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PHOTOCHEMICAL REACTIONS OF 1,2-DIMETHYLCYCLOBUTADIENEIRON TRICARBONYL WITH VARIOUS ACETYLENES

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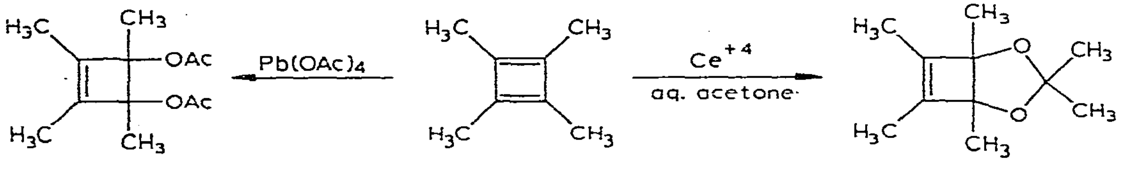
Summary

The photochemical reactions of 1,2-dimethylcyclobutadieneiron tricarbonyl with a variety of acetylenes have been studied. Benzenoid compounds generally are obtained. In particular, irradiation of the 1,2-dimethyl complex with acetylene yields *o*-xylene and *p*-xylene. Reaction with propyne produces 1,2,3- and 1,2,4-trimethylbenzene while 2-butyne forms 1,2,3,4- and 1,2,4,5-tetramethylbenzene. Several possible reaction mechanisms are presented and evaluated in light of the observed product distributions.

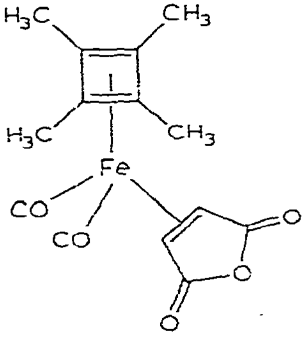
Introduction

The existence of tetramethylcyclobutadiene has been postulated from a variety of reactions that would logically require it as an intermediate [1]. The ease of liberation of cyclobutadiene from its iron tricarbonyl complex (I) by reaction with oxidizing agents [2] such as ceric ammonium nitrate and lead tetraacetate suggested that this method might have wide synthetic applicability for the generation of very reactive molecules. However, reaction of tetramethylcyclobutadieneiron tricarbonyl (II) with ceric ammonium nitrate in aqueous acetone produced the ketal III [3]; while reaction with lead tetraacetate in pyridine yielded the diacetate IV [4]. In neither of these cases could the diene be captured by dienophiles suggesting that the formation of III and IV had occurred prior to complete liberation of the diene from the metal.



(IV) (II) (III)

In 1967 Gunning and his coworkers [5] proposed that cyclobutadiene could be liberated from its metal complex by ultraviolet irradiation. Thus irradiation of I in the presence of dimethyl acetylenedicarboxylate yielded dimethyl phthalate. We [4] attempted to utilize this approach to liberate tetramethylcyclobutadiene from its iron tricarbonyl complex (II). In a series of experiments II was irradiated in ethereal solutions of dimethyl acetylenedicarboxylate, methyl propiolate, and 2-butyne. In each case substantial amounts (50—60% yield) of the corresponding tetramethylbenzene derivative was isolated. However, irradiation in the presence of olefinic dienophiles such as maleic anhydride led to compounds in which a π-bonded olefin has replaced one of the carbon monoxide ligands (V). These complexes were stable at room temperature and showed no tendency to decompose to Diels—Alder adducts. Prolonged irradiation caused decomposition of the complex but did not give rise to Diels—Alder adducts. These experiments and additional studies by Chapman [6] indicated that free cyclobutadiene was not produced in these photolytic reactions and further that the primary photoprocess was dissociation of carbon monoxide.



