portions over a 20 minute period. After the evolution of gases ceased the sodium amalgam was separated out. Another ml of mercury was added, stirred and separated out.

A solution of 5.0 g (2.94 x  $10^{-2}$  m) of 1-methoxymethy1-2-methyl-cis-3,4-carbonyldioxycyclobutene 61 in 100 ml of dry degassed tetrahydrofuran under a nitrogen atmosphere was treated with the above sodium tetracarbonyl ferrate (-II) suspension over a 10 minute period. The reaction mixture was flash distilled under a 0.5 mm vacuum. Distillation of the flash distillate yielded 1.0 g (13%) of 62 as a yellow 55° at 0.5 mm; ir (neat) 2030 (strong, sharp, C=0), oil: bp 1950 (strong, wide, C=0) and 1090 cm<sup>-1</sup> (C-O-C); nmr (CDCl<sub>3</sub>) δ 3.80 (q, 2,  $CH_2O$ ), δ 4.10 (s, 1, ring), δ 4.20 (s, 1, ring),  $\delta$  3.40 (s, 3, methoxyl) and  $\delta$  1.80 (s, 3, methyl); mass spectrum (70 eV) m/e 250 (parent), 222 (P-CO), 194 [P-CO)<sub>2</sub>], 166  $[P-(CO)_3]$  and 110  $[P-Fe(CO)_3]$ ; uv (pentane) 380-200 nm.

1-Chloromethyl-2-methylcyclobutadieneiron Tricarbonyl 65a.

To a solution of 1.0 g  $(4.0 \times 10^{-3} \text{ m})$  of 1-methoxymethyl-2-methylcyclobutadieneiron tricarbonyl 62 in 10 ml of carbon tetrachloride under a nitrogen atmosphere was added 3 ml of concentrated hydrochloric acid. The reaction mixture was stirred for 20 minutes and the organic layer removed, which gave a carbon tetrachloride solution of 65a. This solution was used directly in subsequent reactions: Nmr (CCl<sub>4</sub>)  $\delta$  4.15 (s, 1, ring),  $\delta$  4.05 (s, 1, ring),  $\delta$  3.90 (q, 2, CH<sub>2</sub>Cl),  $\delta$  1.82 (s, 3, methyl). 1-Bromomethy1-2-methylcyclobutadieneiron Tricarbonyl 65b.

To a solution of 1.0 g  $(4.0 \times 10^{-3} \text{ m})$  of 1-methoxymethyl-2-methylcyclobutadieneiron tricarbonyl 62 in 10 ml of carbon tetrachloride under a nitrogen atmosphere was added 3 ml of concentrated hydrobromic acid. The reaction mixture was stirred for 20 minutes, the organic layer was removed which gave a carbon tetrachloride solution of 65b. This solution was used directly in subsequent reactions. Nmr (CCl<sub>4</sub>)  $\delta$  4.12 (s, 1, ring),  $\delta$  4.05 (s, 1, ring),  $\delta$  3.80 (q, 2, CH<sub>2</sub>Br),  $\delta$  1.82 (s, 3, methyl).

1-Methoxymethyl-2-methylcyclobutadieneiron Tricarbonyl ؤرك from ؤيري or ؤي.

To a solution of 65a or 65b as prepared above along with decalin as an internal standard in 10 ml of methanol was added 0.27 g (5.0 x  $10^{-3}$  m) of sodium methoxide and allowed to stir for 1 hr. Enough water was added to separate the layers. Analysis of the organic layer by vpc showed that 62 was reformed in essentially quantitative yield.

# <u>1-(NN-Dimethylamine)methyl-2-methylcyclobutadieneiron</u> Tricarbonyl 62.

To a cooled solution of 1-bromomethyl-2-methylcyclobutadieneiron tricarbonyl  $\xi \xi b$  in 30 ml of pentane under a nitrogen atmosphere was added 10 ml of dimethylamine in one portion. The reaction mixture was warmed to room temperature

and then washed three times with 30 ml portions of water. The organic layer was dried with sodium sulfate, filtered and the solvent removed leaving an orange oil 69. ir (neat) 2030 (strong, sharp, C=0) and 1950 cm<sup>-1</sup> (strong, wide, (C=0); nmr (CDCl<sub>3</sub>)  $\delta$  4.12 (s, 1, ring),  $\delta$  4.10 (s, 1, ring),  $\delta$  2.90 (br s, 12, CH<sub>2</sub>N),  $\delta$  2.33 (s, 6 N-(CH<sub>3</sub>)<sub>2</sub>), and  $\delta$  1.90 (s, 3, methyl); mass spectrum (70 eV) m/e 263 (parent peak), 235 (P-CO), 207 [P-(CO)<sub>2</sub>], 179 [P-(CO)<sub>3</sub>], and 123 [P-Fe(CO)<sub>3</sub>].

