

# CYCLOBUTADIENE AND ITS METAL COMPLEXES

R. PETTIT

*Department of Chemistry, The University of Texas at Austin  
Austin, Texas 78712, U.S.A.*

## INTRODUCTION

The practical and theoretical problems associated with the cyclobutadiene molecule have concerned organic chemists for over one hundred years and, as is well known, this compound has played a particularly interesting role in the development of organic chemistry. The importance of the system to organic chemists stems mainly from the fact that the molecule is a cyclic conjugated system for which, seemingly, two equivalent structures (Ia and Ib) could be written, just as two such structures (IIa and IIb) can be written for benzene. Kekulé and many of his contemporaries associated the peculiar



a



b

(I)



a



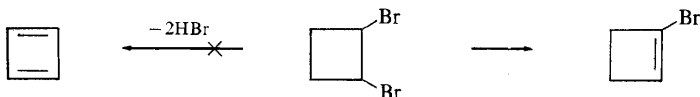
b

(II)

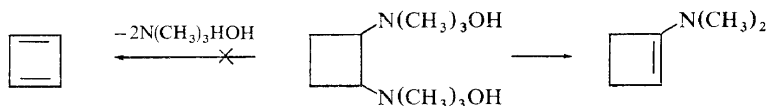
“aromatic” properties of benzene with the fact that it was possible to write two such equivalent structures for the molecule and it was then a logical question to ask whether cyclobutadiene would also be “aromatic” for similar reasons.

Despite the apparent similarity with benzene, it became obvious from the failure of several rational synthetic attempts to prepare the compound that cyclobutadiene does not possess the unusual stability typically associated with aromatic compounds. Three such synthetic attempts which might have been expected to succeed if cyclobutadiene was very stable are indicated in the following reactions<sup>1</sup>; it might be noted at this point that these methods, in common with most of the other published schemes, depended upon some form of a standard elimination reaction from a cyclobutane derivative as the last key step in the synthesis.

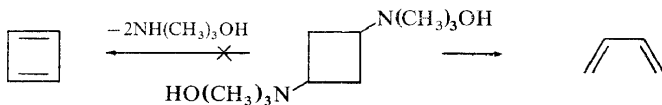
(1) Willstätter (1904)



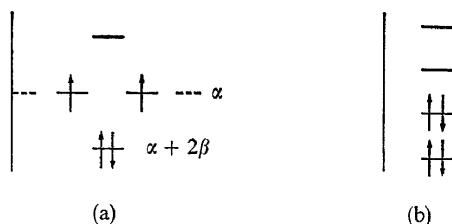
## (2) Buchmann (1942)



## (3) Nenitzescu (1957)



It became clear from such failures as given above that cyclobutadiene, if it existed at all, should certainly not be considered to be "aromatic". The first rationalization of this fact emerged from the application of the Hückel Molecular Orbital Theory to the problem. If one applies the HMO method to a  $\pi$  system covering four  $sp^2$  hybridized carbon atoms situated at the corners of a square, then the energy diagram of the molecular orbitals which result is as shown in *Figure 1(a)*. Application of Hund's rule concerning maximum spin multiplicity leads to the electron energy diagram given in *Figure 1(a)*. The total  $\pi$  electronic energy is seen to be  $(4\alpha + 4\beta)$  which is identical to that of two non-interacting ethylenic bonds. Thus the resonance



*Figure 1.* (a) H.M.O. energy diagram (b) S.C.F.M.O. energy diagram for cyclobutadiene

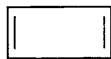
energy for the cyclobutadiene molecule is zero whereas for benzene the method predicts a stabilization of  $2\beta$  ( $\sim 40$  kcal) for the conjugated molecule over a system which contains three non-interacting double bonds. The lack of resonance stabilization energy plus the fact that the molecule is obviously a highly strained system thus afforded a satisfactory explanation for the apparent non-aromaticity of cyclobutadiene. Since this early calculation more sophisticated quantum mechanical treatments have been applied to the cyclobutadiene problem and practically all of these methods lead to the same result, namely, the molecule will not possess significant resonance stabilization energy. A significant fact however emerges from a self consistent field type method in which account is taken of electron repulsion and in which the bond lengths of the molecule are not *a priori* assumed to be equal. One such treatment<sup>2</sup> leads to the energy diagram shown in *Figure 1(b)*. Again is it found that no resonance stabilization energy is present but now there is no orbital degeneracy and the method predicts the ground state to

## CYCLOBUTADIENE AND ITS METAL COMPLEXES

be a singlet electronic state; furthermore, it is found that the molecule has a minimum energy when it adopts a rectangular configuration of carbon atoms with alternating short double bonds and long single bonds. Thus although the earlier problem concerning the non "aromaticity" of cyclobutadiene has been satisfactorily explained, there now emerges another question as to whether the ground state of cyclobutadiene is a square triplet (III) or a rectangular singlet (IV).



(III)

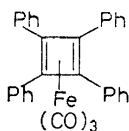


(IV)

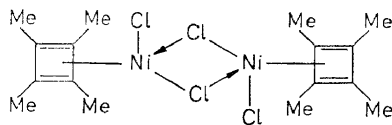
## CYCLOBUTADIENE-METAL COMPLEXES

A most intriguing prediction was made by Longuet-Higgins and Orgel<sup>3</sup> about ten years ago concerning the existence of cyclobutadiene-metal complexes. These authors suggested that despite the notorious instability of cyclobutadiene itself, the hydrocarbon could nonetheless possibly act as a "good" ligand when attached to various transition metals and they surmised that stable cyclobutadiene-metal complexes might exist. The basis for this prediction lay in the fact that there exists a set of atomic orbitals on the transition metal which are of the correct symmetry to allow interaction with the molecular orbitals of a cyclobutadiene ligand. Filled molecular orbitals of the cyclobutadiene ring would be able to interact with empty atomic orbitals of the metal giving rise to "forward coordination" while "back donation" of electrons from the metal to the  $C_4H_4$  ligand would arise from filled  $d$  atomic orbital (or appropriate hybrid atomic orbitals) interacting with vacant molecular orbitals of the cyclobutadiene molecule. This dual type of bonding had been invoked on previous occasions to account for the stability of other organometallic complexes, for example silver olefin complexes and sandwich compounds such as ferrocene.

This suggestion of Longuet-Higgins and Orgel was shown to be essentially correct in the following year by two independent groups of workers. Hubel and coworkers<sup>4</sup> isolated a stable iron tricarbonyl complex of tetraphenylcyclobutadiene (V) following reaction of diphenylacetylene with  $Fe(CO)_5$ . Criegee and Schroder<sup>5</sup>, in the course of their experiments, isolated a dimeric form of tetramethylcyclobutadiene nickel dichloride (VI) upon treatment of dichlorotetramethylcyclobutene with  $Ni(CO)_4$ . X-ray structural determinations<sup>6,7</sup> on these two complexes have confirmed the cyclobutadiene nature



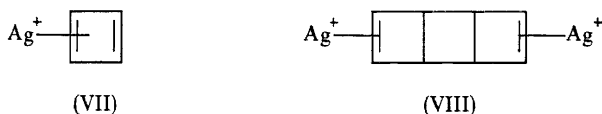
(V)



(VI)

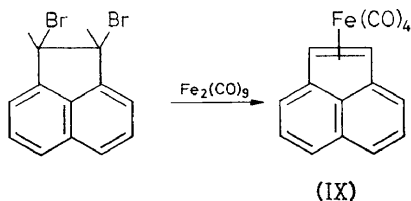
of the ligands. Since this time, quite a few other metal complexes of tetra-substituted cyclobutadiene derivatives have been reported<sup>8</sup>.