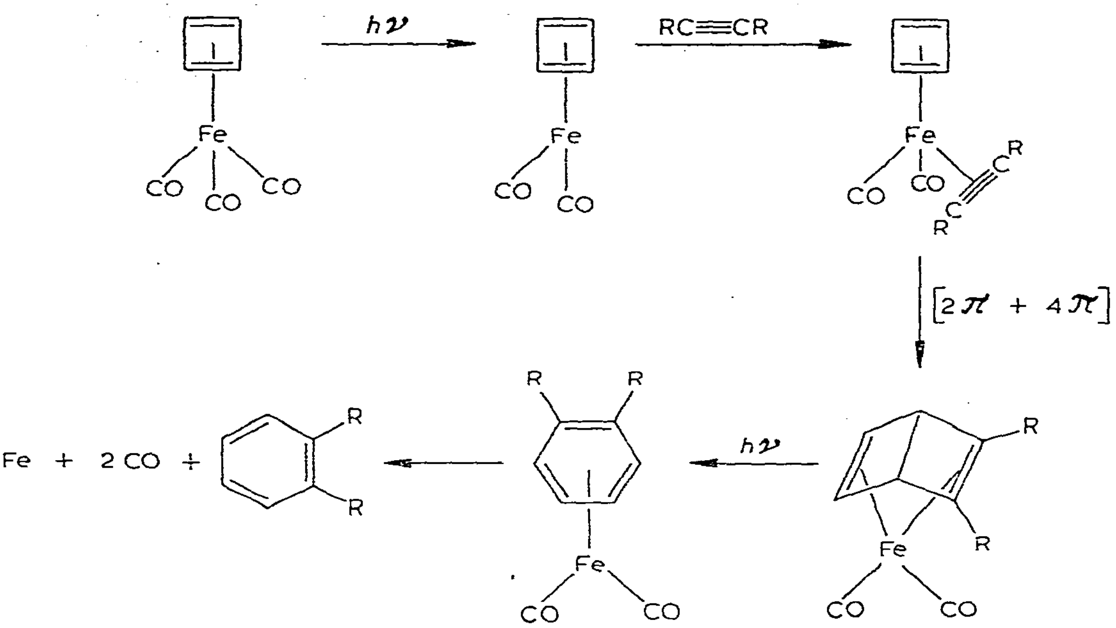
(V)

At least three mechanisms can be envisioned which would explain the formation of benzenoid compounds in these reactions. Mechanism A (Scheme 1) proposes that the reaction proceeds via photochemical dissociation of a carbon monoxide ligand followed by coordination with the acetylene. This π-coordination leaves the other π-bond of the acetylene free to interact with the π-system of the cyclobutadiene by way of an intramolecular 2π + 4π cycloaddition reaction with the resultant formation of a Dewar-benzene metal complex. This coordinately unsaturated molecule could then decompose to liberate a Dewar-benzene which would undergo an allowed ring-opening reaction to produce a benzenoid system. An alternate pathway would involve isomerization of the Dewar-benzene metal complex to a benzenoid iron dicarbonyl species. Complexes of this type are extremely unstable [7] and decomposition would liberate a benzenoid molecule. This mechanism is supported by Chapman's observation that the primary photoprocess is dissociation of a CO ligand; however, to our knowledge no Diels—Alder reaction of this type has been observed. A 2π + 6π cycloaddition between ligands coordinated to an iron atom has been described by Pettit [8].

