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CHEMISTRY OF (CYCLOHEPTATRIENONE)TRICARBONYLIRON AND (CYCLOHEPTADIENONE)TRICARBONYLIRON IN HIGHLY ACIDIC MEDIA

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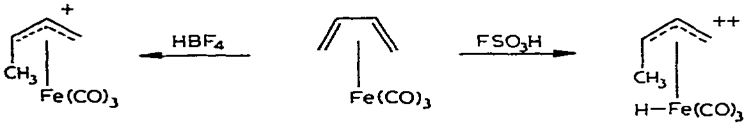
SUMMARY

In trifluoroacetic acid, protonation of (2, 3, 4, 5-*tetrahapto*-cycloheptatrienone)-tricarbonyliron is stereoselective and occurs from the *exo* side of the ring at a coordinated double bond [C(2)]. In sulfuric acid, the protonation is non-stereoselective and probably occurs from either the *exo* or the *endo* side of the ring. Hydride transfer from triethylsilane to the protonated species occurs from the *exo* side of the ring and affords (2,3,4,5-*tetrahapto*-cycloheptadienone)tricarbonyliron. Protonation of this dienone–$Fe(CO)_3$ complex in either trifluoroacetic or sulfuric acid occurs at the oxygen atom of the ketone group.

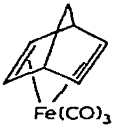
INTRODUCTION

Many π-bonded organo–transition metal complexes suffer protonation in strong acid to give stable cations[1]. (Butadiene)tricarbonyliron (I) is converted to the (π-*anti*-methallyl)tricarbonyliron cation (II) in fluoroboric acid[2] and to the diprotonated species (III) in fluorosulfonic acid[3].



(II) (I) (III)

(Norbornadiene)tricarbonyliron (IV) in contrast to (I), undergoes protonation at iron to give (V), rather than at carbon to give the homoallylic cation (VI)[4]. Transition metal



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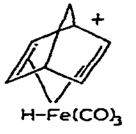

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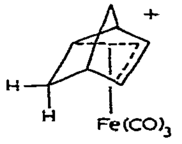

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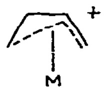

(VII)

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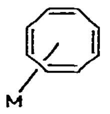
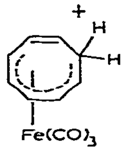
complexes such as (VII), containing the simplest homoallylic cation, are presently unknown. At −120° protonation of (cyclooctatetraene)tricarbonyliron (VIIIa) affords the (cyclooctatrienyl)tricarbonyliron cation (IX)[5]. At higher temperatures (IX) undergoes electrocyclic ring closure to give the homotropylium–$Fe(CO)_3$ cation (Xa)[5,6]. The corresponding ruthenium complex of cyclooctatetraene (VIIIb) is also converted to a homotropylium type complex (Xb) in sulfuric acid, but this, on standing, undergoes an isomerization reaction to give a cation whose NMR spectrum is consistent with either of the structures shown for (XIa)[7]. In sulfuric acid, cyclooctatetraene–$Os(CO)_3$ forms a mixture of (Xc) and (XIb)[7]. In contrast to the iron triad complexes, (cyclooctatetraene)tricarbonylmolybdenum and (cyclooctatetraene)tetracarbonylmolybdenum [(VIIId)[8] and (VIIIe)[9]] afford the homoconjugated cation (XII) on protonation. Thus it appears that the electronic requirements of the metal strongly influence the structure of the cationic ligand obtained in the protonation reactions.



(VIII)

a $M{=}Fe(CO)_3$ c $M{=}Os(CO)_3$
b $M{=}Ru(CO)_3$ d $M{=}Mo(CO)_3$
e $M{=}Mo(CO)_4$



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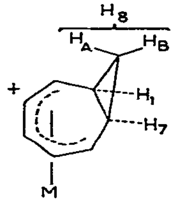
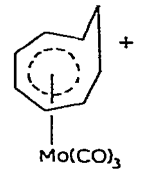


(X)

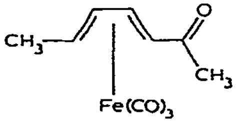
(XI)

a $M{=}Ru(CO)_3$
b $M{=}Os(CO)_3$

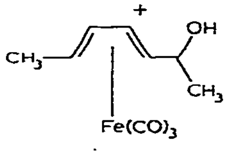


(XII)

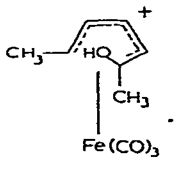
(Dienone)tricarbonyliron complexes have also been studied in strongly acidic media. Protonation of (*trans,trans*-3, 5-heptadien-2-one)tricarbonyliron (XIII) occurs at oxygen to give (XIV) which isomerizes to (XV) on standing[10].