An early report<sup>9</sup> of the isolation of a silver complex of the parent cyclobutadiene molecule (VII) was subsequently shown to be incorrect; the compound was found to be the bis-silver complex of the dimer of cyclobutadiene (VIII) and the single peak found in the n.m.r. spectrum of the substance arose from an isomerization of (VIII) to a silver complex of cyclooctatetraene.

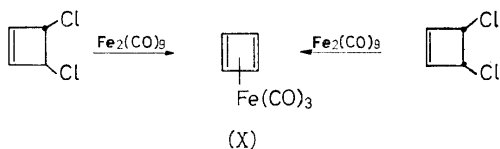


### COMPLEXES OF UNSUBSTITUTED CYCLOBUTADIENE

Our own active interest in cyclobutadiene-metal complexes arose from the observation that diiron enneacarbonyl reacted with acenaphthylene dibromide to produce the iron tetracarbonyl complex of acenaphthylene (IX). This dehalogenation and complexation suggested that the same type of reaction might serve to form the iron carbonyl complex of unsubstituted cyclobutadiene. This subsequently was found to be the case; reaction of



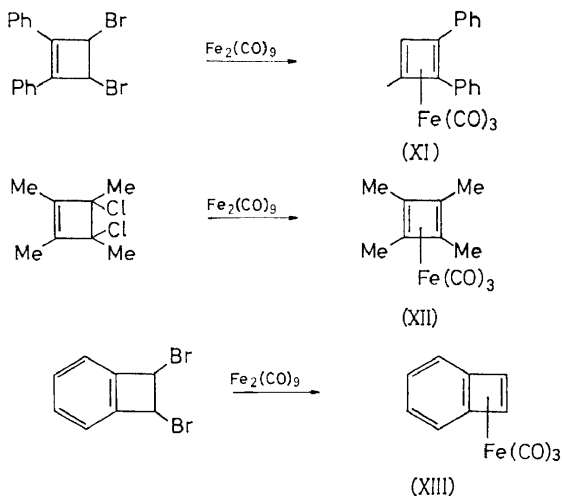
either *cis*- or *trans*-3,4-dichlorocyclobutene with  $\text{Fe}_2(\text{CO})_9$  afforded cyclobutadiene iron tricarbonyl (X) as a stable, pale yellow crystalline solid which melted at  $26^\circ\text{10}$ .



The reaction of 3,4-dihalocyclobutenes with  $\text{Fe}_2(\text{CO})_9$  now appears to be a general method for the preparation of cyclobutadiene iron tricarbonyl complexes. Thus, as indicated in the following reactions, the  $\text{Fe}(\text{CO})_3$  complexes of 1,2-diphenylcyclobutadiene (XI), 1,2,3,4-tetramethylcyclobutadiene (XII), and benzocyclobutadiene (XIII) can be prepared by means of this reaction<sup>11</sup>. The method however has two very severe limitations for the preparation of cyclobutadiene metal complexes in general. First,

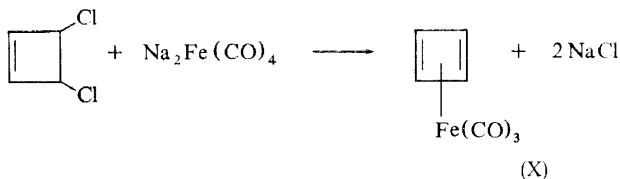
CYCLOBUTADIENE AND ITS METAL COMPLEXES

dihalocyclobutenes are generally very difficult to make; hence, the reaction is not a very attractive one if a large series of substituted cyclobutadiene-iron carbonyl complexes is desired. Secondly, it seems that  $\text{Fe}_2(\text{CO})_9$  is quite unique amongst the various metal carbonyls as far as its reactivity with unsaturated organic molecules is concerned; hence, the method does not

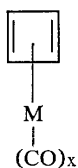


appear to have much utility for the preparation of cyclobutadiene carbonyl complexes of metals other than iron.

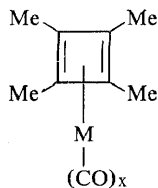
Recently it has been found that cyclobutadiene-iron tricarbonyl can also be prepared through reaction of dichlorocyclobutene with  $\text{Na}_2\text{Fe}(\text{CO})_4$ . While this method has no advantage over the use of  $\text{Fe}_2(\text{CO})_9$  as far as convenience or yields of (X) is concerned, it is of significance because sodium salts of other metal carbonyl anions are known; hence, this reaction could possibly lead to cyclobutadiene carbonyl complexes of metals other than



iron. Although the range of complexes has not yet been fully explored, it does seem that a number of different cyclobutadiene-metal complexes will indeed become available through this reaction. Thus, using such salts as  $\text{Na}_2\text{W}(\text{CO})_4$ ,  $\text{Na}_2\text{Cr}(\text{CO})_4$ , etc., we have recently prepared the complexes indicated below<sup>1,2</sup>. Also indicated is the chemical shift of the n.m.r. singlet displayed by each compound.



M	x	$\tau$
Fe	3	6.09
Ru	3	5.87
Mo	4	5.94
W	4	5.98



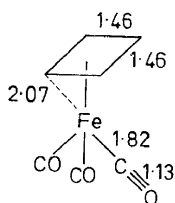
M	x	$\tau$
Fe	3	8.24
Cr	4	8.15
Mo	4	8.06
W	4	7.86

### PROPERTIES OF CYCLOBUTADIENE-IRON TRICARBONYL

Cyclobutadiene-iron tricarbonyl is certainly the most readily available of the metal carbonyl complexes of cyclobutadiene and the chemical properties of this complex have been studied in greatest detail. A brief survey of the chemistry of this system is now given.

Cyclobutadiene-iron tricarbonyl is a pale yellow crystalline solid which melts at  $26^\circ$  and boils at  $60^\circ$  at 0.1 mm; the compound exhibits considerable thermal stability and only very slowly decomposes when exposed to oxygen. In the n.m.r. spectrum the complex shows the expected single sharp singlet at  $\tau$  6.04; one feature of interest here is the coupling constants of the various ring protons (determined from the  $^{13}\text{C}$  satellite spectrum),  $J_{12}$  is very small ( $\sim 0.0$  c/s), whereas the long range coupling  $J_{13}$  is quite large (9.5 c/s). The mass spectral cracking pattern displays a parent molecular ion at  $m/e$  192 then three intense peaks at  $m/e$  165, 136 and 108 corresponding to the successive loss of three carbonyl groups from the iron.

An x-ray determination of the structure has not been attempted as yet. However, electron diffraction studies have been performed and the pertinent bond distances are indicated in *Figure 2*<sup>13</sup>.