A second mechanism is illustrated in Scheme 2. The key step in this mecha-

SCHEME 1

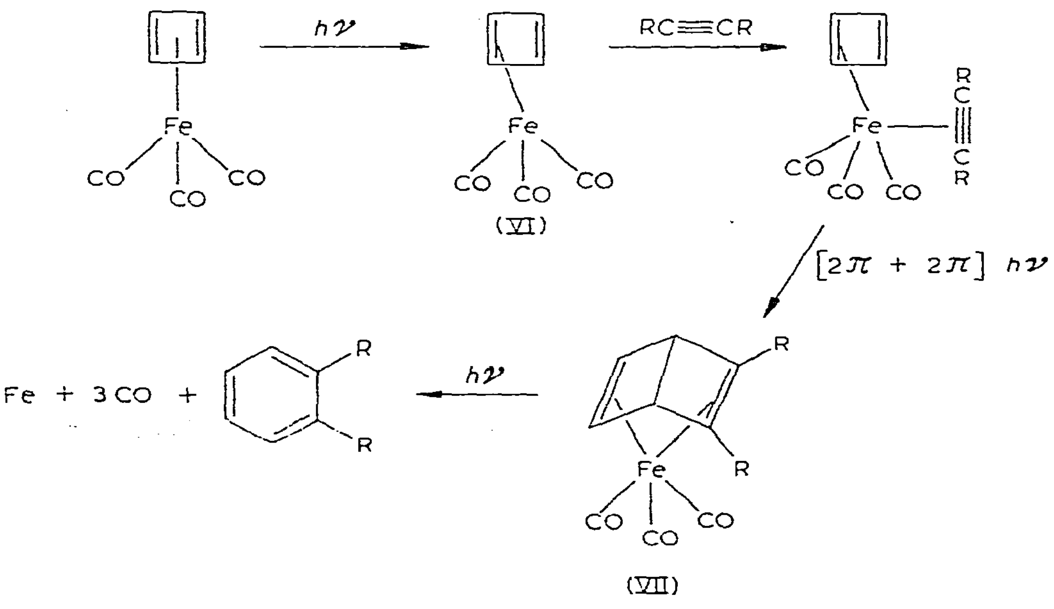
Mechanism A



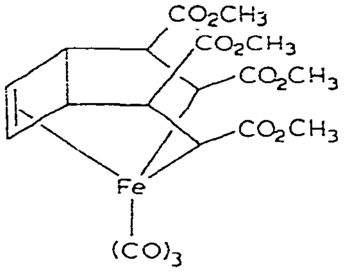
nism is the photochemical formation of the singly-coordinated species VI. Giering and coworkers [9] have been able to synthesize compounds containing singly-coordinated cyclobutadiene, and Pettit [10] has proposed such an intermediate in the formation of compound VIII in the irradiation of I in the presence of di-

SCHEME 2

Mechanism B



methyl maleate. The coordinately unsaturated species VI could then combine with the acetylene. A photochemically allowed $2\pi + 2\pi$ cycloaddition would then lead to VII with decomposition of VII yielding the benzenoid compound. The main objection to this mechanism is that Kerber [11] could find no evidence for a photochemically generated VI in photoreactions of I with trimethylphosphite even though such a species was actively sought.

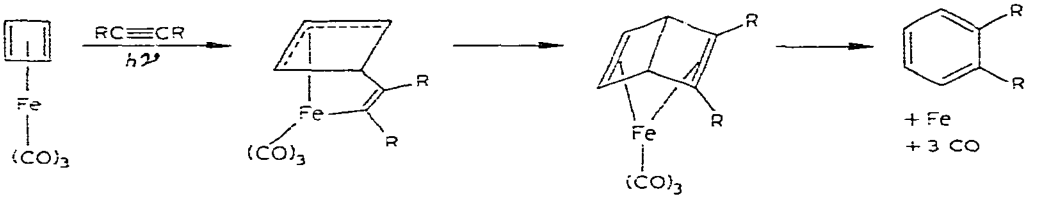


(VIII)

A third mechanism (Scheme 3) involves the photochemically assisted oxidative addition of an acetylene to I followed by reductive elimination to produce the Dewar-benzene complex VII. This mechanism has considerable support in the

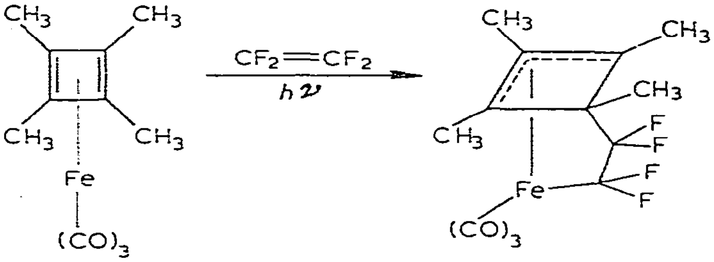
SCHEME 3

Mechanism C



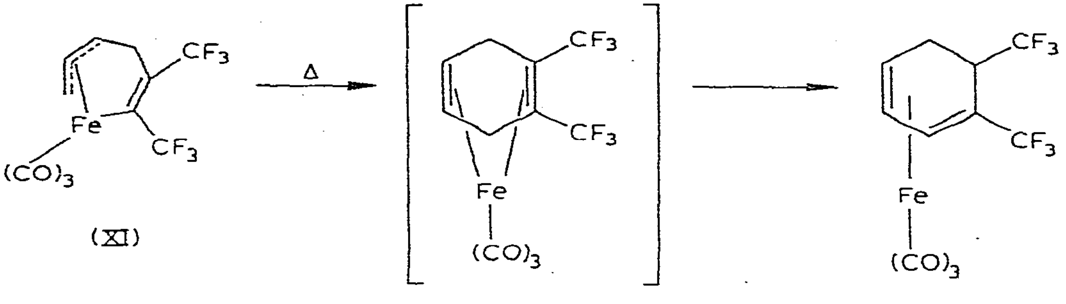
(I) (IX) (VII)

literature. Bond and Green [12] found in their study of the photochemical reactions of tetramethylcyclobutadieneiron tricarbonyl with hexafluoro-2-butyne and tetrafluoroethylene that crystalline 1/1 adducts were formed. Several structures were proposed for these adducts. A later report [16] confirmed that the compound formed in the reaction with tetrafluoroethylene possessed structure X.