1-Methoxymethyl-2-methylcyclobutadieneiron Tricarbonyl 62 from 69.

To a solution of 0.1 g  $(3.8 \times 10^{-4} \text{ m})$  of 1-(NN-dimethylamine)methyl-2-methylcyclobutadieneiron tricarbonyl 69 in 30 ml of diethyl ether was added 0.284 g  $(2.0 \times 10^{-3} \text{ m})$  of methyl iodide. The reaction mixture was allowed to stir at room temperature for 20 hr. This solution was treated with 20 ml of methanol and 0.54 g  $(1.0 \times 10^{-2} \text{ m})$  of sodium methoxide. The reaction mixture after stirring for 20 hr was treated with water to separate the layers. The water layer removed and the organic layer washed two more times with 10 ml portions of water; dried with magnesium sulfate, and the solvent removed (vpc analysis shows essentially quantitative yield of 62 using decalin as an internal standard). Three microdistillations yielded pure 62.

Potassium  $(+) - \alpha$ -Methoxy- $\alpha$ -trifluoromethyl- $\alpha$ -phenylacetate.

To a solution of 0.234 g  $(1.0 \times 10^{-3} \text{ m})$  of  $(+) - \alpha$ -methoxy- $\alpha$ trifluoromethyl- $\alpha$ -phenylacetic acid in 10 ml of ethanol was added 0.0464 g  $(8.3 \times 10^{-4} \text{ m})$  of potassium hydroxide. After stirring for 1/2 hr, diethyl ether and water was added giving two layers. The water layer separated out and then the water removed leaving .18 g of the acid salt as a white precipitate.

 $1-(+)-\alpha$ -Methoxy- $\alpha$ -trifluoromethy $1-\alpha$ -phenylacetoxymethy1-2methylcyclobutadieneiron Tricarbonyl <u>76</u>.

To a solution of 35 mg  $(1.17 \times 10^{-4} \text{ m})$  of 1-bromomethy1-2-methylcyclobutadieneiron tricarbonyl 65b prepared as previously described in 30 ml of tetrahydrofuran under a nitrogen atmosphere was added 40 mg (1.53 x  $10^{-4}$  m) of potassium (+)- $\alpha$ -methoxy- $\alpha$ -trifluoromethyl- $\alpha$ -phenylacetate. After stirring for 4 hr, 20 ml of diethyl ether and water was added to give two layers. The water layer was removed and the organic layer washed several times with a 5% solution of sodium bicarbonate. The organic layer was dried with magnesium sulfate, filtered and the solvent removed leaving a brown oil 76. Microdistillation yields 23 mg (43%) of 76; bp 100° at 0.5 mm; ir (neat) 2140 (strong, sharp, C=0), 1970 (strong, wide, C=O), and 1750  $\text{cm}^{-1}$  (strong, C=O); nmr  $(CDC1_3)$  & 7.47 (m, 5, aromatic), & 4.73 (q, 2,  $CH_2$ -0),  $\delta$  4.18 (s, 1, ring),  $\delta$  4.08 (d, 1, ring, J=4 Hz),  $\delta$  = 3.58 m, 3, methoxyl) and  $\delta = 1.73$  (d, 3, methyl, J=6 Hz); mass

spectrum m/e 452 (parent), 424 (P-CO), 396  $[P-(CO)_2]$ , 368  $[P-(CO)_3]$ , and 312  $[P-Fe(CO)_3]$ .