(XIII)



(XIV)



(XV)

As part of an effort to explore the properties and chemical reactions of highly reactive neutral and cationic organic molecules stabilized by coordination to transi-

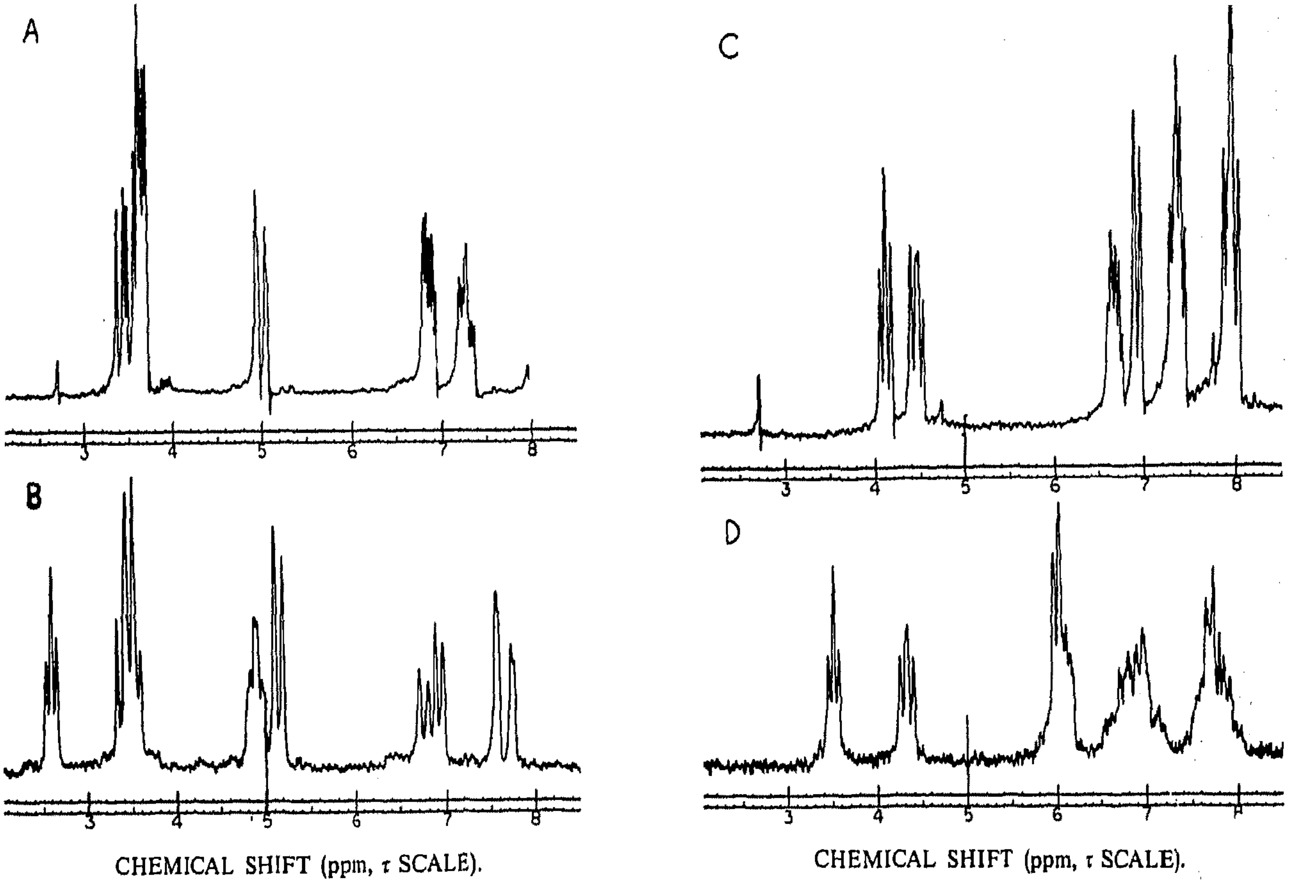


Fig. 1. NMR spectra of: (A) (cycloheptatrienone)tricarbonyliron (XVIa) in $CDCl_3$; (B) (cycloheptatrienone)-tricarbonyliron (XVIa) in CF_3COOH; (C) (cycloheptadienone)tricarbonyliron (XVIIa) in $CDCl_3$; (D) (cycloheptadienone)tricarbonyliron (XVIIa) in CF_3COOH.

tion metals, we undertook a study of (cycloheptatrienone)tricarbonyliron (XVI) and (cycloheptadienone)tricarbonyliron (XVII) in highly acidic media*.

RESULTS

Tropone–Fe(CO)$_3$ (XVIa) was prepared in 62% yield from diiron enneacarbonyl and tropone. Previously, (XVIa) had been obtained in 28% yield from the reaction of acetylene with diiron enneacarbonyl[12] and in 7.4% yield by refluxing a benzene solution of tropone and triiron dodecacarbonyl[13].