(II) (X)

Complexes with similar structures were obtained with other fluoroalkenes. In a further study [14] they have found that the photoproduct XI (obtained by irradiating butadieneiron tricarbonyl and hexafluoro-2-butyne) rearranges to XII upon heating at 70—80°C indicating that the reductive elimination step is feasible in these reactions. We have studied the photochemical reactions of 1-methyl- and 1,2-dimethyl-cyclobutadieneiron tricarbonyl with various acetylenes in hope of clarifying the mechanism by which these benzenoid compounds are formed.



(XI)

(XII)

Results and discussion

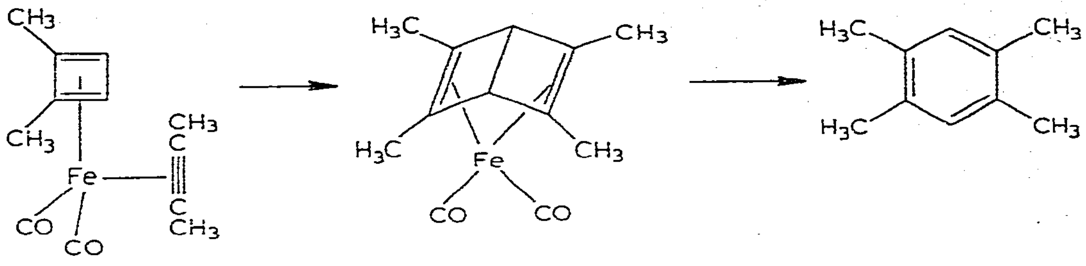
Solutions of 1,2-dimethylcyclobutadieneiron tricarbonyl (XIII) and various acetylenes in anhydrous ethyl ether were irradiated with a 450-Watt Hanovia mercury vapor lamp (borosilicate glass immersion well). A nitrogen atmosphere was maintained and the progress of the reaction was followed by the disappearance of the metal carbonyl absorption bands in the infrared spectrum. Complete disappearance occurred within 1.5 h. After filtration (to remove iron byproducts) and concentration of the filtrate, the residue was analyzed by GLPC.

When XIII was irradiated in the presence of acetylene, *o*-xylene and *p*-xylene were obtained in a ratio of 82/18. Analysis of the photoreaction with 2-butyne revealed that 1,2,3,4-tetramethyl- and 1,2,4,5-tetramethyl-benzene had been formed in a ratio of 97/3. Reaction with propyne yielded 1,2,3-trimethyl- and 1,2,4-trimethyl-benzene in a ratio of 68/32.

In order to establish that the observed products and their ratios were not due to some isomerization, we irradiated the authentic compounds in the presence and absence of added iron pentacarbonyl. No isomerization was detected; thus, it appears that the observed hydrocarbons are the initial products of the photoreactions.

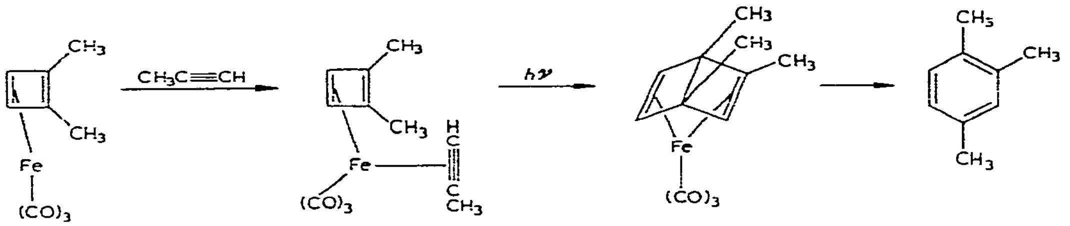
With these data in hand, one can consider the relative merits of each of the previously mentioned mechanisms. The results of the experiment with 2-butyne reveal a severe problem with mechanism A. Since the Diels—Alder reaction is known to be very sensitive to steric interactions, the preferred intermediate would appear to be XIV. Internal cycloaddition would produce XV which would ultimately yield 1,2,4,5-tetramethylbenzene. However, 1,2,4,5-tetramethylbenzene is a very minor product of the reaction.

