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REACTIONS OF UNSYMMETRICALLY SUBSTITUTED PENTADIENYLIRON TRICARBONYL CATIONS WITH WATER

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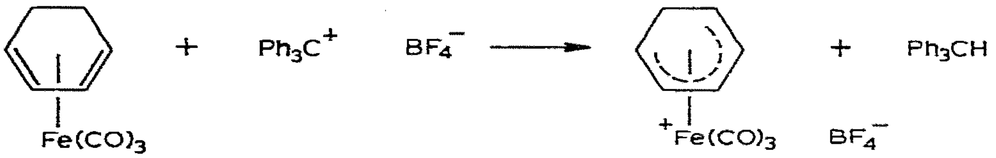
Summary

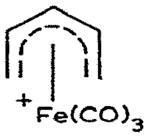
The reactions of unsymmetrically-substituted pentadienyliron tricarbonyl cations with water have been studied in order to learn more about the relative importance of steric and electronic factors in determining the position of nucleophilic attack.

Introduction

A transition metal stabilized pentadienyl cation was first isolated by Fischer in 1960 when cyclohexadieneiron tricarbonyl was treated with triphenylmethyl fluoroborate [1]. This cation (I) was found to be remarkably stable. Not only did its mode of formation indicate that it was more stable than the triphenylmethyl cation, but its salts could be readily recrystallized from water. Since this cation was part of a cyclic system, the carbons were of necessity arranged in a completely *cisoid* fashion. However, in acyclic systems one might predict that two isomeric cations (II, III) could exist. In order to study the geometrical pre-



(I)



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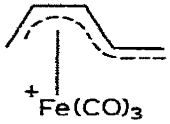
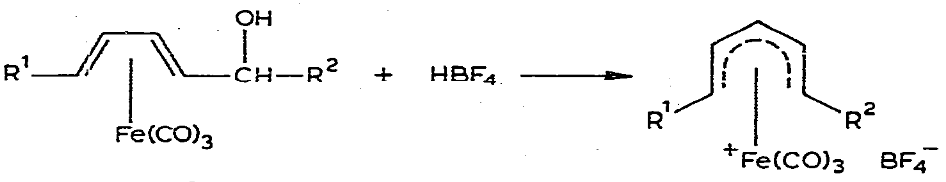


(III)

ference of these cations, Pettit and Mahler [2] treated a series of pentadienol-iron tricarbonyl complexes (IV) with fluoroboric acid. Addition of ether to the reaction mixture caused precipitation of the cation salts as bright yellow crystals. In all cases NMR analysis of the salts indicated that they possessed an arrangement of atoms similar to structure II.