The NMR spectrum of (XVIa) is shown in Fig. 1A.** Assignment (Fig. 2) of the low-field pair of doublets at τ 3.44 to H(6) coupled to both H(7) (J 10.8 Hz) and H(5) (J 8.0 Hz) is consistent with the chemical shifts observed in other dienones and trienones[10,14].

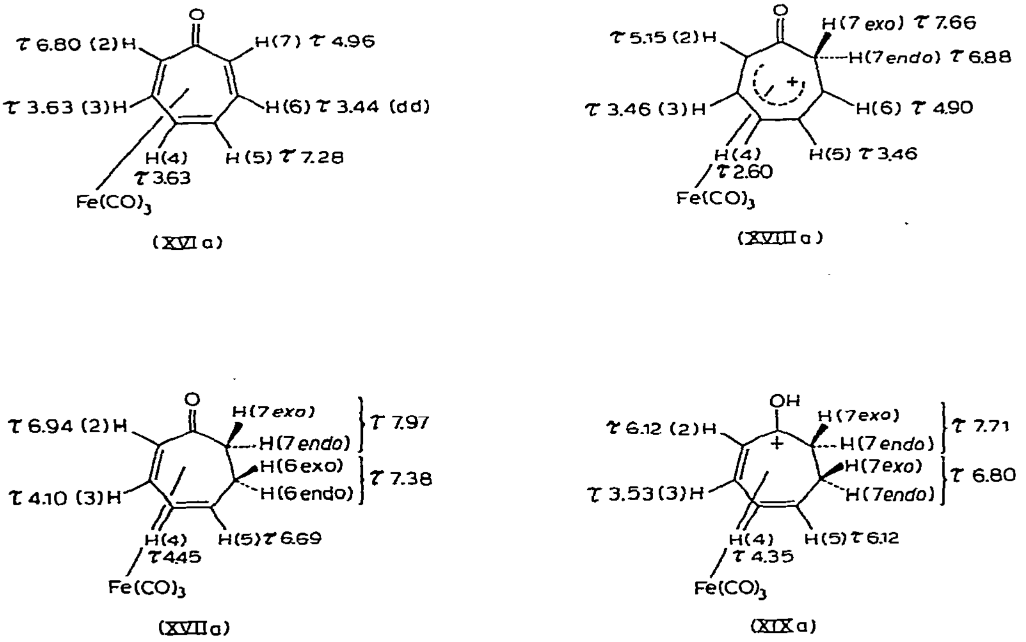


Fig. 2. NMR chemical shift assignments for compounds (XVIa), (XVIIa), (XVIIIa), and (XIXa).

Since protons on the central carbons of diene–Fe(CO)$_3$ complexes generally appear at lower field than those on terminal carbons[15], the multiplet at τ 3.63 is assigned to H(3) and H(4). H(3) is virtually coupled[16] to H(5) and H(4) is virtually coupled to H(2). In the d_2-derivative (XVIb), the multiplet at τ 6.80 H(2) and the doublet at τ 4.96 H(7) disappear, H(3) and H(4) appear as a doublet with virtual coupling

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* Presented in part at the Southeast-Southwest Regional Meeting of the American Chemical Society. New Orleans, La., December 1970, Abstr. No. 327. A preliminary report of a similar study on (XVI) has recently appeared[11].