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2-methylcyclobutadieneiron tricarbonyl 62 and 22 mg of tetracyanoethylene 78 in 7 ml of dry degassed tetrahydrofuran under a nitrogen atomsphere was added 390 mg (7.1 x  $10^{-4}$  m) of ceric ammonium nitrate as a powder over a 4 minute period. The reaction mixture was allowed to stir vigorously for 15 more minutes. Diethyl ether was added and the organic layer was washed several times with 7 ml portions of a saturated salt water solution until the aqueous layer became colorless. The organic layer was dried with magnesium sulfate, filtered and the solvent removed leaving 43 mg (100%) of  $\chi_2^0$ ,  $\xi_2^0$ ,  $\xi_2^1$ and &2 as an orange oil. Isomer 22 can be titurated out as a solid by addition of diethyl ether to the oil; mp 124-125° ir (neat) 2240 (weak, sharp, CN) and 1090  $\text{cm}^{-1}$  (C-O-C); nmr  $\delta$  6.46 (br s, viny1),  $\delta$  6.36 (br s, viny1),  $\delta$  5.50 (br s, viny1), δ 4.20 (m,  $CH_2O$ ), δ 4.03 (m,  $CH_2O$ ), δ 3.80 (m,  $CH_2O$ ), δ 3.43,  $\delta$  3.40,  $\delta$  3.33 (s, methoxyls) and  $\delta$  2.08,  $\delta$  1.9,  $\delta$  1.7 (s, methyls); mass spectrum m/e 238 (parent peak); uv (diethyl ether) 345-200 nm, sh 270 nm.

 $\frac{3-\text{Methoxymethyl-4-methyl-8-azatricyclo[4.3.0.0<sup>2,5</sup>]nona-3-ene-}{7,9-\text{dione-8-phenyl} 84 and Isomers 85, 86 and 87.}$ To a solution of 50 mg (2.0 x 10<sup>-4</sup> m) of 1-methoxymethyl-

2-methylcyclobutadieneiron tricarbonyl  $\delta_{2}^{2}$  and 32 mg (1.85 x  $10^{-4}$  m) of N-phenyl maleimide <u>83</u> in 7 ml of degassed acetone under a nitrogen atmosphere was added 390 mg (7.1 x  $10^{-4}$  m) of ceric ammonium nitrate as a powder over a 3 minute period. The reaction mixture was allowed to stir vigorously for 5 more minutes. Diethyl ether was added and the organic layer was washed several times with 7 ml portions of a saturated salt water solution until the aqueous layer became colorless. The organic layer was dried with magnesium sulfate, filtered and the solvent removed leaving 50 mg (100%) of 84, 85, 86 and <u>87</u> as a tan oil. ir (neat) 1690 (strong, wide, C=O), 2900  $\text{cm}^{-1}$  (strong, broad, aromatic), and 1100  $\text{cm}^{-1}$  (C-O-C), nmr (CDC1<sub>3</sub>) δ 7.5 (m, aromatic), δ 6.17, δ 6.03, δ 5.53 (br s, viny1),  $\delta$  3.93 (br s, CH<sub>2</sub>O),  $\delta$  3.57 (m, ring),  $\delta$  3.33, 3.40 (s, methoxyls) and  $\delta$  1.83,  $\delta$  1.73,  $\delta$  1.27 (s, methyls); mass spectrum m/e 283 (parent); uv (CHC1<sub>3</sub>) 340-200 nm.

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To a solution of 50 mg  $(2.0 \times 10^{-4} \text{ m})$  of 1-methoxymethyl-2-methylcyclobutadieneiron tricarbonyl 62 and 20 mg  $(1.85 \times 10^{-4} \text{ m})$  of benzoquinone 82 in 7 ml of degassed acetone under a nitrogen atmosphere was added 390 mg  $(7.1 \times 10^{-4} \text{ m})$  of ceric ammonium nitrate as a powder over a 3 minute period. The reaction mixture was allowed to stir for five more minutes. Diethyl ether added and the organic layer washed several times with 7 ml portions of a saturated salt solution until the aqueous layer became colorless. The organic layer was dried with magnesium sulfate, filtered and the solvent removed yielding 40 mg (100%) of &9, 90, 91 and 92 as a yellow oil. ir (neat) 1675 (strong, wide, C=O) and 1100 cm<sup>-1</sup> (C-O-C); nmr (CDCl<sub>3</sub>) & 6.9 (m, carbonyl vinyl), & 5.90, & 5.62 (br s, vinyl), & 4.1-3.5 (m, CH<sub>2</sub>O and ring), & 3.43, & 3.40, & 3.3 (s, methoxyls) and & 1.93, & 1.63, & 1.57, & 1.5 (s, methyls); mass spectrum m/e 218 (parent); uv diethyl ether) 400 to 200 nm, sh 285 nm.