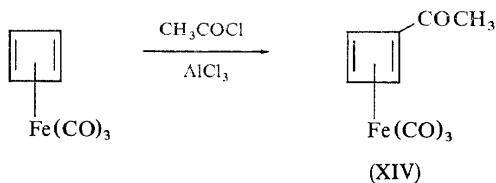


*Figure 2.* Bond distances in angstrom units for cyclobutadiene-iron tricarbonyl as determined by electron diffraction studies.

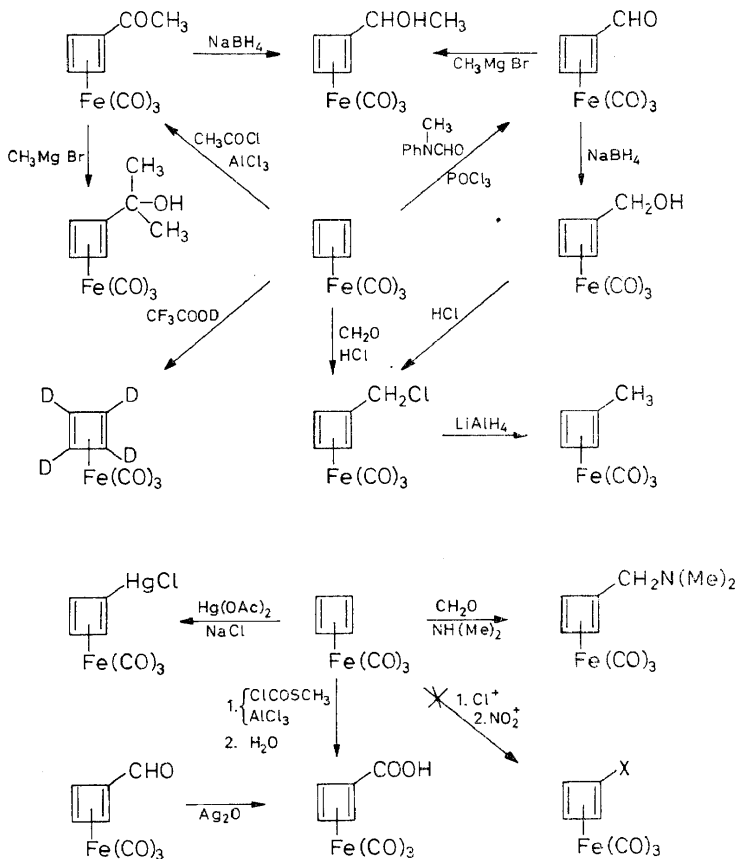
Certainly one of the most interesting properties concerning the complex (X) is that it is found to be an "aromatic" system in the sense that it readily undergoes electrophilic substitution reactions leading to substituted cyclobutadiene-iron tricarbonyl complexes. For example, treatment of cyclobutadiene-iron tricarbonyl with acetyl chloride and aluminium chloride in a typical Friedel-Crafts type reaction leads to the formation of acetyl-

CYCLOBUTADIENE AND ITS METAL COMPLEXES

cyclobutadiene-iron tricarbonyl (XIV) in practically quantitative yields. Similar results are found using benzoyl chloride to give the corresponding benzoyl derivative.



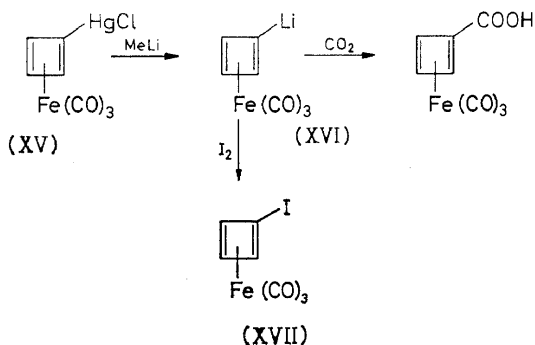
Competition experiments have shown that in this reaction cyclobutadiene-iron tricarbonyl is almost as reactive as ferrocene and much more reactive than benzene. The chemical properties of functional groups in substituted derivatives of (IX) appear to be normal, for example reduction of the acetyl derivative (XIV) with  $\text{NaBH}_4$  gives  $\alpha$ -hydroxyethylcyclobutadiene-iron tricarbonyl in excellent yield. Thus the direct introduction of substituents into the  $\text{C}_4\text{H}_4$  ligand together with further modification has allowed for the



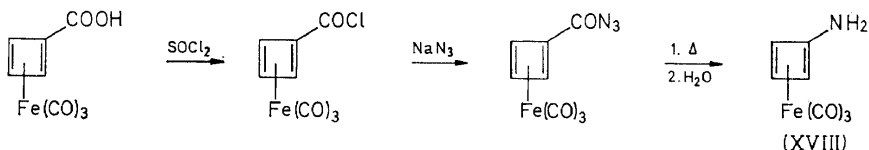
preparation of a much larger number of substituted cyclobutadiene-iron tricarbonyl complexes than would be possible from the direct reactions alone. To indicate the range of complexes which can be formed, several such reactions and interconversions which have been carried out are indicated below. The reactions employ fairly standard conditions with the reagents indicated and further elaboration will not be given now.

It should be pointed out that chlorination and nitration of (X) failed to yield the chloro- and nitro-derivatives. As will be seen presently, the complex (X) can suffer oxidation degradation fairly easily and the reactive species  $\text{Cl}^+$  and  $\text{NO}_2^+$  in these two reactions are known to be oxidizing agents as well as electrophiles in substitution process; this then probably explains the failure to isolate the chloro- and nitro-cyclobutadiene complexes.

The chloromercury derivative (XV) has recently been found to be a useful source for the lithio derivative (XVI) which in turn should prove to be a valuable intermediate for further synthesis<sup>14</sup>. Thus the iodocyclobutadiene complex (XVII) has now been prepared by means of the scheme:



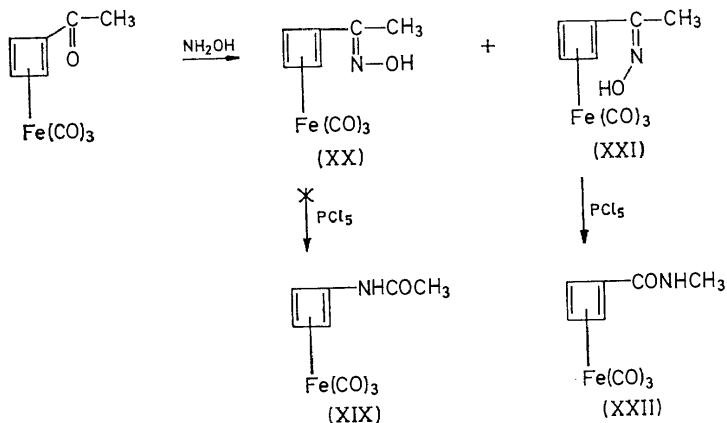
Aminocyclobutadiene-iron tricarbonyl (XVIII) can be prepared via a Curtius rearrangement as shown below. The mechanism of the Curtius rearrangement is believed to involve migration of a substituent to an electron deficient nitrogen atom and it is of interest to note that the cyclobutadienyl- $\text{Fe}(\text{CO})_3$  group will undergo such a migration. On the other hand, we have not been able to isolate acetamidocyclobutadiene- $\text{Fe}(\text{CO})_3$  (XIX) from the oxime (XX) under conditions used for the Beckmann rearrangement;