Difficulties are also encountered in the use of mechanism B. It has been estab-



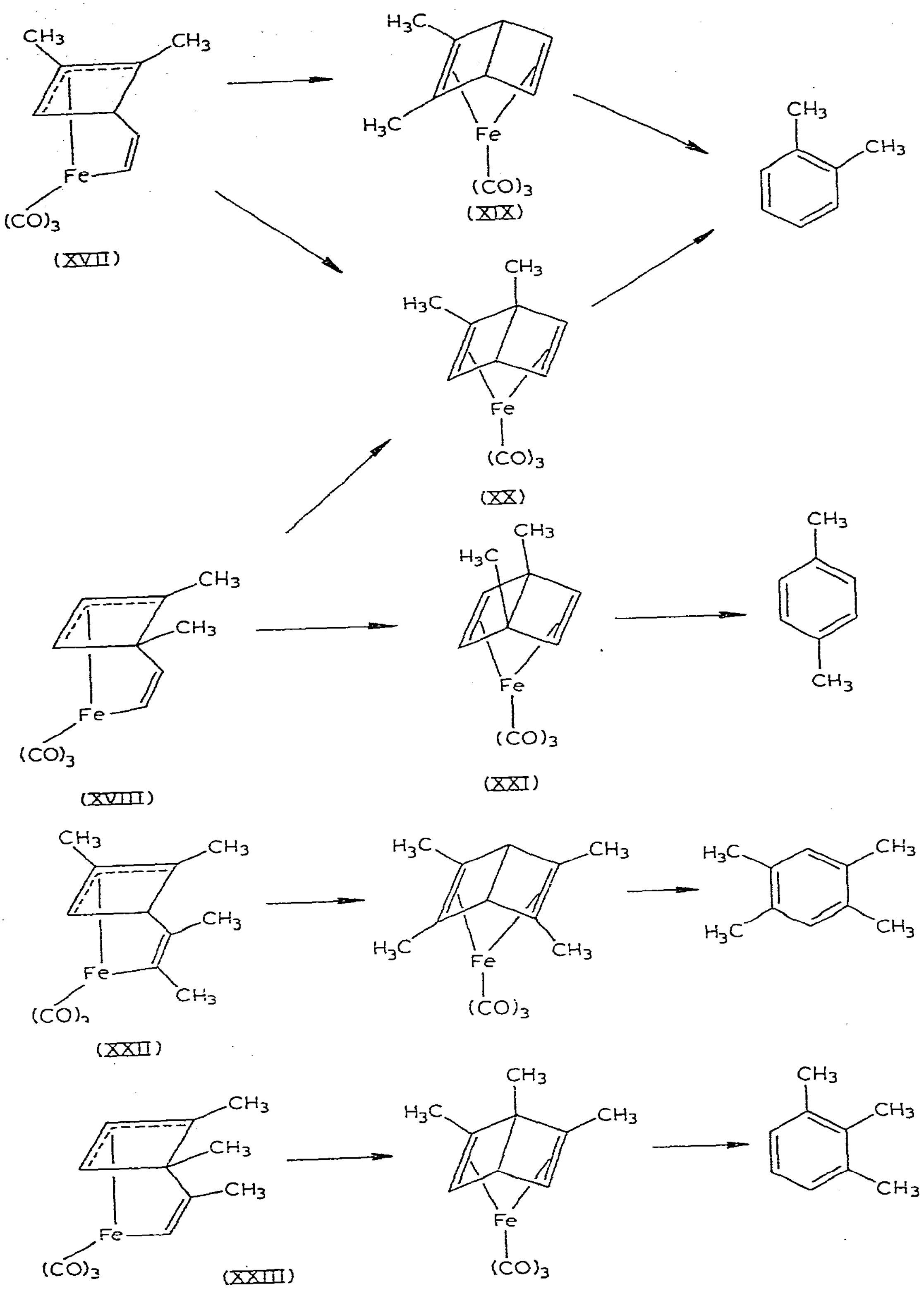
(XIV) (XV)

lished that the most stable olefin—metal complexes are formed from the least substituted olefins [13]. Therefore, the most stable singly-bonded cyclobutadiene intermediate would be XVI, which would react with propyne to yield 1,2,4-trimethylbenzene. However, 1,2,3-trimethylbenzene is the predominant product of this reaction.