** Signal assignments have not been reported in detail previously[13].

between H(3) and H(5) and an observed value for $J(4, 5)$ of 5.0 Hz. H(5) appears as a quintet (pair of overlapping triplets) $J(5,4\text{–}3)$ 5.0 Hz and $J(5, 6)$ 8.0 Hz.

On treatment of (XVIa) with either sulfuric acid or trifluoroacetic acid (Scheme 1) a deep red solution was obtained having the NMR spectrum shown in Fig. 1b. We assign structure (XVIIIa) to the cation produced in the above media for the following reasons. In trifluoroacetic acid-*d* the doublet at τ 7.66 (J 17 Hz) disappears and the quartet at τ 6.88 collapses to a doublet (J 8.2 Hz). Thus the chemical shift of the proton derived from the acid is in the region normally associated with hydrogen attached to saturated carbon[17] and the coupling constant agrees with that expected for geminal protons[17]. The absence of signals at high field (τ 15–30)[4,18] suggests that protonation does not occur at iron. Protonation at oxygen also seems unlikely since the coupling constant for the proton derived from the acid is several times larger than that expected for a proton on oxygen separated from its nearest neighbor by four bonds. Tropone–$Fe(CO)_3$ (XVIa), recovered in 50% yield from trifluoroacetic acid-*d* by neutralizing the acidic solution with potassium carbonate, was shown by mass spectrometry to be devoid of deuterium. Thus, incorporation of deuterium into (XVIa) does not occur in trifluoroacetic acid-*d*.

In contrast to the above result, the signals at τ 6.88, τ 7.66 and τ 5.15 all disappear when (XVIa) is allowed to stand over night in sulfuric acid-d_2. Neutralization of the latter solution with a slurry of potassium carbonate in methylene chloride afforded 2,7-tropone-d_2–$Fe(CO)_3$ (XVIb). This result facilitated the assignment of H(2) in (XVIIIa) to the doublet at τ 5.15. Assignments for the two protons at C(7) can also be made if the following two assumptions are valid: (*a*) the structure of tropone–$Fe(CO)_3$ (XVIa) in solution is identical to that in the crystalline state; (*b*) inversion of the cycloheptatrienone ring does not occur during the protonation step.

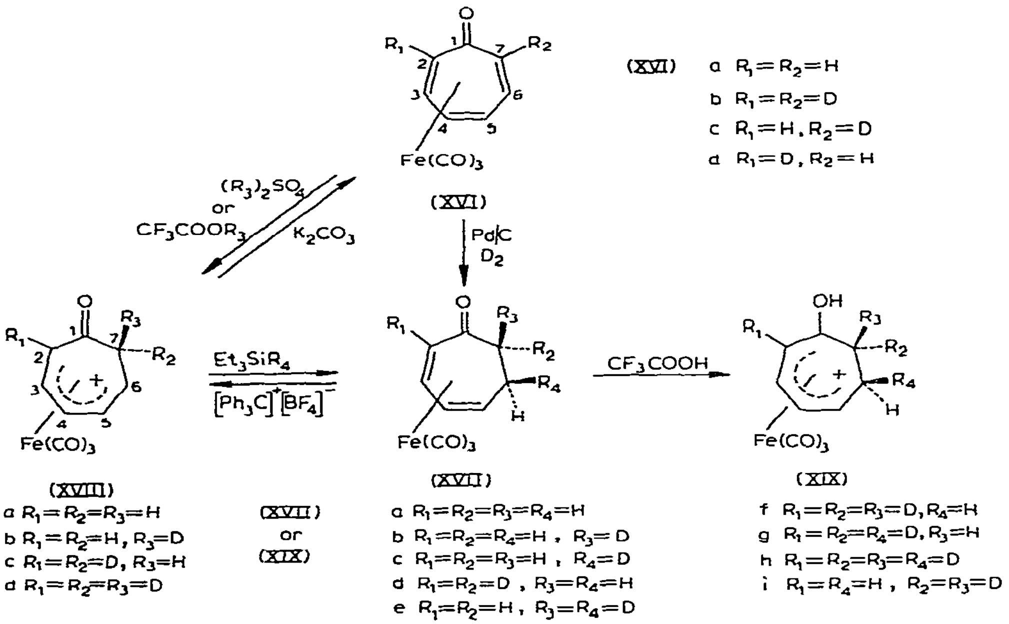
An X-ray structure determination on (XVIa) indicates that the $Fe(CO)_3$ group is bonded to only four of the carbon atoms in the cycloheptatrienone ring, C(2)–C(3)–C(4)–C(5)[19]. As a consequence of this interaction, the tropone ring becomes distinctly nonplanar. The remaining carbon atoms, C(1)–C(6)–C(7), are bent away from the metal atom and exist in a plane that makes a dihedral angle of 47° with the plane containing C(2)–C(3)–C(4)–C(5).