# Resolution of 1-(NN-Dimethylamine)methyl-2-methylcyclobutadieneiron Tricarbonyl 69.

A heated solution of 1.05 g  $(4.0 \times 10^{-3} \text{ m})$  of 1-(NNdimethylamine)methyl-2-methylcyclobutadieneiron tricarbonyl 69 and 0.928 g  $(4.0 \times 10^{-3} \text{ m})$  of d-10-camphor sulfonic acid 72 in 3.5 ml of dry degassed ethanol under a nitrogen atmosphere was allowed to cool to room temperature for 48 hr. The reaction mixture was then cooled at 0°C for 24 hr. Diethyl ether is then added to double the total volume and the reaction mixture was centrifuged. The yellow liquid was decanted and the white crystals washed 5 times with a 50/50, v/v ethanol, diethyl ether solution by centrifugation and decantation. The crystals dissolved in hot methanol were added to an excess of aqueous sodium hydroxide. The free amine 62 was extracted into diethyl ether. The ether layer was dried with sodium sulfate, filtered and the solvent removed. A polarimeter revealed that the crystals yielded the positive rotamer and the decantates yielded the negative rotamer. The amine 62 thus formed is used directly in subsequent reactions. See Table 8 for details of representative resolutions.

Nmr Experiments with the Trapped Adducts and Eu(hfbc)<sub>3</sub>.

Decompositions of 62 were done as previously described on pages 49, 50, and 51. As much of the sample as possible was dissolved in 0.15 ml of deuterated chloroform (note that with pure isomer 72, vigorous heating was required to get dissolution). The solution was transferred to a thick walled nmr tube and a nmr spectrum was taken. Solid  $Eu(hfbc)_3$  was added in 5 mg portions directly into the nmr The nmr tube was tipped up and down until the solid tube. dissolved and the solution was thoroughly mixed. After the solution was allowed to come to equilibrium at the nmr spectrometer temperature for 10-15 minutes an nmr was taken. Further 5 mg portions of  $Eu(hfbc)_3$  were added as needed to obtain a satisfactory shifted spectrum.

Decomposition of Optically Active 1-Methoxymethyl-2-methylcyclobutadieneiron Tricarbonyl 62 with 78, 83 and 88.

Decompositions with optically active iron complex 62 with the dienophiles 78, 83 and 88 were done almost identically to those with racemic 62. However instead of completely removing the solvent after filtering, the solvent was evaporated down to 6 ml and polarimeter measurements were taken. See Table 8 for details of representative decompositions.

## B I B L I O G R A P H Y

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APPENDIX

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Figure 2. Infrared spectrum of 1-methoxymethyl-2-methyl-<u>cis</u>-3,4-carbonyldioxycyclobutene <u>61</u> (neat).


Figure 3. Infrared spectrum of 1-methoxymethy1-2-methy1cyclobutadieneiron tricarbony1 62 (neat).



Figure 4. Infrared spectrum of 1-(NN-dimethyl amine)methyl-2-methylcyclobutadieneiron tricarbonyl 69 (neat).



Figure 5. Infrared spectrum of 1-(+)-a-methoxy-a-trifluoromethyl-a-phenylacetoxymethyl-2-methylcyclobutadiene-iron tricarbonyl <u>76</u> (neat).



Figure 6. Infrared spectrum of 2,2,3,3-tetracyano-5methoxymethyl-6-methylbicyclo[2.2.0]hex-5-ene 2,9 and isomers 20, 81 and 82 (neat).



Figure 7. Infrared spectrum of 3-methoxymethyl-4-methyl-8azatricyclo[4.3.0.0<sup>2,5</sup>]nona-3-ene-7,9-dione-8phenyl §4 and isomers §5, §5 and §7 (neat).



Figure 8. Infrared spectrum of 3-methoxymethyl-4-methyltricyclo[4,4.0.0<sup>2,5</sup>]deca-3,8-diene-7,10-dione 2Q and isomers 2Q, 9Q and 9Z (neat).



Figure 9. Nmr spectrum of 1-methoxymethyl-2-methyl-<u>cis</u>-3,4-carbonyldioxycyclobutene §2 (CDCl<sub>3</sub>).



Figure 10. Nmr spectrum of 1-methoxymethyl-2-methylcyclobutadieneiron tricarbonyl §2 (CDCl<sub>3</sub>).



Figure 11. Nmr spectrum of 1-chloromethyl-2-methylcyclobutadieneiron tricarbonyl 65a (CC1<sub>4</sub>).



Figure 12. Nmr spectrum of 1-bromomethy1-2-methylcyclobutadieneiron tricarbony1 §\$b (CC1<sub>4</sub>).



