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PHOTOCHEMICAL REACTIONS OF SUBSTITUTED CYCLOBUTADIENEIRON TRICARBONYL COMPLEXES WITH ACETYLENES

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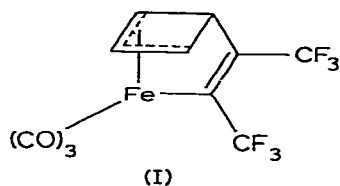
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Summary

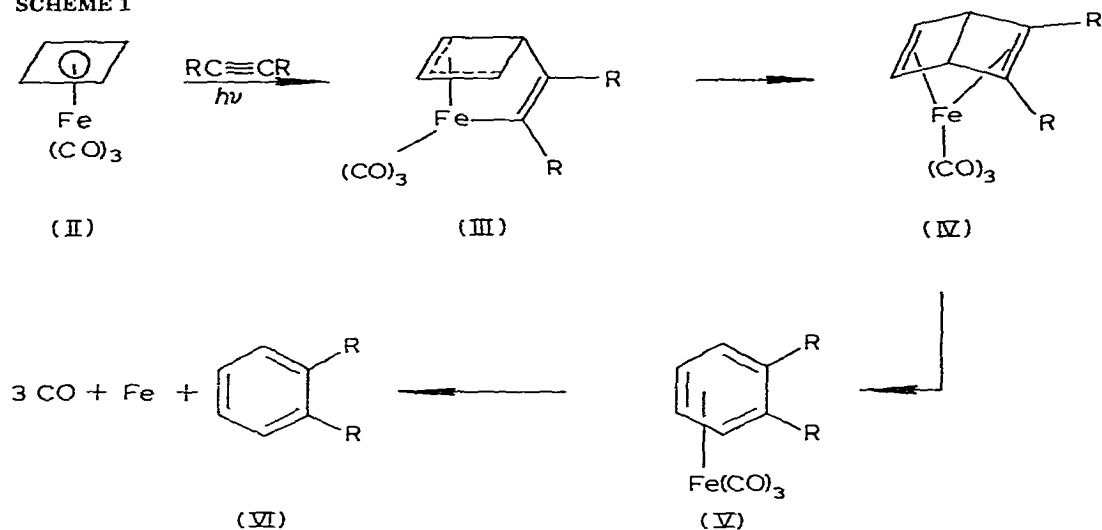
When mixtures of monosubstituted cyclobutadieneiron tricarbonyl complexes and propyne are irradiated, substituted toluenes are obtained. The composition of the isomeric mixture is influenced by the nature of the substituent in the metal complex. Electron-withdrawing groups produce mixtures containing a very large percent of the *ortho* isomer while electron-releasing groups yield mixtures rich in the *para* isomer. Complex mixtures of isomeric benzene compounds are obtained when substituted acetylenes are allowed to react with methyl- or isopropylcyclobutadieneiron tricarbonyl.

Introduction

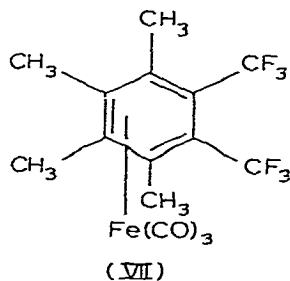
The observation that irradiation of cyclobutadieneiron tricarbonyl in the presence of dimethyl acetylenedicarboxylate yielded dimethyl phthalate led Gunning and coworkers [1] to propose that cyclobutadiene could be liberated from its metal complex by ultraviolet irradiation. Later experiments [2,3] indicated that free cyclobutadiene was not produced in these photolytic reactions and further that the primary photoprocess was dissociation of carbon monoxide. Bond and Green [4,5] reported reactions soon thereafter where UV irradiation of cyclobutadieneiron tricarbonyl complexes in the presence of fluoro-olefins or -acetylenes afforded novel π -allylic complexes (I) in which the unsaturated molecule linked the C_4 ring and the metal atom. A mechanism (Scheme 1) has



SCHEME 1



been proposed to explain the origin of benzenoid compounds formed in some reactions of this type [6,7]. The mechanism for the oxidative addition of the acetylene to II to form III has been studied [8,9] and, while it is difficult at the present time to distinguish with certainty among various possible paths, orientation effects are best explained by intermediates having some ionic character. The reductive elimination step (conversion of III to IV) has precedent in the literature [10] and the isolation of VII from the photochemical reaction of tetramethylcyclobutadieneiron tricarbonyl with hexafluorobut-2-yne [7] supports the proposed intermediacy of V.