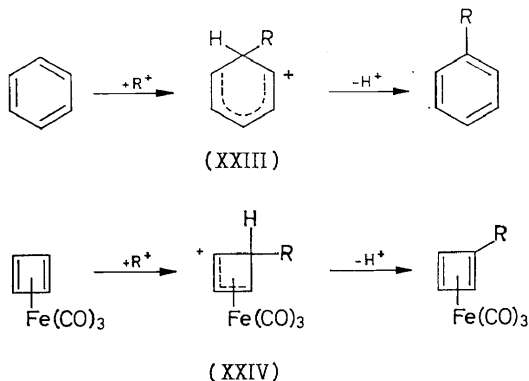
whereas the geometrical isomeric oxime (XXI) does yield the *N*-methanamide of cyclobutadiene carboxylic acid- $\text{Fe}(\text{CO})_3$  (XXII) under the same conditions. In the latter reaction it is the methyl group which migrates while in the former, the cyclobutadiene- $\text{Fe}(\text{CO})_3$  unit would be required to migrate.



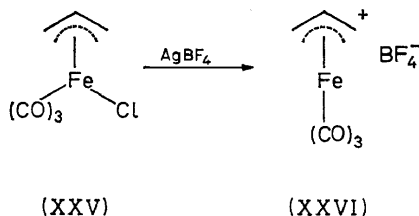
CYCLOBUTADIENE AND ITS METAL COMPLEXES



The mechanism of the electrophilic substitution of cyclobutadiene-iron tricarbonyl has not been established but it seems reasonable to expect that an analogous scheme to that proposed for benzene and other aromatic hydrocarbons is operative. In the substitution of benzene the electrophile adds to the ring, removing one carbon atom from conjugation, and yielding a pentadienyl cation (XXIII) as a metastable intermediate; loss of a proton then affords the substituted benzene. In an analogous scheme an electrophile

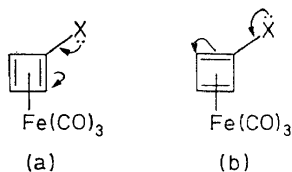


could add to the complex (X) to give the  $\pi$ -allyliron tricarbonyl intermediate (XXIV); loss of a proton from (XXIV) would then yield the substituted cyclobutadiene complex. We had previously found that reaction of  $\text{AgBF}_4$  with  $\pi$ -allylchloroiron tricarbonyl (XXV) leads to the formation of the fluoroborate salt of the  $\pi$ -allyliron tricarbonyl cation (XXVI); such salts are



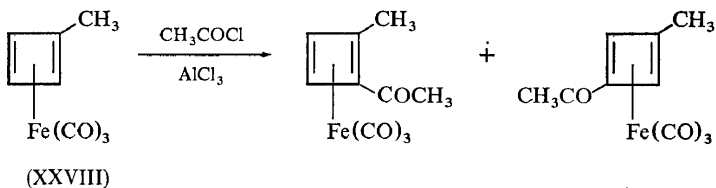
stable and frequently can be isolated as crystalline compounds<sup>15</sup>. It is the thermodynamic stability of the  $\pi$ -allyl cation (XXIV) which then allows a low energy pathway for proceeding from the parent complex (X) to the substituted complex (XXV) and accounts for the high degree of reactivity of the complex (X) in electrophilic substitution reactions.

One further interesting point deals with the orientation effects of substituents towards further substitution. For example, it would be of interest to determine whether the familiar techniques devised for substituted benzene derivatives concerning the orientation effects will also apply to the cyclobutadiene ligand. Thus if a substituent Y carries a lone pair of electrons should the complex (XXVII) undergo further substitution in the 2- position

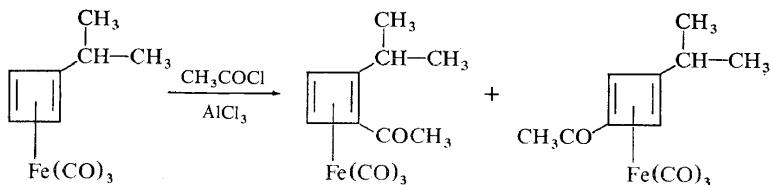


(XXVII)

according to the "electron pushing" scheme indicated in XXVII (a) and (b). The methyl group in toluene is an activating and ortho-para directing substituent and if the same rules can be applied to the complex (X) then methyl cyclobutadiene- $\text{Fe}(\text{CO})_3$  (XXVIII) should acetylate predominantly in the



(XXVIII)

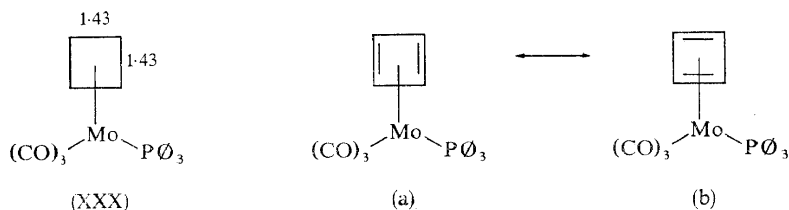


(XXIX)

2- position. This is not found to be the case, acetylation of (XXVIII) yields both the 2- and 3- acetyl derivatives indicated in a 1:2 ratio respectively despite the statistical factor alone favouring the reverse order. To test

whether predominant substitution at the 3- position resulted from unfavourable steric factors acting at the 2- position, the isopropyl complex (XXIX) was acetylated; once again two isomers were produced and in the same 1:2 ratio for 2- versus 3- substitution as found for the methyl derivative. Therefore, in this example at least, the rules established for benzene do not apply for the substitution of cyclobutadiene-iron tricarbonyl. This is perhaps not surprising for, in the case of benzene, the orientation effects of a substituent are determined by how the substituent effects the stability of the pentadienyl cation (XXIII) while in the case of the complex (X) it will be determined by how the substituent effects the stability of the  $\pi$ -allyl  $\text{Fe}(\text{CO})_3$  complex (XXIV). The electronic demands may well be different in the two cases.

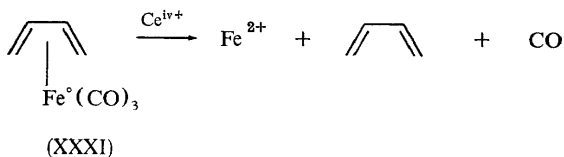
Finally, mention may be made concerning the aromaticity of cyclobutadiene metal carbonyls other than the iron system (X). Only very preliminary data have been collected so far. In one experiment it has been shown that under conditions where cyclobutadiene- $\text{Fe}(\text{CO})_3$  is acetylated in better than 95 per cent yield, cyclobutadiene- $\text{Mo}(\text{CO})_4$ , on the other hand, gives no such acetyl derivative. Thus it appears, perhaps not surprisingly,



that the chemical properties of the complexes will be very much dependent on the nature of the transition metal. It should be noted here that an x-ray structure of cyclobutadiene-molybdenum tricarbonyl triphenylphosphine (XXX) reveals that the  $\text{C}_4$  ligand adopts a square configuration<sup>16</sup>; hence, the molecule is a resonance hybrid of the two canonical forms (a) and (b) and, in the physical sense of the word, can be classified as aromatic.