Figure 13. Nmr spectrum of 1-(N,N-dimethyl amine)methyl-2methylcyclobutadieneiron tricarbonyl §2 (CDC1<sub>3</sub>).



Figure 14. Nmr spectrum of 1-(+)-a-methoxy-a-trifluoromethyla-phenylacetoxymethyl-2-methylcyclobutadieneiron tricarbonyl ζ6 from racemic 62 (CDCl<sub>3</sub>).



Figure 15. Nmr spectrum of 1-(+)-a-methoxy-a-trifluoromethy1a-phenylacetoxymethy1-2-methylcyclobutadieneiron tricarbonyl 76 from (-) 62 (CDCl<sub>3</sub>).



Figure 16. Nmr spectrum of 1-(+)-a-methoxy-a-trifluoromethyla-phenylacetoxymethyl-2-methylcyclobutadieneiron tricarbonyl 76 from (+) 62 (CDCl<sub>3</sub>).



Figure 17. Nnr spectrum of 3-methoxymethyl-4-methyl-8azatricyclo[4.3.0.0<sup>2</sup>, <sup>5</sup>]nona-3-ene-7,9-dione-8phenyl & and isomers & 5, & 6, and & 7 (COCl<sub>3</sub>).



Figure 18. Nmr spectrum of 3-methoxymethyl-4-methyl-8azatricyclo[4.3.0.0<sup>2</sup> f<sup>5</sup>]nona-3-ene-7,9-dione-8phenyl 84 and isomers 85, 86 and 87 with Eu(hfbc)<sub>3</sub> in CDCl..



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Figure 24. Nmr spectrum of 2,2,3,3-tetracyano-5-methoxymethyl-6-methylbicyclo[2.2.0]hex-5-ene 72 with Eu(DMP)3 in CDCl3.





Figure 27. Nmr spectrum of 2,2,3,3-tetracyano-5-methoxymethyl-6-methylbicyclo[2.2.0]hex-5-ene Zg from 39% (-) g2 with Eu(hfbc)<sub>3</sub> in CDCl<sub>3</sub>.

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Figure 28. CD spectrum of 52.5% (+) 1-methoxymethyl-2methylcyclobutadieneiron tricarbonyl 62 (pentane).



Figure 29. CD spectrum of 32.2% (-) 1-methoxymethyl-2methylcyclobutadieneiron tricarbonyl 62 (pentane).



Figure 30. CD spectrum of 2,2,3,3-tetracyano-5-methoxymethyl-6-methylbicyclo[2.2.0]hex-5-ene 79 and isomers &Q, &L, and & from 52.5% (+) & & (CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>).



Figure 31. CD spectrum of 2,2,3,3-tetracyano-5-methoxymethyl-6-methylbicyclo[2.2.0]hex-5-ene 79 and isomers &&, && and && from 32\* (-) && (CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>).



Figure 32. CD spectrum of 3-methoxymethyl-4-methyltricyclo-[4.4.0.0<sup>2,5</sup>]deca-3,8-diene-7,10-dione 89 and isomers 99, 91 and 92 from 52% (\*) 62 (CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>).



Figure 33. CD spectrum of 3-methoxymethyl-4-methyl-8azatricyclo[ $4.3.0.0^2$ ,<sup>5</sup>]nona-3-ene-7,9-dione-8phenyl 84 and isomers 85, 86 and 87 from 50% (+) 62 (CHCl<sub>3</sub>).

Table 1.	Mass Spectrum of 3-Methoxymethy1-4-methy1-
	tricyclo[4.4.0.0 <sup>2</sup> , <sup>5</sup> ]deca-3,8-diene-7,10-dione
	by and isomers 90, 91, and 94

m/e	Rel. Intensity	m/e	Rel. Intensity
218	1.0	91	12.5
203	1.17	82	27.0
186	2.83	77	13.0
175	2.83	76	16.0
158	3.0	65	7.84
149	4.84	56	25.3
145	4.84	54	26.0
129	5.0	45	17.8
121	3.83	43	18.8
115	8.5	41	26.5
105	20.2	32	26.0
104	22.6	31	24.2
		28	26.0

	m/e	Rel. Intensity
_	126	1.0
	112	2.58
	95	2.54
	83	2.37
	65	1.27
	45	1.0

Table 2.Mass Spectrum of 1-Methoxymethyl-2-methyl-<br/>cis-3,4-carbonyldioxycyclobutene §1

m/e	Rel Intensity
250	1.0
222	2.84
194	2.5
166	1.5
136	6.34
135	1.0
134	3.17
110	2.58
96	2.17
56	4.67
28	19.16