On protonation of (XVIa), C(6) should become ca. coplanar with the diene–$Fe(CO)_3$ group and both C(1) and C(7) should remain above the plane of the other ring atoms. In this conformation the chemical shift (τ) of H(7-*exo*) should be greater than that of H(7-*endo*) since the *exo* hydrogen experiences shielding from the π-electrons of both the carbonyl group and the diene–$Fe(CO)_3$ moiety. H(7-*exo*) should also appear as a doublet, J(7-*exo*, 7-*endo*)$\approx$15 Hz[17]. Coupling between H(7-*exo*) and H(6) would not be expected since a model of (XVIIIa) indicates that the dihedral angle between the two hydrogens is almost 90°[20]. The dihedral angle between H(7-*endo*) and H(6) is ca. 30°, however, and H(7-*endo*) should, therefore, appear as a pair of doublets. The above reasoning leads to the assignment of H(7-*exo*) in (XVIIIa) to the doublet at τ 7.66, J(7-*exo*, 7-*endo*) 17 Hz and H(7-*endo*) to the quartet (pair of doublets) at τ 6.88, J(7-*exo*, 7-*endo*) 17 Hz, J(7-*endo*, 6) 8.1 Hz.

Assignments for the remaining protons in the cation (XVIIIa) were made from the simplified NMR spectrum of the d_3-derivative, (XVIIId)/(D_2SO_4). In the spectrum of (XVIIId) the broad triplet (pair of overlapping doublets) at τ 4.90 (Fig. 1b) appears as a sharp doublet and is, therefore, assigned to H(6), $J(5,6)$ 8.2 Hz. The quartet (four pairs of overlapping doublets) at τ 3.46 appears as a doublet at τ 3.28 and a triplet (pair of overlapping doublets) at τ 3.48 and is assigned to H(3), J(2,3) 9.6 Hz, J(3,4) 7.2 Hz and H(5), J(4, 5) 5.8 Hz, J(5, 6) 8.2 Hz. The triplet (pair of overlapping doublets) at τ 2.60 remains a triplet and is assigned to H(4), J(3,4) 7.2 Hz, J(4, 5) 5.8 Hz.

Additional support for the assignment of structure (XVIIIa) to protonated (XVI) was obtained by reducing the cation in a solution of trifluoroacetic acid with triethylsilane. The yellow solid obtained in 80% yield from this reaction possessed physical properties (m.p. and IR spectrum) identical to those reported for dihydrotropone–Fe(CO)$_3$ (XVIIa). The NMR (Fig. 1c) and mass spectrum of the isolated compound were also consistent with structure (XVIIa). Unambiguous NMR assignments (Fig. 2) for the protons in (XVIIa) were made from spectra of the deuterated derivatives (XVIIb)–(XVIIh). The latter compounds were prepared by treating cycloheptatrienone–Fe(CO)$_3$ (XVIa) with various combinations of deuterated and undeuterated acids and silanes as shown in Scheme 1.