Photoinsertion reactions of haloalkenes also occur with acyclic dieneiron tricarbonyl complexes and substituents on the diene have been shown to influence the position of bond formation. Reports indicate that 1,3-pentadieneiron tricarbonyl [10] and 1-phenylbutadieneiron tricarbonyl [8] undergo insertion exclusively at the unsubstituted end of the diene system while reaction at C(4) of 2-methyl-1,3-butadieneiron tricarbonyl [10] is five times more likely than at C(1). This is in sharp contrast to reactions with 1,2-dimethylcyclobutadieneiron tricarbonyl [6] where the preferred position of insertion appears to be one of the substituted ring-carbon atoms. Therefore we have investigated reactions of a number of cyclobutadieneiron tricarbonyl complexes in order to determine how substituents influence the position of the photoinsertion reaction.

Results and discussion

The photolytic reaction of a series of monosubstituted cyclobutadieneiron tricarbonyl complexes with unsymmetric acetylenes has been studied. Substituents on the acetylenes and cyclobutadiene ring were chosen for their steric and/or electronic characteristics. The reactants (in ether solution) were irradiated generally for one hour with a 450 watt Hanovia mercury vapor lamp and the progress of the reaction was monitored by the disappearance of the infrared Fe—CO stretching absorptions. Gas chromatographic analysis of the organic reaction products gave relative abundances of *ortho*, *meta* and *para* isomers. The possible orientations upon photoinsertion can be envisioned by following the mechanism presented in Scheme 1. Statistical orientations during bond formation were determined by considering all possible attacks as equally likely. When the acetylene used is propyne, Fe—C bonding at the least substituted end of the unsymmetric acetylene is predicted because of the preferential attachment of the bulky iron carbonyl moiety to the least hindered end of the acetylene molecule. It is also the preferred direction of addition if one invokes an ionic intermediate in the oxidative-addition step [9]. A statistical distribution of 25% *ortho*, 25% *para*, and 50% *meta* is predicted by this model. Identical statistical distributions are obtained if the opposite direction of addition to propyne is invoked.

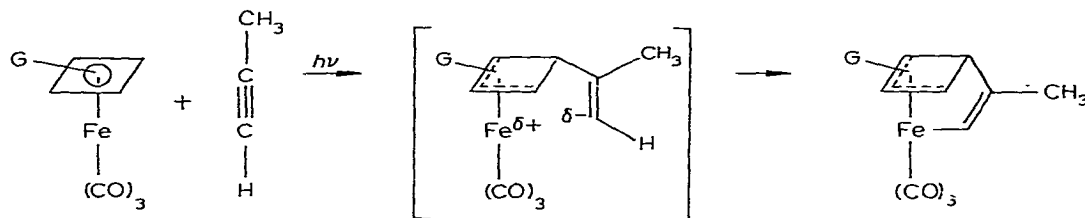
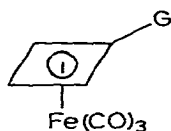


TABLE I

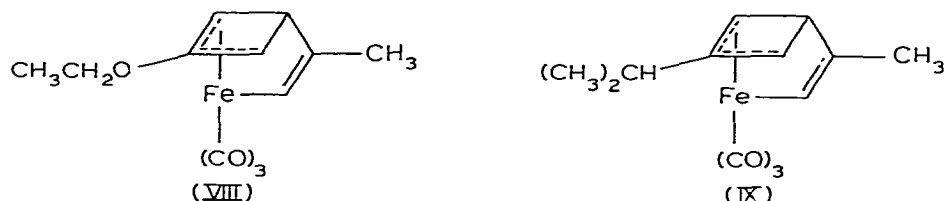
PRODUCTS FROM IRRADIATION OF SUBSTITUTED CYCLOBUTADIENEIRON TRICARBONYL COMPLEXES WITH PROPYNE



G	Relative percent abundance		
	<i>Ortho</i>	<i>Meta</i>	<i>Para</i>
Statistical norm	25	50	25
-CH ₃	26 (+4)	49 (-2)	25 (0)
-CH(CH ₃) ₂	16 (-36)	46 (-8)	38 (+52)
-COOH ₃	88 (+252)	4 (-92)	8 (-68)
-CO ₂ CH ₃	79 (+216)	9 (-82)	12 (-52)
-OCH ₂ CH ₃	2 (-92)	12 (-76)	86 (+244)

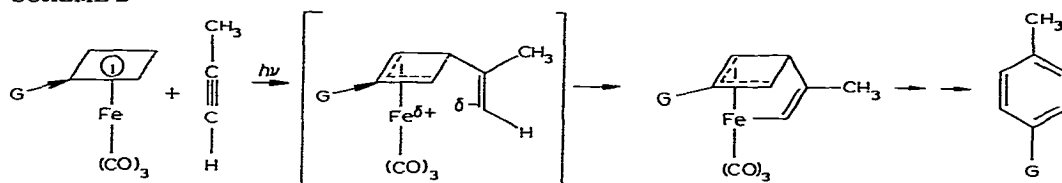
Table 1 lists the distribution of products obtained from irradiation of substituted cyclobutadieneiron tricarbonyl complexes in the presence of propyne. The values in the parentheses are the percent of increase or decrease relative to the statistical probability values. Substituent effects can be seen to have a marked effect on the isomer distribution, with the strong electron-withdrawing groups (by induction and resonance) $-\text{COCH}_3$ and $-\text{CO}_2\text{CH}_3$ deviating widely from the strong electron-donating (by resonance) substituent $-\text{OCH}_2\text{CH}_3$. The methyl substituent being the weakest contributor to electronic and steric effects would be expected to follow most nearly the random orientation model.