Table	3.	Mass Spectrum of 1-Methoxymethy1-	
		2-methylcyclobutadieneiron Tricarbonyl	б2

m/e	Rel. Intensity	m/e	Rel. Intensity
263	1.0	122	14.4
235	>22.2	121	10.7
219	1.14	110	15.1
207	>22.2	108	13.3
179	18.7	99	22.2
171	16.3	95	20.2
151	>22.2	84	18.7
149	3.57	83	14.7
136	>22.2	65	4.87
134	>22.2	56	>22.2
123	9.55	44	>22.2

Table 4.Mass Spectrum of 1-(NN-Dimethyl amine)methyl-<br/>2-methylcyclobutadieneiron Tricarbonyl 69

m/e	Rel. Intensity	m/e	Rel. Intensity
452	1.0	189	19.0
424	1.6	174	5.0
396	1.0	163	21.5
368	5.5	155	20.0
312	1.0	136	5.0
263	4.2	135	5.6
236	6.6	117	8.6
233	1.0	105	22.8
219	70.0	79	14.0
217	9.0	77	16.0
191	2.0		

Table 5. Mass Spectrum of  $1-(+)\alpha$ -Methoxy- $\alpha$ -trifluoromethyl- $\alpha$ -phenylacetoxymethyl-2-methylcyclobutadieneiron Tricarbonyl  $\chi_0^{\alpha}$ 

m/e	Rel. Intensity
238	1.0
223	1.38
206	1.12
179	2.25
173	2.63
141	1.75
110	2.5
109	2.5
95	7.38
77	1.88
76	2.0
67	6.0
51	3.38
4 5	4.0
31	11.2
28	19.4

Table 6.Mass Spectrum of 2,2,3,3-Tetracyano-5-methoxymethyl-<br/>6-methylbicyclo[2.2.0]hex-5-ene 79 and Isomers 80,<br/>81, and 82

m/e	Rel. Intensity	m/e	Rel. Intensity
283	1.0	132	0.675
268	4.25	127	0.432
255	0.405	121	4.2
240	0.216	119	2.16
222	0.243	105	4.05
199	0.243	104	3.78
184	0.378	91	3.97
174	0.945	77	3.64
171	0.838	65	1.65
163	0.189	45	3.11
149	0.433	41	2.18
136	3.14	39	1.95
135	3.02	32	2.62
		28	4.18

Table 7.Mass Spectrum of 3-Methoxymethyl-4-methyl-<br/>8-azatricyclo[4.3.0.02,5]nona-3-ene-7,9-dione-<br/>8-phenyl §4 and Isomers §5, §6, and §7