SCHEME 1



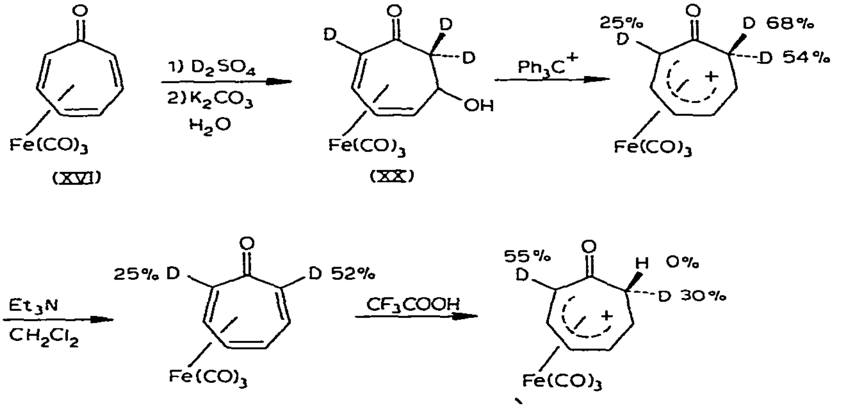
In the NMR spectrum of the d_3-derivative (XVIIf); the two-proton signal at τ 7.97 and the one-proton signal at τ 6.94 are both absent and are, therefore, assigned to H(7-*endo*, 7-*exo*) and H(2) respectively; the triplet (pair of overlapping doublets) at τ 4.10 collapses to a doublet and is assigned to H(3), J(2,3) 6.6 Hz, J(3,4) 5.5 Hz; the quartet (pair of doublets) at τ 4.45 remains and is assigned to H(4), J(3, 4) 5.5 Hz, J(4, 5) 8.1 Hz; the two-proton quartet at τ 7.38 collapses to a broad doublet and is assigned to H(6-*exo*, -*endo*) virtually coupled to H(5), J(5,6) 4.0 Hz; H(5) appears as a quintet (pair of overlapping triplets) at τ 6.69 J(5,6) 4.0 Hz, J(4,5) 8.1 Hz.

In the d_1-derivative (XVIIc), H(5) appears as a sharp doublet at τ 6.69 J(4, 5)

8.1 Hz, J(5, 6-*endo*) $\approx$ 0. Therefore, H(5) does not couple to H(6-*endo*) and the observed coupling in (XVIIa) J(5, 6) 4.0 Hz represents the average of J(5, 6-*endo*) $\approx$ 0 and J-(5, 6-*exo*) $\approx$ 8.0. A similar situation exists for protons H(7-*endo*) and H(7-*exo*). In (XVIIc) the two-proton signal at τ 7.97 appears as a doublet; J(6-*endo*, 7-*endo*-*exo*) 9.2 Hz and the quartet τ 7.38 assigned to H(6-*endo*) appears as a triplet J(6-*endo*, 7-*endo*-*exo*) 9.2 Hz. Thus H(6-*endo*) is virtually coupled to H(7-*endo*, 7-*exo*) and the observed coupling constant (9.2 Hz) represents the average of J(6-*endo*, 7-*endo*) $\approx$ 0 and J(6-*endo*, 7-*exo*) $\approx$ 18 Hz. The spectrum of (XVIIe) confirms the above assignments since H(5) appears as a doublet J(4, 5) 8.1 Hz, J(5, 6-*endo*) $\approx$ 0 and H(6-*endo*) and H-(7-*endo*) appear as broad singlets J(6-*endo*, 7-*endo*) $\approx$ 0.

As indicated earlier when (XVIa) was allowed to stand in sulfuric acid-d_2 for several hours, the NMR signals corresponding to H(7-*exo*), H(7-*endo*) and H(2) disappeared completely. Spectra recorded at frequent intervals during the exchange process indicated that the rate of deuterium incorporation into (XVIIIa) was several times greater at C(7) than at C(2). Termination of the exchange process at an early stage by quenching the reaction mixture with an aqueous solution of sodium carbonate afforded a 70% yield of d_2- and d_3-6-hydroxycycloheptadienone–Fe(CO)$_3$ (XX) (Scheme 2). Treatment of (XX) with triphenylmethyl fluoroborate in methylene chloride gave a 78% yield of d_2- and d_3-(XVIII). The NMR spectrum of this material (liquid SO$_2$) indicated that the extent of deuterium incorporation was 68% at the 7-*exo*, 54% at the 7-*endo* and 25% at the 2 positions. Treatment of this mixture with triethylamine in methylene chloride afforded an 80% yield of d_1- and d_2-(XVI). Deuterium incorporation at the 2 and 7 positions in the latter mixture was found to be 25% and 52% respectively. When the NMR spectrum of this material was recorded in trifluoroacetic acid, the extent of deuterium incorporation was found to be 30% at the 7-*endo*, ~0% at the 7-*exo* and 55% at the 2 positions. Thus protonation in trifluoroacetic acid occurs stereoselectively from the *exo* side of the ring at a coordinated double bond.