(XVI)

The applicability of mechanism C is best illustrated by considering the photoreaction with acetylene. The oxidative addition reaction could lead to two isomeric compounds (XVII, XVIII). Each of these intermediates could in turn give rise to two products. For example, XVII could undergo reductive elimination to form XIX (carbon—carbon bond formation at the unsubstituted ring position) or XX (carbon—carbon bond formation at the substituted ring position). Similarly XVIII could yield XX and XXI. Only XXI would lead to production of *p*-xylene. On a statistical basis one would predict an *o*-xylene to *p*-xylene ratio of 75/25, while the observed ratio is 82/18. Since a statistical approach so nearly approximates the observed values, one might suspect that formation of each of the intermediates (XVII, XVIII) is equally likely and further that the directions of the reductive elimination steps are also equally likely. The values obtained in the reaction with 2-butyne suggest that this is not true. If this mechanism is operative, the compound 1,2,4,5-tetramethylbenzene is produced by a single pathway involving formation of XXII followed by reductive elimination with carbon—carbon bond formation at the unsubstituted ring position. Statistically the 1,2,4,5-isomer should comprise 25% of the aromatic hydrocarbon product; however, only 3% was found. The propyne reaction which produces 1,2,3-trimethylbenzene as the major product (68/32) is even more revealing. Once again, a single reaction pathway would lead to formation of the 1,2,3-isomer. All other pathways would produce the 1,2,4-isomer. This unique pathway involves formation of intermediate XXIII in which the acetylenic carbon has become bonded to the methyl-substituted cyclobutadiene ring carbon


(XVII)
(XIX)
(XX)
(XVIII)
(XXI)
(XXII)
(XXIII)
CH3
H3C
Fe
(CO)3

followed by reductive elimination with bond formation to the adjacent unsubstituted ring carbon. In reactions with unsymmetrical acetylenes (i.e. propyne), the oxidative addition is proposed to occur in a manner in which the bulky iron tricarbonyl group would become attached to the least-hindered end of the triple bond. Thus, a consideration of this mechanism reveals that the initial carbon—carbon bond formation preferentially occurs between the acetylenic carbon and a carbon of the cyclobutadiene ring bearing a methyl group. While a detailed mechanism for the insertion step cannot be written at this time, it appears that some ionic character must be generated in order to achieve the observed orientation.

To further test this hypothesis, 1-methylcyclobutadieneiron tricarbonyl was treated with propyne and methyl propiolate. The *ortho* isomers (*o*-xylene and methyl *o*-toluate) were formed in yields (based on total isomeric hydrocarbon produced) of 35—40% and the *para* isomer in less than 10%. This gives additional support for an increased tendency for bond formation at the ring carbon bearing a methyl group.

Orientations in these reactions are in stark contrast to those observed in photoinsertion reactions of haloalkenes into the iron—carbon bonds of dieneiron tricarbonyl. Reports by Kerber [11] and Green [14] indicate that unsymmetrical diene complexes, 1,3-pentadiene- and 1-phenylbutadieneiron tricarbonyl, undergo insertion exclusively at the unsubstituted carbon of the butadiene system. Further studies of these orientation effects are currently under investigation in this laboratory.

Experimental

Gas chromatographic analysis

Gas chromatography was accomplished on a Hewlett—Packard 5200 series gas chromatograph equipped with a flame ionization detector, a 5' × 1/8" column of 7.5% Bentoin-7.5% diisodecylphthalate on Chromosorb W and a nitrogen carrier gas system.

Methylcyclobutadieneiron tricarbonyl [3] and 1,2-dimethylcyclobutadieneiron tricarbonyl [15] were prepared according to literature procedures. The photochemical reaction procedure given below in detail is typical of all the photoreactions.

Photochemical reaction of 1,2-dimethylcyclobutadieneiron tricarbonyl with propyne

Dimethylcyclobutadieneiron tricarbonyl (0.3 g, 1.36 mmol) and propyne (2 g, 50 mmol) were dissolved in 200 ml of anhydrous ethyl ether and the solution cooled (under N_2 atmosphere) in an ice-salt bath. The mixture was irradiated for 1 h with a 450 Watt Hanovia mercury vapor lamp in a borosilicate immersion well. The reaction was followed by the disappearance of the metal carbonyl peaks in the infrared spectrum. The resultant brown slurry was filtered through a thin Celite pad and the solvent removed from the filtrate on a rotary evaporator. The residue was chromatographed over a 2 × 5 cm alumina column and eluted with ether. Concentration of the eluant produced 0.12 g (74% yield) of a mixture of 1,2,3-trimethyl and 1,2,4-trimethyl-benzene in a ratio of 68/32.

Acknowledgements

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