(+)0.238° (+)0.347° (+)0.266° 180 mg 79.0   (+)0.132° (+)0.185° (+)0.120° 150 mg 42.8   (+)0.132° (+)0.185° (+)0.130° 133 mg 69.6   (+)0.179° (+)0.154° (+)0.130° 133 mg 69.6   (+)0.179° (+)0.154° (+)0.130° 133 mg 52.5   (+)0.179° (-)0.1254° (-)0.110° 195 mg 52.5   (-)0.375° (-)0.201° (-)0.110° 195 mg 52.5   (-)0.225° (-)0.221° (-)0.075° 100 mg 38.6   (+)0.225° (-)0.125° (-)0.075° 127 mg 32.0   (+)0.225° (+)0.101° 150 mg 50.0 50.0   (+)0.252° (+)0.123° (+)0.101° 80 mg 52.5   (+)0.179° (+)0.125° (-)0.213° (-)0.275° 480 mg 52.5   (-)0.335° (-)0.210° (-)0.100° 157 mg 53.0 52.5   (-)0.155° (-)0.100° 157 mg 53.0 52.5 52.5   (-)0.155° (-)0.100° 157 mg		578 nm <sup>a</sup>	Adducts	OF Adducts	
(+)0.258° (+)0.197° (+)0.120° 150 mg 42.8   (+)0.132° (+)0.185° (+)0.130° 133 mg 52.5   (+)0.179° (+)0.154° (+)0.130° 133 mg 52.5   (+)0.179° (+)0.154° (+)0.130° 133 mg 52.5   (+)0.179° (+)0.154° (+)0.184° 213 mg 52.5   (-)0.375° (-)0.201° (-)0.110° 195 mg 52.6   (-)0.229° (-)0.125° (-)0.072° 100 mg 38.6   (+)0.229° (+)0.140° 127 mg 32.0   (+)0.229° (+)0.140° 150 mg 50.0   (+)0.221° (+)0.140° 150 mg 50.0   (+)0.221° (+)0.130° 133 mg 52.5   (+)0.215° (-)0.215° (-)0.215° 50.0   (+)0.155° (-)0.215° (-)0.215° 52.5   (-)0.235° (-)0.100° 133 mg 52.5   (-)0.235° (-)0.100° 133 mg 52.5   (-)0.155° (-)0.100° 130 mg 53.0	TCNE <sup>a</sup>	(+)0.010			
(+)0.132° (+)0.185° (+)0.130° 133 mg 69.6   (+)0.179° (+)0.154° (+)0.130° 133 mg 69.6   (+)0.179° (+)0.184° 213 mg 64.3   (-)0.375° (-)0.184° 213 mg 64.3   (-)0.155° (-)0.110° 195 mg 28.0   (-)0.201° (-)0.072° 100 mg 38.6   (+)0.229° (-)0.072° 127 mg 38.6   (+)0.229° (+)0.140° 150 mg 50.0   (+)0.229° (+)0.140° 150 mg 50.0   (+)0.229° (+)0.140° 150 mg 50.0   (+)0.215° (+)0.130° 133 mg 50.0   (+)0.179° (+)0.155° (+)0.130° 333.0   (-)0.215° (-)0.215° (-)0.275° 480 mg 50.0   (-)0.155° (-)0.100° 133 mg 53.3 50.0   (-)0.155° (-)0.100° 136 33.3 50.0	TCNE	(+)0.004			
(+)0.179* (+)0.154* (+)0.184* 213 mg 52.5   (-)0.375* (-)0.184* 213 mg 46.3   (-)0.375* (-)0.201* (-)0.184* 213 mg 46.3   (-)0.375* (-)0.201* (-)0.110* 195 mg 46.3   (-)0.125* (-)0.072* 100 mg 38.6   (+)0.125* (-)0.076* 127 mg 38.6   (+)0.229* (+)0.140* 150 mg 50.0   (+)0.221* (+)0.140* 150 mg 50.0   (+)0.179* (+)0.213* (+)0.130* 133 mg 52.5   (+)0.179* (+)0.154* (+)0.130* 133 mg 52.5   (-)0.215* (-)0.213* (-)0.275* 480 mg 52.5   (-)0.155* (-)0.100* 140 mg 33.3   (-)0.155* (-)0.100* 140 mg 33.3	TCNE	(+)0.056°			Reacted with 1/2
(+)0.184* 213 mg 46.3   (-)0.375* (-)0.201* (-)0.110* 195 mg 28.0   (-)0.375* (-)0.201* (-)0.072* 100 mg 28.0   (+)0.125* (-)0.076* 127 mg 38.6   (+)0.125* (-)0.076* 127 mg 32.0   (+)0.229* (+)0.140* 150 mg 50.0   (+)0.222* (+)0.130* 150 mg 69.0   (+)0.179* (+)0.130* 153 mg 52.5   (+)0.179* (+)0.130* 153 mg 52.5   (-)0.215* (-)0.215* (-)0.275* 480 mg 52.5   (-)0.155* (-)0.100* 175 mg 33.0   (-)0.155* (-)0.100* 140 mg 38.3	TCNE		×	×	$CD of (\bullet) 22$