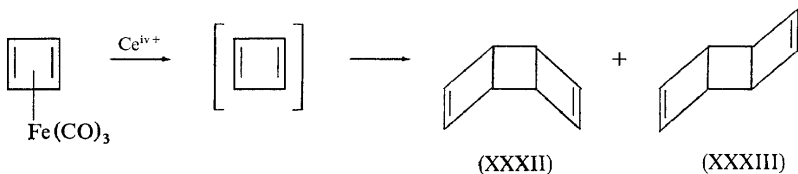
### OXIDATIVE DECOMPOSITION OF CYCLOBUTADIENE-IRON TRICARBONYL

Prior to the isolation of cyclobutadiene-iron tricarbonyl it had been established in our laboratories as well as those of others that diene-iron tricarbonyl complexes very readily suffer oxidative decomposition with accompanying liberation of the ligands. Thus treatment of butadiene-iron tricarbonyl (XXXI) with ferric, silver or ceric salts, at temperatures as low as  $0^\circ$ , resulted in oxidation of  $\text{Fe}^0$  in the complex to  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  ions and liberation of carbon monoxide and butadiene. This immediately suggested then a possible synthesis of cyclobutadiene by means of a similar oxidation of the corresponding iron carbonyl complex (X). The really attractive feature of the proposed synthesis is that the last step of the scheme could be extremely

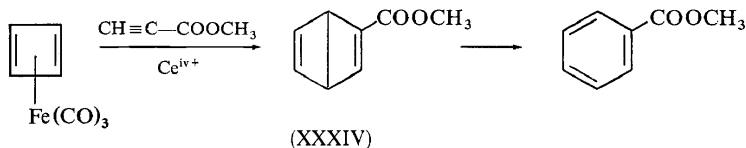


mild, i.e., temperatures of 0°C and reagents as innocuous as ferric ion; it will be recalled that in most previous attempted synthesis the last step involved a thermal elimination of one sort or another. It may well have been that cyclobutadiene was produced in some earlier cases but that it failed to survive the vigorous conditions required to generate it.

Cyclobutadiene-iron tricarbonyl was therefore subjected to oxidation with ceric ammonium nitrate in aqueous ethanol solutions. The major organic products isolated were *syn*- and *anti*-tricyclooctadiene (XXXII)



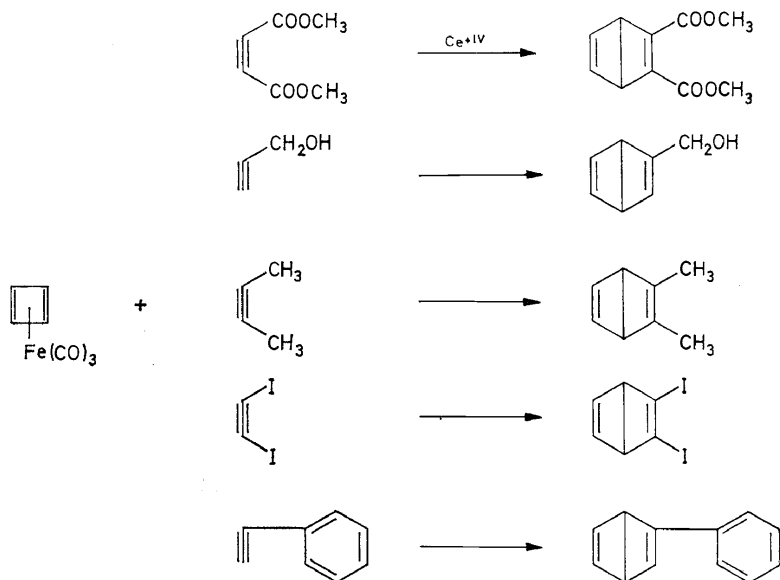
and (XXXIII), in ratio of 8:1 respectively. The formation of these products was most encouraging for cyclobutadiene would be expected to be a good diene in Diels-Alder type reactions and, being a highly strained olefin, should also be a reactive dienophile; hence Diels-Alder type dimerization leading to (XXXII) and (XXXIII) would be most reasonable. Furthermore the predominance of the *syn* isomer also pointed to free cyclobutadiene being liberated which then dimerized in a Diels-Alder manner according to the usual preference for "*endo-cis*" addition. Oxidative decomposition of the cyclobutadiene complex was then carried out in the presence of dienophilic reagents which would be expected to trap the liberated cyclobutadiene. In the presence of acetylene carboxylic acid ester, the reaction thus led to the bicyclohexadiene carboxylic ester (XXXIV). The structure of (XXXIV) is clearly indicated by its n.m.r. spectrum which



consists of three olefinic type absorptions at  $\tau$  2.90, 3.37 and 3.51, two allylic protons at  $\tau$  6.00 and 6.16 and one methyl ester absorption at  $\tau$  6.32; furthermore, the product quantitatively isomerized to methyl benzoate upon heating to 90° for thirty minutes.

CYCLOBUTADIENE AND ITS METAL COMPLEXES

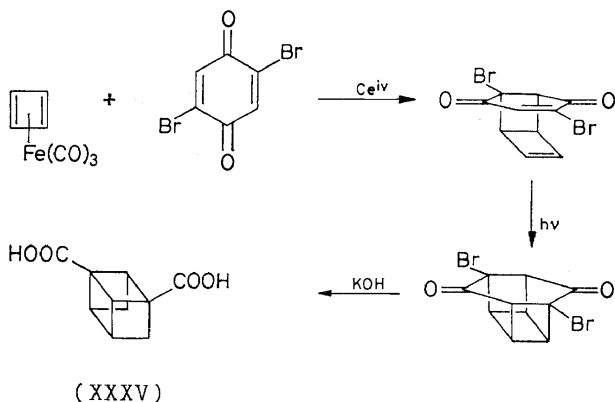
Compound (XXXIV) is a "Dewar benzene" form of methylbenzoate and the oxidative degradation of (X) in the presence of acetylenes now provides a fairly general and extremely simple method for the preparation of Dewar benzene derivatives. The utility of the method for such synthesis is indicated in the following reactions.



The last of these reactions, where phenylacetylene is used as the dienophile, is amusing in that it leads to Hemi-Dewar biphenyl—a molecule in which one ring has the Dewar structure while the other has the Kekulé structure.

The isolation of the various Dewar benzene derivatives now points out another interesting aspect of cyclobutadiene-iron tricarbonyl, namely its potential utility in organic synthesis.

One other example of the use of complex X in organic synthesis is the following simple synthesis of cubane dicarboxylic acid (XXXV) the ring

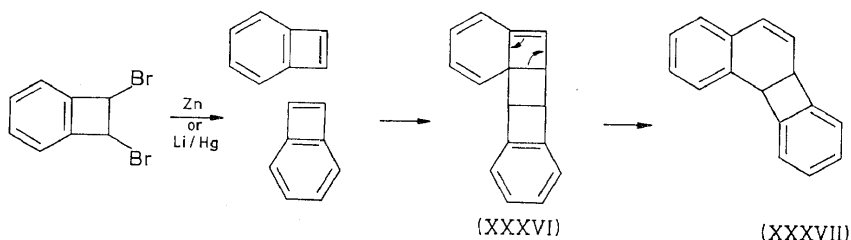


system of which was previously accessible only by an elaborate sequence of chemical reactions<sup>17</sup>.