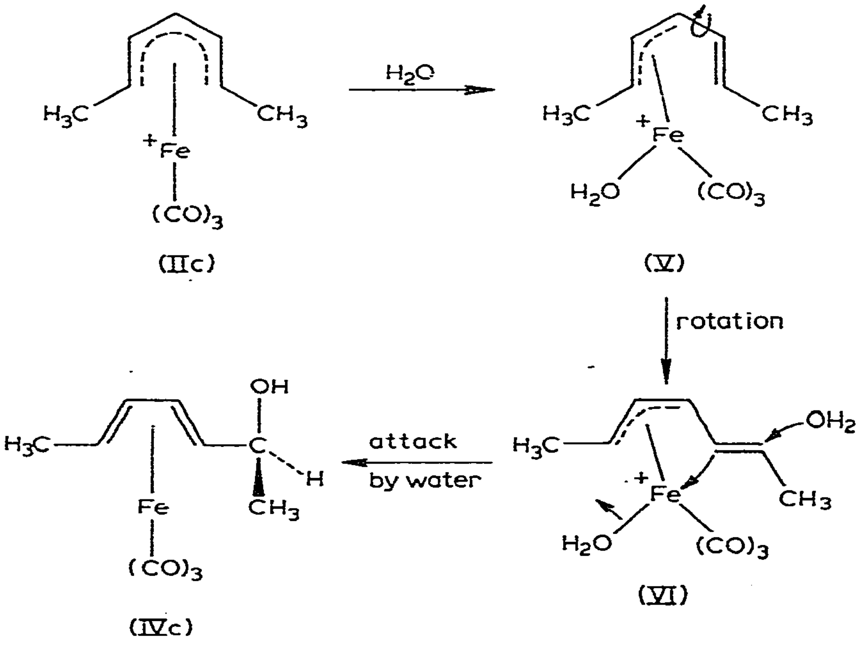


(IVa) $R^1 = R^2 = H$
(IVb) $R^1 = H, R^2 = CH_3$
(IVc) $R^1 = R^2 = CH_3$

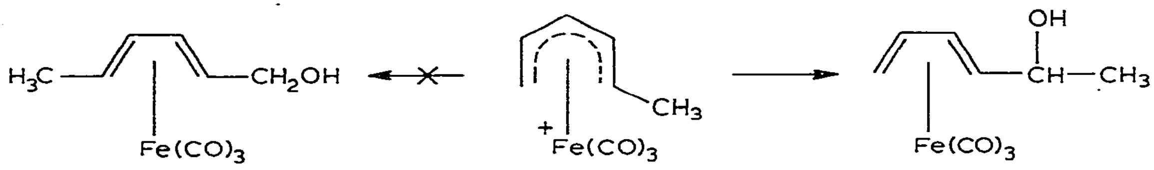
(II)

These cations were also found to be stable; however, they have been found to react with a variety of nucleophiles such as water [2], alcohols [2,3], amines [4], hydride ions [2,3], organocadmium reagents [5], and electron-rich aromatic compounds [6]. The hydrolysis reaction has been studied in some detail and reveals several interesting facts. For example, cation IIc reacts immediately with water to generate only one of the possible diastereoisomers of alcohol IVc. Pettit's assignment [3] of a configuration of *SS* (or *RR*) to this alcohol has been confirmed by Riley and Davis [7]. A mechanism (Scheme 1) was proposed to account for this observation. Important aspects of the mechanism are the hydrated π-allyliron cation (V) and the attack by the nucleophile from the least hindered face.

SCHEME 1

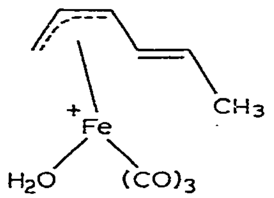


Another interesting facet of the hydrolysis reaction is that the unsymmetrical cation IIb produced alcohol IVb to the total exclusion of alcohol VII [3]. According to the previously described mechanism there must be a strong preference for reactive intermediate VIII as compared to intermediate IX. This was

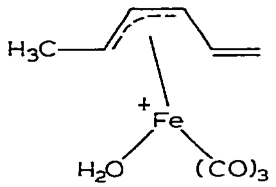


(VII) (IIb) (IVb)

rationalized on the basis that VIII contained the most substituted alkene and the

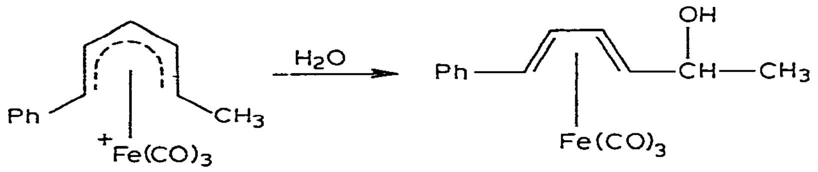


(VIII)



(IX)

least sterically crowded hydrated π-allyliron cation. The recent report [8] that hydrolysis of the unsymmetrical cation X produced only XI complicates this explanation. This would necessitate a reactive intermediate in which the methyl



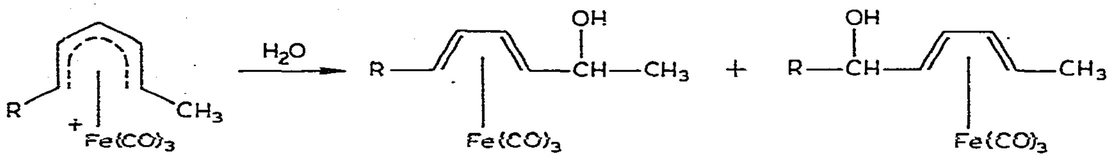
(X) (XI)

group was substituted on the double bond instead of the phenyl group even though this would not yield the most stable alkene. Additionally, substitution of the bulky phenyl group on the π-allyl system would yield a more crowded π-allyliron cation. In order to elucidate the role of electronic and steric effects in these reactions, we have studied the reactions of a variety of unsymmetrically substituted pentadienyliron tricarbonyl cations with water.

Results and discussion

The unsymmetrically substituted pentadienyliron tricarbonyl cations used in this study were prepared from either of the corresponding alcohols by dissolving the alcohols in a mixture of acetic anhydride and fluoroboric acid. The bright yellow fluoroborate salts were precipitated by dilution of the reaction mixture with ether and isolated by filtration. These salts were obtained in high yield and were found to be air and light stable. The hydrolysis reactions were accomplished by gradual addition of the salts to large quantities of water with vigorous stirring. The alcohols which were formed were isolated by filtration or extraction.