A consideration of these results allows one to draw some conclusions concerning the effect of substituents on these photolytic reactions. A strong electron-donating group such as ethoxy produces a very large amount of the *para* isomer. The isopropyl group, which is a weak electron donor, also shows a moderate increase in the amount of the *para* isomer. This suggests that intermediate VIII is greatly preferred and that IX is important, but to a lesser extent. *Para* orientation could be predicted for electron-releasing groups in the light of

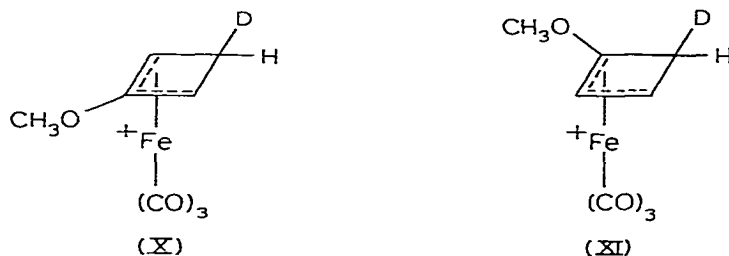


a mechanism that has considerable ionic character. In this pathway (Scheme 2), the electron-donating substituent stabilizes a π -allyl cationic intermediate in the *para* position more than in alternate positions.

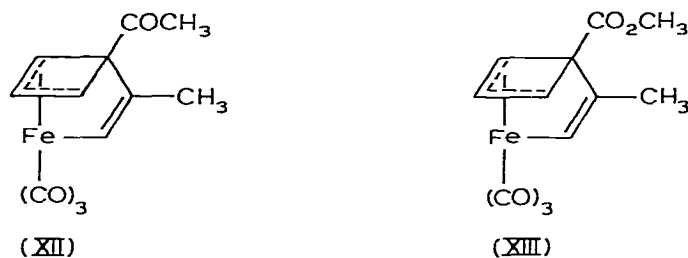
SCHEME 2



Broussard [11] investigated the isotopic exchange reaction of methoxycyclobutadieneiron tricarbonyl with $\text{CF}_3\text{CO}_2\text{D}$ and found that deuterium was incorporated exclusively at the *para* position, whereas reaction with unsubstituted cyclobutadieneiron tricarbonyl resulted in total deuterium exchange although at a slower rate. A detailed molecular orbital treatment which included the effects of the iron carbonyl moiety on the organic ligand was used to account for the increased stability of cation X relative to XI.

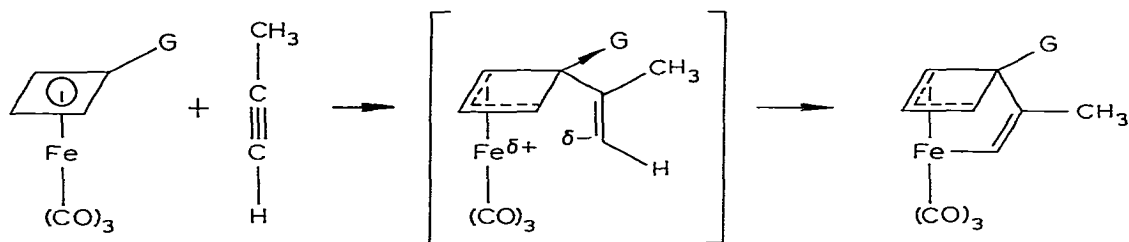


The results also reveal that strong electron-withdrawing groups lead to preferred formation of the *ortho* isomer. This suggests the importance of intermediates such as XII and XIII, and a mechanistic pathway as in Scheme 3. Even though initial attack would appear to be at an electron-deficient site, the posi-



tion of G allows for the least amount of electron withdrawal from the already electron-deficient π -allyl cationic intermediate.

SCHEME 3

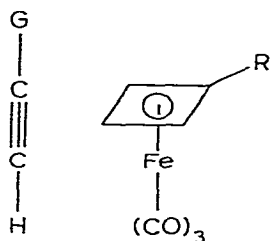


Little mention has been made concerning the origin of the *meta* products. When the substituent is weak electronically (i.e., alkyl groups), the *meta* product is formed essentially in statistical amounts, indicating random attack. There is a slight decrease in amount of *ortho* product (steric factor) and a slight increase in *para* product (electronic factor) as the bulk of the group increases. When the substituents are strongly electron-releasing or -withdrawing, the *meta* products become minor products, indicating the great importance of electronic effects.