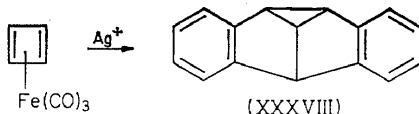
Other interesting organic synthesis are possible utilizing the complex (X); however, these will not be discussed further now for they lead us into the realm of pure organic chemistry and away from organometallic chemistry which is the topic of this meeting.

### BENZOCYCLOBUTADIENE-IRON TRICARBONYL

As mentioned earlier, benzocyclobutadiene-iron tricarbonyl is produced following reaction of dibromobenzocyclobutene with  $\text{Fe}_2(\text{CO})_9$  and it was of interest to determine whether this complex could also serve as a convenient source of benzocyclobutadiene. Unlike cyclobutadiene, it was almost certain that benzocyclobutadiene had been synthesized earlier by two independent groups. Cava<sup>19</sup> and Nenitzescu<sup>20</sup> and their coworkers had shown that dehalogenation of dibromobenzocyclobutene with zinc or with lithium amalgam gave rise to benzocyclobutadiene which, in the presence of dienes, could be trapped as a Diels-Alder adduct. In the absence of any trapping agent, benzocyclobutadiene dimerized in the manner indicated to yield the stable  $\text{C}_{16}\text{H}_{12}$  compound (XXXVII) via the initial unstable Diels-Alder adduct (XXXVI).



Oxidative decomposition of benzocyclobutadiene-iron tricarbonyl with ceric ammonium nitrate yielded only polymeric organic material so a milder oxidizing agent *viz.* silver ions was used. This latter reaction led to the decomposition of the complex but the organic product contained none of the expected  $\text{C}_{16}\text{H}_{12}$  compound (XXXVII) but instead consisted of an isomer of this having the structural formula (XXXVIII).

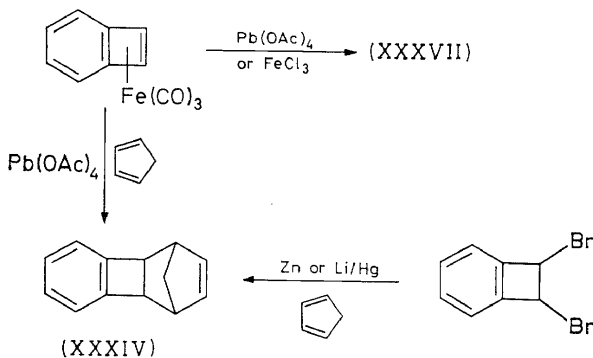


On the other hand, when lead tetraacetate or ferric chloride was used as the oxidant, the degradation proceeded as expected to yield the "normal" dimer (XXXVII). Furthermore, when the complex was oxidized with  $\text{Pb}(\text{OAc})_4$  in the presence of cyclopentadiene, there resulted the Diels-Alder adduct (XXXIX) identical to that previously obtained by dehalogenation of dibromobenzocyclobutene in the presence of cyclopentadiene<sup>21</sup>.

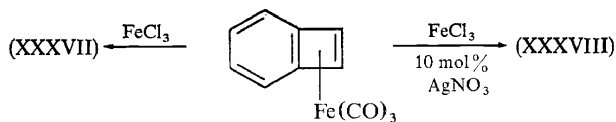
CYCLOBUTADIENE AND ITS METAL COMPLEXES

Evidently these latter oxidizing agents decompose the complex and effect the liberation of benzocyclobutadiene as expected.

Clearly an interesting puzzle existed in the case of the oxidation with  $\text{AgNO}_3$  and one in which the role of silver ion was largely implicated. This latter fact was even more readily apparent when it was found that while



benzocyclobutadiene-iron tricarbonyl was oxidized to give the normal  $\text{C}_{16}\text{H}_{12}$  hydrocarbon (XXXVII) with ferric chloride alone, when ferric chloride plus catalytic amounts of  $\text{AgNO}_3$  were used then the only  $\text{C}_{16}\text{H}_{12}$  hydrocarbon produced was the abnormal dimer (XXXVIII).

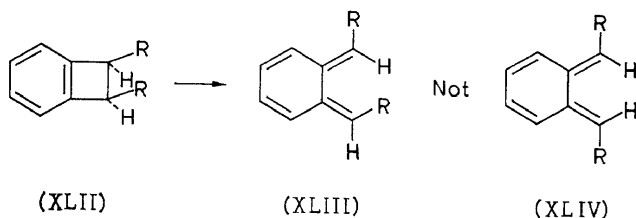


We consider that the key to this interesting problem lies in a novel reaction of an organo-silver intermediate briefly described below and one which could well develop into a significant area of organometallic chemistry.

Only a very brief outline of the arguments used to explain the formation of the abnormal dimer can be given at this time.

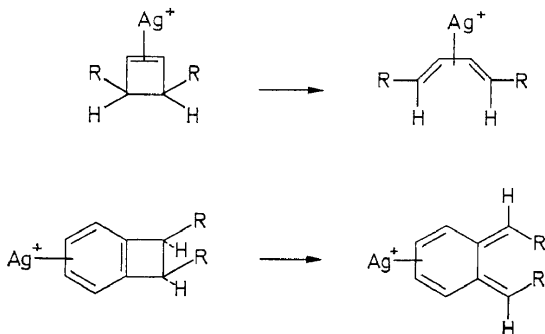
If the thermal isomerization of the cyclobutene derivative (XXXIX) to butadiene is considered it is now recognized that the conrotatory ring





opening process leading to the *cis-trans* isomer (XL) will be the reaction path followed; the alternant disrotatory process leading to the *trans-trans* isomer (XLI) is not an "allowed" process. The explanation of this is embodied in a set of postulates known as the Woodward-Hoffman Rules<sup>22</sup>. Likewise the thermal ring opening of a benzocyclobutene such as (XLII) to *o*-xylene must proceed via a conrotatory process to yield (XLIII) rather than by a disrotatory process to give the isomer (XLIV).

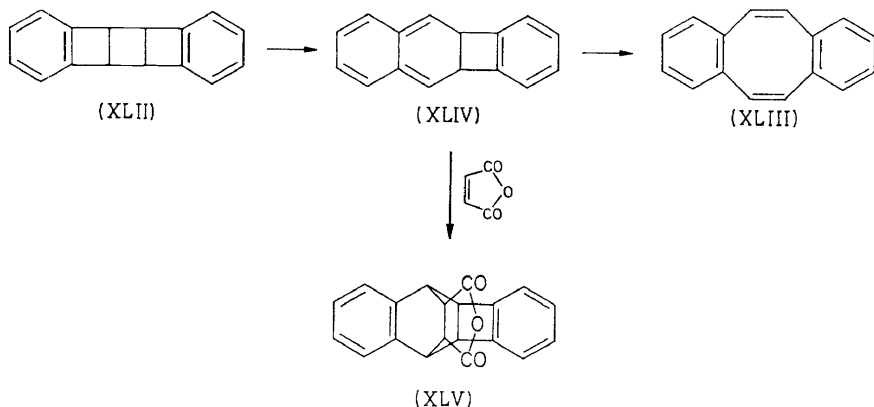
However, arguments can be given to indicate that the thermal ring opening of the silver or cuprous complexes of cyclobutenes and benzocyclobutenes to the silver or cuprous complexes of butadienes and *o*-xylenes by a disrotatory process is now an allowed process<sup>23</sup>. Thus:



Consider now the highly strained hydrocarbon (XLII). The isomerization of this compound to the relatively unstrained molecule dibenzocyclooctatetraene (XLIII) would certainly be expected to be an exothermic reaction; however, neither of the two following pathways by which the isomerization could conceivably occur in a concerted manner are "allowed" according to the Woodward-Hoffmann rules. The ring opening of the central cyclobutane ring leading to (XLIII) directly is not an allowed process, while the stepwise rearrangement proceeding via the *o*-xylylene intermediate (XLIV) would of course require a disrotatory type ring opening which is also not allowed. Hence the hydrocarbon (XLII) is thermally fairly stable and it is reported that isomerization to (XLIII) only occurs upon heating to 180° for several hours. On the other hand, addition of a small amount of silver ion to a solution of (XLII) effects the complete isomerization of (XLII) to (XLIII) at room temperature within ten seconds. Furthermore, addition of AgNO<sub>3</sub> to a solution of (XLII) and maleic anhydride leads to the immediate formation of the Diels-Alder adduct (XLV),



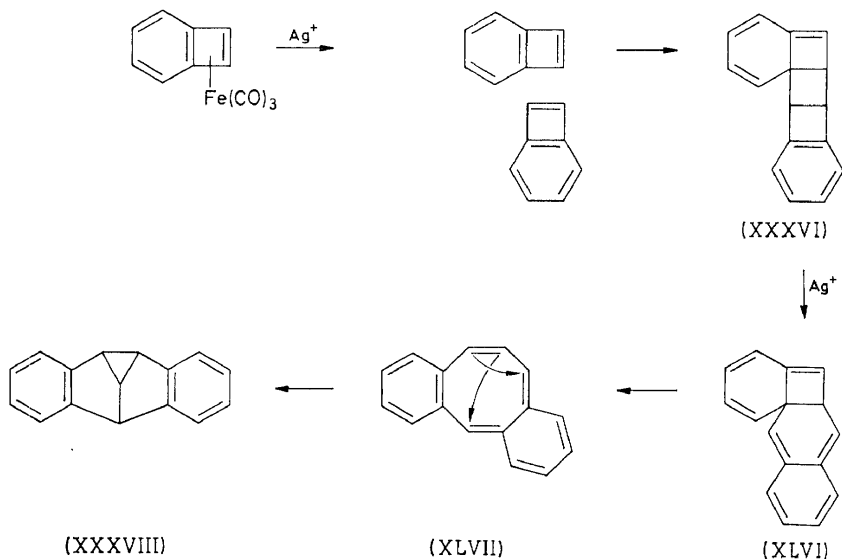
## CYCLOBUTADIENE AND ITS METAL COMPLEXES



demonstrating that the isomerization of (XLII), under the influence of  $\text{Ag}^+$  ions, proceeds via the *o*-xylylene derivative (XLIV).

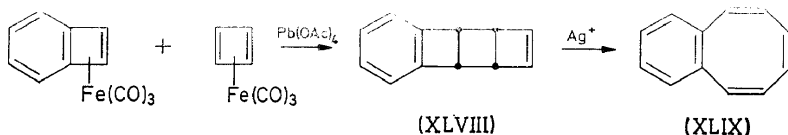
Other similar examples of the "apparent" change in the Woodward-Hoffmann rules in the presence of metal ions have been found but these lie outside the scope of the present lecture. The pertinent point now established is that highly strained benzocyclobutene derivatives may isomerize to *o*-xylylene systems by a disrotatory process in the presence of silver ions.

Returning now to the formation of the abnormal dimer of benzocyclobutadiene upon oxidation of benzocyclobutadiene-iron tricarbonyl with silver ions. We believe now that benzocyclobutadiene is indeed liberated in this reaction and that it dimerizes to the system (XXXVI) in the manner indicated previously. The hydrocarbon (XXXVI) is highly strained benzocyclobutene derivative and, before it isomerizes to the normal dimer (XXXVII), it undergoes the facile silver ion catalyzed isomerization to



the *o*-xylylene derivative (XLVI) analogous to that described in the previous paragraph. Further isomerization of (XLVI) to the 1,4-dibenzocyclo-octatetraene (XLVII) and subsequent internal Diels–Alder type addition would then lead to the formation of the abnormal dimer (XXXVIII).

One final comment concerning the benzocyclobutadiene complex. The rate of oxidative decomposition of this material appeared to be comparable to that of the decomposition of the parent system itself. This then suggested the intriguing possibility of being able to generate cyclobutadiene and

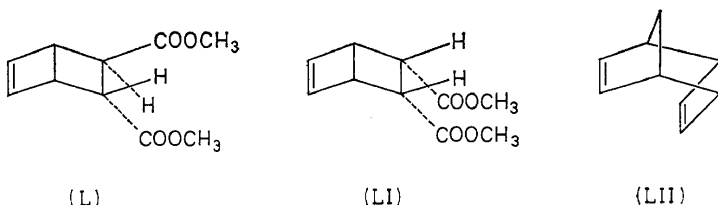


benzocyclobutadiene simultaneously and in practice this appears to be the case. Addition of Pb(OAc)<sub>4</sub> to a mixture of benzocyclobutadiene–iron tricarbonyl and cyclobutadiene–iron tricarbonyl afforded the expected Diels–Alder adduct (XLVIII) in yields of 75 per cent. It is interesting to note that the stereochemistry of (XLVII) is that indicated, which again is expected on the basis of “*endo-cis*” addition of Diels–Alder reactions. The compound (XLVIII) undergoes very facile silver ion catalyzed isomerization to benzocyclooctatetraene (XLIX) and the reaction sequence incidentally provides a useful synthesis of this hydrocarbon.

### ON THE NATURE OF THE GROUND STATE OF CYCLOBUTADIENE

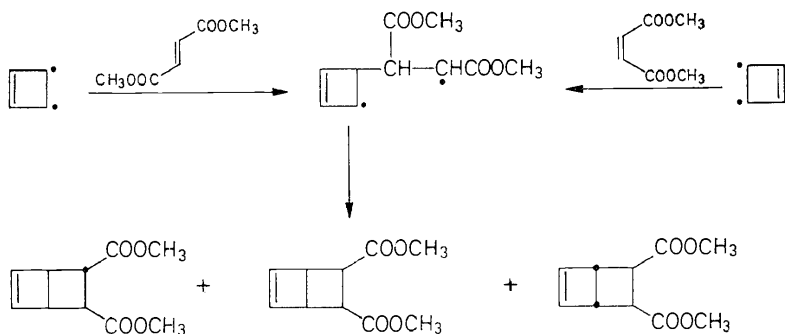
Although a definitive answer concerning the nature of the ground state of cyclobutadiene remains to be given, an argument can be developed which points to a singlet ground state.