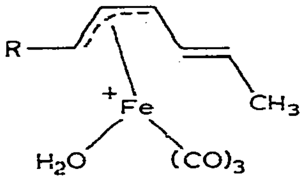
Two families of cations were studied. In the first (XII), one of the substituents was maintained as the methyl group and the other was varied. Hydrolysis of these cations could lead to alcohols of general structures XIII or XIV. The results are listed in Table 1. The product ratios were determined by NMR analysis of the crude hydrolysis product. The methyl protons of alcohols of type XIII appear as a doublet located at τ 8.7—8.8 ppm while the methyl protons of XIV appear as a doublet located at τ 8.5—8.6 ppm. The separation of these peaks is adequate for accurate area determination. An examination of the results indicates that steric factors are important. In the trivial case XIIa attack is equally favored at either end of the cation; however, as the bulk of one of the substituents increases the water molecule becomes more selective in the position of its attack with attack at the least sterically hindered position predominating. In terms of the possible intermediates suggested by Pettit's mechanism (XV, XVI), several factors should be considered. Since all of the substituents (with the exception of the phenyl group) have approximately the same stabilizing influence on the free alkene, there seems to be little reason to prefer one intermediate over another. An attempt to minimize crowding about the allyliron cation would favor an



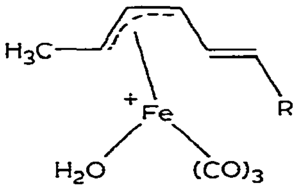
(XIIa) R = methyl
(XIIb) R = ethyl
(XIIc) R = isopropyl
(XIId) R = phenyl

(XIII)

(XIV)



(XV)



(XVI)

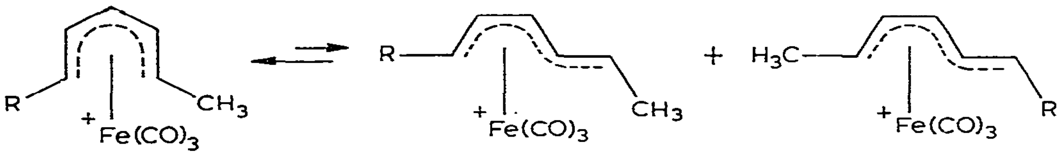
TABLE 1

PRODUCT RATIOS OF COMPOUNDS XIII/XIV OBTAINED BY HYDROLYSIS REACTIONS OF COMPOUNDS XIIa—XIId

Cation	XIII/XIV
XIIa	50/50
XIIb	61/39
XIIc	90/10
XIId	100/ 0

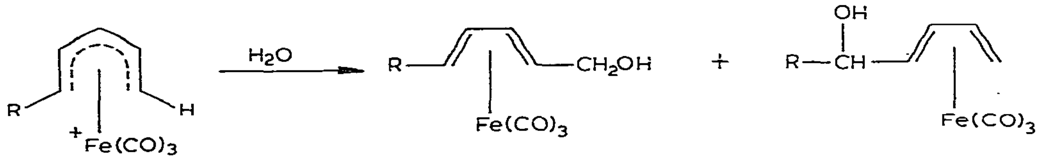
intermediate such as XVI. As can be seen, however, an increase in the bulk of R favors product arising from intermediate XV. This can be rationalized in terms of the ease of attack of the water molecule at a less hindered position. Since substituents have been shown to have little effect on the stability of allyliron tricarbonyl cations [8], the steric demand of the phenyl group is proposed to be of prime importance in determining the course of the hydrolysis reaction of cation XIId.

Since many of the other nucleophilic additions proceed in the absence of water or other solvents which could efficiently solvate the metal, another mechanism should be considered. In this mechanism the *cisoid* cation XII is in equilibrium with the corresponding *transoid* cations XVII, XVIII. Both direct [10] and indirect [6] evidence for this type of equilibrium has been found. Cation XII is more abundant than XVII of XVIII, but is also apparently much less reactive [6]. Reaction of these *transoid* cations with water at the incompletely coordinated end could lead to the observed products. The increasing preference for reaction with cation XVII as the bulk of R increases can be rationalized in terms of steric hindrance to nucleophilic attack.