Ultraviolet irradiation of methyl- and isopropyl-cyclobutadieneiron tricarbonyl with ethoxyacetylene, methyl propiolate, and propyne resulted in observable trends when considering an increase in alkyl substituent size. Results are given in Table 2. In each case there is a decrease in the amount of *ortho* product and an increase in the amount of *para* product as the bulk of the substituent on the cyclobutadiene ring increases. The intermediate giving rise to *para* product would have the least steric hindrance. Steric crowding in the initial oxidative-addition step could explain the decrease in amount of *ortho* isomer formed as the substituent is changed from methyl to isopropyl. This explanation is complicated by the observation [9] that 3,3,3-trifluoro-1-propyne adds in a direction opposite to that proposed for propyne. The trifluoro methyl group stabilizes the incipient "vinyl anionic" intermediate. In a similar fashion the carbomethoxy and ethoxy groups might be predicted to add in a different direction to that proposed for propyne. Additional studies are currently underway in an attempt to explore the role of substituents on the acetylene in determining the direction of the photoinsertion reaction.

TABLE 2

BENZENOID PRODUCTS FROM IRRADIATION OF ALKYL-SUBSTITUTED CYCLOBUTADIENE-IRON TRICARBONYL COMPLEXES WITH UNSYMMETRIC ACETYLENES



G	R	Relative percent abundance		
		Ortho	Meta	Para
-OCH ₂ CH ₃	-CH ₃	23 (-8)	14 (-72)	63 (+152)
	-CH(CH ₃) ₂	21 (-16)	15 (-70)	64 (+156)
-CO ₂ CH ₃	-CH ₃	29 (+16)	40 (-20)	31 (+24)
	-CH(CH ₃) ₂	2 (-92)	21 (-58)	77 (+208)
-CH ₃	-CH ₃	26 (+4)	49 (-2)	25 (0)
	-CH(CH ₃) ₂	16 (-36)	46 (-8)	38 (+52)

Experimental

A. Photolytic experiments

1. Source of compounds

a. *Cyclobutadieneiron tricarbonyl complexes.* The preparation of methyl- [12], ethyl- [13], isopropyl- [14], acetyl- [15], ethoxy- [11], and carbomethoxy- [2] cyclobutadieneiron tricarbonyl compounds was accomplished according to literature procedures.

b. *Acetylenes.* Ethoxyacetylene and methyl propiolate were purchased from Farchan Division of Story Chemical Corporation. Propyne was commercially available from Linde Division of Union Carbide Company in a pressurized gas cylinder. All acetylenes were used without purification.

2. Typical photolysis procedure

Photolytic reaction of methylcyclobutadieneiron tricarbonyl with propyne. Methylcyclobutadieneiron tricarbonyl, 0.2 g, was dissolved in 20 ml of anhydrous ether and cooled to 0°C. Two hundred fifty millimeters of anhydrous ether were cooled to 0°C and propyne gas was bubbled through the solution with stirring for 15 min. After saturation was complete, the cold solutions were added to a photolytic reactor immersed in an ice-water bath. The photolytic reactor consisted of a borosilicate immersion well, available from Ace Glass, fitted into a large test tube. The total volume of the reactor was 250 ml. A 450-watt Hanovia mercury vapor lamp was inserted into the water-cooled immersion well. The mixture was irradiated under a N₂ atmosphere with stirring for approximately 1 h while the disappearance of the metal carbonyl peak in the infrared spectrum at 2038 cm⁻¹ was monitored. The resulting brown slurry was

filtered through a 1-inch Celite pad and the solvent removed by rotary evaporation. The remaining oil was chromatographed over a 1 × 2 inch alumina column with 75 ml of ether. The solvent was removed from the eluant and the residue analyzed by gas chromatography. When liquid acetylenes were used, 2.0 g of the acetylene and 0.2 g of the complex were dissolved in 250 ml of ether and allowed to react as described above.

3. Analysis of reaction products

Gas chromatographic analyses were performed on a Hewlett-Packard 5720 Series Gas Chromatograph equipped with a flame detector and a 4' × 1/8" glass column packed with 5% Bentoin-5% SP 1200 on Chromosorb W or a 4' × 1/8" column packed with 5% Bentoin 34 on Chromosorb W. Peaks were identified by comparison with retention times of authentic compounds. No isomerization of the authentic compounds was observed when they were subjected to the reaction conditions. The distribution of the isomeric cymenes was determined by infrared spectroscopy [16].

Acknowledgement

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