If cyclobutadiene were to be a singlet, then the Diels–Alder rules suggest that reactions with dimethylfumarate and dimethylmaleate should be stereospecific and lead to compounds (L) and (LI) respectively. Likewise addition to the diene cyclopentadiene in the concerted Diels–Alder reaction should yield the hydrocarbon (LII).

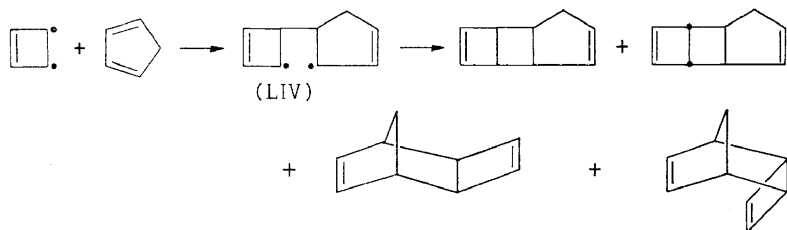


On the other hand, it can be argued that if cyclobutadiene were to have a triplet ground state then its addition to dimethylmaleate and dimethylfumarate should be non-stereospecific and that the same products should result from each of these reactions. A diradical might be expected to add to

## CYCLOBUTADIENE AND ITS METAL COMPLEXES



dimethylmaleate to give the diradical (LIII); assuming rotation about the bond between the two carbon atoms bearing the two COOCH<sub>3</sub> groups is fast compared to the rate ring closure to form the bicyclohexene ring, then the ring closure should yield the three stereoisomers indicated. By an analogous argument, addition of triplet cyclobutadiene to cyclopentadiene should proceed via the diradical (LIV), which could then undergo ring closure to yield one or more of the four hydrocarbons indicated.



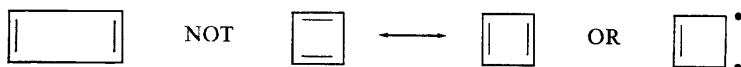
In practice it is found that the reactions of cyclobutadiene-iron tricarbonyl and dimethylfumarate, dimethylmaleate and cyclopentadiene in the presence of oxidizing agents are stereospecific, the products being (L), (LI), and (LII) respectively. The stereochemistry of these products is just that expected on the basis of the Diels-Alder rules. Therefore, within the limitations of the assumptions made, the ground state of cyclobutadiene appears to be a singlet electronic state. Furthermore, quantum mechanical treatments which predict a singlet ground state also predict a rectangular configuration for the molecule; therefore, arguments can be made for the case that cyclobutadiene possesses alternating short double bonds and long single bonds.

A more desirable experiment to determine the nature of the ground state of cyclobutadiene of course would be to take physical measurements directly on a sample of pure cyclobutadiene. However the practical difficulties associated with this approach have, to say the least, proved to be extremely difficult and so far insurmountable.

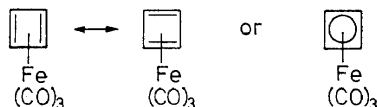
### SUMMARY

In summary, we consider that the theoretical and experimental evidence points rather strongly to a ground state singlet for cyclobutadiene in which

the molecule possesses alternating short double bonds and long single bonds just as cyclooctatetraene does. That is:



On the other hand, the metal complexes of cyclobutadiene have been shown to have a square configuration; hence, are best represented as follows:



Finally I wish to thank the National Science Foundation, the U.S. Army Research Office (Durham) and the Robert A. Welch Foundation for providing support for this research. I also thank Badische Anilin und Soda Fabrik and General Anilin and Film Corporation for donating generous samples of cyclooctatetraene and iron pentacarbonyl respectively.

## References

- <sup>1</sup> aR. Willstätter and W. von Schmaedel. *Ber. dtsch. Chem. Ges.* **38**, 1992 (1905).
- <sup>b</sup>E. R. Buchman, A. O. Reims and M. J. Schlatter. *J. Am. Chem. Soc.* **64**, 2701 (1942).
- <sup>c</sup>M. Avram, C. D. Nenitzescu and E. Marica. *Chem. Ber.* **90**, 1857 (1957).
- <sup>2</sup> See M. J. S. Dewar and G. J. Gleicher. *J. Am. Chem. Soc.* **87**, 3255 (1965) and references therein.
- <sup>3</sup> H. C. Longuet-Higgins and L. E. Orgel. *J. Chem. Soc.* 1969 (1956).
- <sup>4</sup> W. Hubel and E. H. Braye. *J. Inorg. Nucl. Chem.* **10**, 250 (1959).
- <sup>5</sup> R. Criegee and G. Schröder. *Liebigs Ann.* **623**, 1 (1959).
- <sup>6</sup> R. P. Dodge and V. Schomaker. *Nature*, **196**, 798 (1960).
- <sup>7</sup> J. D. Dumitz, H. C. Mey, O. S. Mills and H. M. M. Shearer. *Helv. Chim. Acta.* **45**, 627 (1962).
- <sup>8</sup> For a recent review of cyclobutadiene-metal complexes see P. M. Maitlis in *Advances in Organometallic Chemistry*, vol. IV, F. G. A. Stone and Robert West, Eds., Academic Press, New York, 1966, p. 95.
- <sup>9</sup> M. Avram, G. Mateescu, I. G. Dinulescu, E. Marica and C. D. Nenitzescu, *Tetrahedron Letters* No. 1, 21 (1961). M. Avram, H. P. Fritz, H. J. Keller, C. G. Lreotzer, G. Mateescu, J. F. W. McOmie, N. Sheppard and C. D. Nenitzescu, *Tetrahedron Letters* 1611 (1963).
- <sup>10</sup> G. F. Emerson, L. Watts and R. Pettit. *J. Am. Chem. Soc.* 131 (1965).
- <sup>11</sup> J. D. Fitzpatrick and R. Pettit, to be published.
- <sup>12</sup> R. G. Amiet, P. C. Reeves and R. Pettit. *Chem. Comm.* 1208 (1967).
- <sup>13</sup> M. Davis, personal communication.
- <sup>14</sup> H. Dieck and R. Pettit, to be published.
- <sup>15</sup> G. F. Emerson and R. Pettit. *J. Am. Chem. Soc.* **84**, 4591 (1962).
- <sup>16</sup> G. F. Emerson, J. E. Mahler and R. Pettit. *Chem. & Ind. (London)*, 836 (1964).
- <sup>17</sup> M. Davis, Personal communication.
- <sup>18</sup> P. E. Eaton and T. W. Cole, Jr. *J. Am. Chem. Soc.* **86**, 962 (1964).
- <sup>19</sup> W. Merk and R. Pettit. *J. Am. Chem. Soc.* **89**, 4788 (1967).
- <sup>20</sup> M. P. Cava and D. R. Napier. *J. Am. Chem. Soc.* **79**, 1701 (1957).
- <sup>21</sup> C. D. Nenitzescu, M. Avram and D. Dinu. *Chem. Ber.* **90**, 2541 (1957).
- <sup>22</sup> M. P. Cava and M. J. Mitchell. *J. Am. Chem. Soc.* **81**, 5409 (1959).
- <sup>23</sup> R. B. Woodward and R. Hoffmann. *J. Am. Chem. Soc.* **87**, 395 (1965).
- <sup>24</sup> W. Merk and R. Pettit. *J. Am. Chem. Soc.* **89**, 4788 (1967).