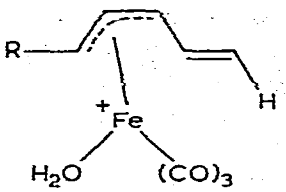
(XII) (XVII) (XVIII)

The second series of cations studied (XIX) consisted of mono-substituted pentadienyliron tricarbonyl cations. The results of their hydrolysis reactions are quite different from those of XIIa—XIId. No trace of alcohols of structure XX could be found. The presence of a pair of doublets in the τ 9.6—9.8 ppm region of the NMR spectrum (characteristic of *trans*-1-substituted dieneiron tricarbonyl complexes [11]) simplifies the structure assignment. These results seem to indicate that steric effects are of no importance in determining the position of attack on these cations. Examination of the intermediates (XXII, XXIII) reveals that the free double bond is stabilized by alkyl substitution in XXIII. As previously stated, substituents have little influence on the stability of allyliron tricarbonyl cations; thus the preferred intermediate would seem to be XXIII in spite of the

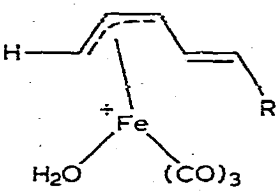


(XX) (XXI)

(XIXa) R = methyl
(XIXb) R = ethyl
(XIXc) R = isopropyl
(XIXd) R = t-butyl
(XIXe) R = phenyl

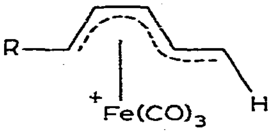


(XXII)

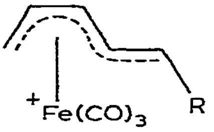


(XXIII)

fact that attack by water would seem to be more difficult. In terms of the alternate mechanism XXV would be preferred because of the ability of R to better stabilize the increased charge density at the terminus [10].



(XXIV)



(XXV)

The results can be summarized as follows. If a pentadienyliron tricarbonyl cation is substituted at the termini, water will attack preferentially at the carbon bearing the smallest substituent. When only one end of the cation bears a substituent, attack will occur at the substituted position because of the ability of the substituent to stabilize the reactive intermediate.

Experimental

Microanalyses were performed by Chemalytics, Inc., Tempe, Arizona. NMR spectra were determined on a Perkin—Elmer model R32 nuclear magnetic resonance spectrometer.

Table 2 lists the previously unreported alcohols used in this study along with their melting or boiling points and elemental analysis. Table 3 is a tabulation of the NMR spectral data for the complexes.

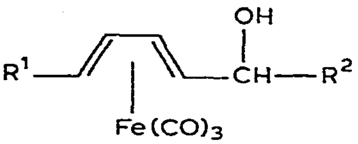
Two general pathways were followed in the synthesis of previously unknown alcohols. The first involves the reaction of the desired alcohol with triiron dodecacarbonyl in benzene while the second involves acylation of a dieneiron tricarbonyl complex followed by reduction of the resultant ketone. The following examples are illustrative of these pathways.

Preparation of 2-methyl-4,6-octadiene-3-oliron tricarbonyl (XIVc). A mixture of 3.94 g (28 mmol) of 2-methyl-4,6-octadien-3-ol (prepared from 2,4-hexadienal and isopropylmagnesium bromide), 10.89 g (22 mmol) of $Fe_3(CO)_{12}$ and 500 ml of benzene was refluxed overnight (nitrogen atmosphere). The cooled solution was filtered and concentrated leaving a thick oil. The crude product was chromatographed over Al_2O_3 (ether) to remove iron by-products. This material was then vacuum distilled to yield 4.04 g (51% yield) of the desired compound as an orange oil (b.p. 94—100°C/0.4 mmHg). In similar fashion, 2,4-octadien-5-oliron tricarbonyl (XIVb) was prepared in 52% yield.

Preparation of 1,3-heptadien-5-oliron tricarbonyl (XXIb). To 50 ml of dry CH_2Cl_2 (cooled to 0°C) was added 2.40 g (26 mmol) of propionyl chloride and

TABLE 2

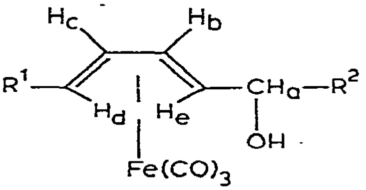
PHYSICAL PROPERTIES OF DIENOLIRON TRICARBONYL COMPLEXES



Compound	R¹	R²	M.p. (°C)	B.p. (°C/mmHg)	Elemental analysis (Found (calcd.) (%))	
					C	H
XIIIb	ethyl	methyl	—	88—90/0.5	49.39 (49.64)	5.48 (5.31)
XIVb	methyl	ethyl	—	96—98/0.5	49.91 (49.64)	5.36 (5.31)
XIIIc	isopropyl	methyl	83—85	—	51.73 (51.45)	5.72 (5.77)
XIVc	methyl	isopropyl	—	94—96/0.4	51.91 (51.45)	5.89 (5.77)
XXIb	H	ethyl	—	92—94/0.5	47.76 (47.68)	4.85 (4.85)
XXIc	H	isopropyl		92—94/0.4	49.66 (49.67)	5.02 (5.26)
XXId	H	t-butyl	49—52	—	51.52 (51.48)	5.57 (5.72)
XXIe	H	phenyl	98—99	—	55.48 (56.03)	3.59 (4.00)