SCHEME 2



Additional information concerning the stereochemistry of the protonation-reduction sequence using trifluoroacetic acid-*d* and triethylsilane-*d* was obtained from the catalytic reduction of (XVIa) over Pd/C catalyst at 167 atm of deuterium gas.

A 30% yield of a compound having an NMR spectrum identical to that of (XVIIe) was obtained in this experiment. Thus if catalytic reduction proceeds by the normal *cis* addition mechanism, introduction of two deuterium atoms by the deuteration/hydride reduction sequence must also occur in a *cis* manner.

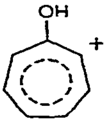
Treatment of (XVIIe) with triphenylmethyl fluoroborate in methylene chloride afforded (XVIIIb) which was converted to tropone–$Fe(CO)_3$ (XVIa) by neutralizing a trifluoroacetic acid solution of (XVIIIb) with potassium carbonate. A mass spectrum of recovered (XVIa) showed that it did not contain any deuterium. Thus, the above oxidation sequence is stereoselective and removes the same two hydrogen atoms introduced into (XVI) by the protonation/hydride reduction procedure.

Prolonged treatment with sodium tert-butoxide in tert-butyl alcohol-*d* converted (XVIIa) to a monodeuterated derivative having an NMR spectrum identical to that of (XVIIb). As expected, oxidation of this material with triphenylmethyl fluoroborate and potassium carbonate (Scheme 1) produced (XVI) which was devoid of deuterium. Thus in the base catalyzed exchange reaction the 7-*exo* hydrogen is removed stereoselectively.

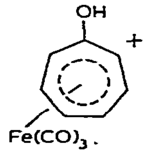
In trifluoroacetic or sulfuric acid, (XVIIa) is protonated at oxygen to give cation (XIX). Deuterium incorporation into (XIX) does not occur when either trifluoroacetic acid-*d* or sulfuric acid-d_2 is employed as a reagent*. The NMR spectrum of XIXa (Fig. 1d) is almost identical to that of (XVIIa) except that all of the signals are shifted to lower field, H(2) is deshielded more than H(5) and the two corresponding signals have the same chemical shift. Chemical shift assignments for the protons in (XIXa) are shown in Fig. 2. The following coupling constants were determined: $J(2,3)$ 5.6 Hz; $J(3,4)$ 6.0 Hz; $J(4,5)$ 8.4 Hz; J(6-*endo*, 6-*exo*) 16 Hz; J(6-*endo*, 7-*endo*) 4.0 Hz. No signal was observed for the OH proton, presumably because it undergoes rapid exchange with solvent. In (XIXe) the signals at τ 6.98 and τ 7.17 appear as broad doublets J(6-*endo*, 7-*exo*) 4 Hz, J(5, 6-*endo*) ≈ 0.

DISCUSSION

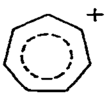
Cycloheptatrienone is protonated at oxygen in ethereal hydrochloric acid to give the 6-π electron hydroxytropylium cation (XXI)[21]. Acyclic dienone–$Fe(CO)_3$ complexes also suffer protonation at oxygen[10]. In contrast we find that tropone–$Fe(CO)_3$ (XVIa) acquires a proton at carbon to give (XVIIIa) in either trifluoroacetic or sulfuric acid. This result suggests that (XVIIIa) is more stable than (XXII) and is consistent with the observation that the pK_{R^+} for the tropylium cation (XXIII) and the cycloheptadienyl–$Fe(CO)_3$ cation (XXIV) are identical (4.7) and greater than that of the tropylium–$Fe(CO)_3$ cation (4.5)[22].