(-)0.375° (-)0.201° (-)0.110° 195 mg 28.0   (-)0.375° (-)0.125° (-)0.072° 100 mg 38.6   (+)0.229° (-)0.125° (-)0.076° 127 mg 32.0   (+)0.229° (+)0.121° (+)0.140° 150 mg 50.0   (+)0.252° (+)0.213° (+)0.110° 80 mg 69.0   (+)0.179° (+)0.213° (+)0.130° 133 mg 52.5   (-)0.215° (-)0.213° (-)0.275° 480 mg 52.5   (-)0.215° (-)0.213° (-)0.275° 480 mg 52.5   (-)0.155° (-)0.100° 175 mg 33.0   (-)0.155° (-)0.100° 140 mg 38.3	TCNE			×	
(-)0.375° (-)0.201° (-)0.110° 195 mg 28.0   (-)0.125° (-)0.072° 100 mg 38.6   (+)0.125° (-)0.076° 127 mg 32.0   (+)0.229° (+)0.125° (-)0.0140° 150 mg 50.0   (+)0.222° (+)0.140° 150 mg 50.0 1   (+)0.179° (+)0.213° (+)0.130° 133 mg 52.5   (-)0.215° (+)0.130° 133 mg 52.5 1   (-)0.215° (-)0.213° (-)0.275° 480 mg 52.5 1   (-)0.215° (-)0.213° (-)0.275° 480 mg 52.5 1   (-)0.215° (-)0.210° (-)0.275° 480 mg 53.0 1   (-)0.155° (-)0.100° 175 mg 33.3 1	TCNE			×	
(-)0.125° (-)0.072° 100 mg 38.6   (+)0.229° (-)0.125° (-)0.076° 127 mg 32.0   (+)0.229° (+)0.221° (+)0.140° 150 mg 50.0 1   (+)0.252° (+)0.213° (+)0.101° 80 mg 50.0 1   (+)0.179° (+)0.154° (+)0.130° 133 mg 52.5 1   (-)0.215° (-)0.213° (-)0.275° 480 mg 52.5 1   (-)0.235° (-)0.210° (-)0.275° 480 mg 33.0 1   (-)0.155° (-)0.100° 175 mg 33.3 38.3 1	TCNE	(-)0.004			
(-)0.125° (-)0.076° 127 mg 32.0   (+)0.229° (+)0.221° (+)0.140° 150 mg 50.0   (+)0.252° (+)0.213° (+)0.140° 150 mg 50.0   (+)0.252° (+)0.213° (+)0.101° 80 mg 69.0   (+)0.179° (+)0.154° (+)0.130° 133 mg 52.5   (-)0.215° (-)0.213° (-)0.275° 480 mg 30.0   (-)0.215° (-)0.210° (-)0.275° 480 mg 33.0   (-)0.155° (-)0.100° 140 mg 38.3 38.3	TCNE			×	
(+) 0.229° (+) 0.221° (+) 0.140° 150 mg 50.0 N   (+) 0.252° (+) 0.213° (+) 0.101° 80 mg 69.0 N   (+) 0.179° (+) 0.154° (+) 0.130° 133 mg 52.5 N   (-) 0.215° (-) 0.313° (-) 0.275° 480 mg 52.5 N   (-) 0.215° (-) 0.313° (-) 0.275° 480 mg 30.0 N   (-) 0.215° (-) 0.210° (-) 0.100° 175 mg 33.3 N   (-) 0.155° (-) 0.100° 140 mg 38.3 N N N	TCNE		×	×	87
(+)0.252° (+)0.213° (+)0.101° 80 mg 69.0 8   (+)0.179° (+)0.154° (+)0.130° 133 mg 52.5 1   (-)0.215° (-)0.313° (-)0.275° 480 mg 30.0 1   (-)0.335° (-)0.210° (-)0.108° 175 mg 33.0 1   (-)0.155° (-)0.100° 140 mg 38.3 3	<sub>q</sub> ₩dΝ	(+)0.005	×		
(+)0.179* (+)0.154* (+)0.130* 133 mg 52.5 8   (-)0.215* (-)0.313* (-)0.275* 480 mg 30.0 1   (-)0.215* (-)0.210* (-)0.275* 480 mg 30.0 1   (-)0.335* (-)0.210* (-)0.108* 175 mg 33.0 1   (-)0.155* (-)0.100* 140 mg 38.3 38.3 1	BQC	(+)0.003			
(-)0.215* (-)0.313* (-)0.275* 480 mg 30.0 1   (-)0.335* (-)0.210* (-)0.108* 175 mg 33.0 1   (-)0.155* (-)0.100* 140 mg 38.3 1	BQ		×		
(-)0.335° (-)0.210° (-)0.108° 175 mg 33.0 1 (-)0.153° (-)0.155° (-)0.100° 140 mg 38.3	BQ	(-)0.01			
(-)0.153° (-)0.155° (-)0.100° 140 mg 38.3 ]	BQ	(-)0.004			
	BQ	(-)0.003			
	BQ	:		×	
(-)0.097° 104 mg 50.0					of 76 [Adduct of (+
(+)0.019° 24 mg 42.5				Dar Dar est	of 76 [Adduct of (+) er 75 and (+) 62]

Table 8. Resolution and Decomposition Data