TABLE 3

CHEMICAL SHIFTS OF PROTONS IN DIENOLIRON TRICARBONYL COMPLEXES



Compound		Chemical shifts τ (ppm) (solvent CS_2)					
R¹	R²	H_a	$H_{b,c}$	H_d	H_e	R¹	R²
methyl	ethyl	6.60	4.90	9.00		8.57	8.35, 9.00
methyl	isopropyl	6.50	4.95	9.10		8.55	8.31, 9.01
methyl	phenyl	5.62	4.90	8.90		8.60	2.78
ethyl	methyl	6.28	4.90	8.90		8.40, 8.97	8.75
isopropyl	methyl	6.45	4.88	9.00		8.50, 8.93	8.72
phenyl	methyl	6.35	4.50	8.80		2.87	8.65
H	methyl	6.50	4.70	9.73	9.10	8.25	8.75
H	ethyl	6.50	4.70	9.72	8.95	8.35	8.48, 9.05
H	isopropyl	6.50	4.70	9.75	8.95	8.31	8.40, 9.10
H	t-butyl	6.50	4.70	9.80	8.94	8.31	9.10
H	phenyl	5.90	4.65	9.85	8.94	8.40	2.83

2.40 g (18 mmol) of anhydrous $AlCl_3$. The mixture was stirred under N_2 for 20 min. A solution of 3.00 g (15 mmol) of butadieneiron tricarbonyl and 20 ml of CH_2Cl_2 was added dropwise over a period of 5 min. The reaction mixture was stirred for an additional 15 min at 0°C and then poured into a stirred mixture of 75 ml of NH_4OH and 50 g of ice. After the mixture was stirred for 5 min, the layers were separated. The aqueous layer was extracted with CH_2Cl_2 and the combined CH_2Cl_2 extracts were washed with water and dried ($MgSO_4$). The solvent was removed and the crude *cis*-dienone complex was dissolved in 25 ml of 1 *M* sodium methoxide in methanol and stirred at room temperature for 3 h in order to cause isomerization to the *trans*-dienone complex. The methanol solution was poured into water and the solution extracted with CH_2Cl_2. The dried organic extracts were concentrated and the residue chromatographed over Al_2O_3 (ether) to yield 1.69 g of *trans*-1,3-heptadien-5-oneiron tricarbonyl. The ketone was dissolved in 20 ml of methanol and 0.40 g (105 mmol) of $NaBH_4$ was added over a period of 15 min. After a further 15 min, the solution was poured into water and extracted with ether. The product was purified by chromatography and distilled (92—94°C/0.4 mmHg) to yield 0.90 g (23%) of the desired product as a pale yellow liquid. Alcohols XXIc (24%), XXId (16%), and XIIIb (5%) were prepared by identical procedures.

Typical procedure for preparation of pentadienyliron tricarbonyl cations and their reaction with water

1-Isopropylpentadienyliron tricarbonyl fluoroborate (XIXc). Alcohol XXIc (0.73 g, 2.7 mmol) was dissolved in 2 ml of acetic anhydride. A solution of 0.95 g (4.3 mmol) of 40% fluoroboric acid and 2 ml of acetic anhydride was prepared (caution) with stirring at 5—10°C. The alcohol was then added slowly to the stirred solution keeping the temperature at 5—10°C throughout the addition. The solution was allowed to stir for 30 min following the addition and then poured into 30 ml of ether. The precipitated product (0.62 g, 67%) was isolated by filtration, washed with ether and air dried. The cation (0.55 g) was added slowly to 700 ml of H_2O with vigorous stirring. The clear solution turned milky and after being stirred for 1 h was extracted with ether. The ether extracts were concentrated and the residue (0.31 g, 71%) analyzed by NMR. If desired the alcohol can be purified by chromatography over deactivated Al_2O_3 with ether serving as the eluting agent.

Acknowledgment

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