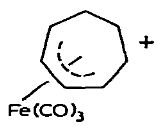
(XXI)



(XXII)



(XXIII)



(XXIV)

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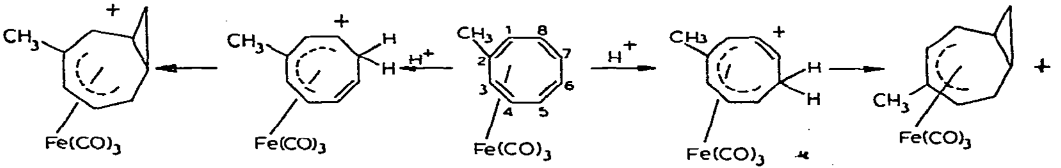
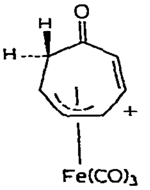
* Similar results were obtained by Clinton and Lillya in their study of protonated acyclic dienone–$Fe(CO)_3$ complexes[10].

Experiments with deuterated derivatives of (XVI) (Scheme 2) indicate that in trifluoroacetic acid the protonation reaction is also stereoselective and occurs from the *exo* side of the ring at a coordinated double bond. In contrast to this result, Brookhart and Davis find that (1,2,3,4-*tetrahapto*-2-methylcyclooctatetraene)tricarbonyl iron (XXV) suffers stereoselective protonation in fluorosulfonic acid from the *exo* side of the eight-membered ring at an uncoordinated double bond, C(6) or C(7) in (XXV)[23].



(XXVIIb) 66%   (XXVIb) 66%   (XXV)   (XXVIa) 33%   (XXVIIa) 33%

X-ray data indicate that the iron tricarbonyl complexes of the cycloheptatrienone[19] and cyclooctatetraene[24] ring systems possess similar geometries. In (XVIa) the plane defined by the four carbon atoms of the diene–Fe(CO)$_3$ moiety makes a dihedral angle of 47° with the plane occupied by C(1)–C(6)–C(7)[19]. In (VIIIa) the dihedral angle between the two planes containing C(1)–C(2)–C(3)–C(4) and C(5)–C(6)–C(7)–C(8) is 41° [24]. Thus, the reason for the protonation occurring at different sites in (XVIa) and (XXV) is probably not related to geometric considerations.



(XXVIII)

Protonation at an uncoordinated double bond in (XXV) leads directly to the observed pentadienyl cations and involves minimal changes in the position of the nuclei. In contrast, formation of (XVIIIa) by protonation at C(2) of (XVI) requires that the iron–tricarbonyl group migrate to the free double bond during the course of the reaction. Since energy is generally required to move nuclei from their stable ground-state equilibrium positions, it is not surprising that protonation of (XXV) occurs at C(6) and C(7). In (XVI) the electron density in the free double bond is somewhat depleted as a result of conjugation with the carbonyl group and protonation occurs preferentially at the terminal carbon of the diene–Fe(CO)$_3$ moiety. Presumably formation of (XVIIIa) by this pathway proceeds through the relatively stable π-allyl structure (XXVIII).

Why the protonation occurs stereoselectively from the *exo* rather than the *endo* side of the coordinated double bond is not clear. On coordination of an olefin to a transition metal the electron density in the π-orbital of the olefin is reduced on the *exo* side and becomes concentrated in the bonding region between the organic ligand and the metal[25]. All other things being equal, protonation should take place at the site of highest electron density and, therefore, occur from the *endo* side of (XVIa). That this is not the observed result suggests that electron density is not the only factor controlling the stereochemistry of the protonation.

Alternately, we suggest that perhaps the stereochemistry of protonation at metal–olefin-π-bonds is influenced by the nature of the interaction between the incoming electrophile and the highest occupied molecular orbital in the complex. For a diene–$Fe(CO)_3$ compound this latter orbital would result from a combination of the first antibonding orbital of the diene with a filled orbital of appropriate symmetry on the metal and thus increase the electron density on both the *exo* and *endo* sides of the terminal carbon atoms of the diene unit[26]. Protonation from the *exo* side of C(2) in (XVI) would be favored if the three-centered bond formed in the transition state for protonation from the front side of the iron–carbon-π-bond on the *endo* side of the ligand was less stable than the transition state involving a back side attack of the electrophile from the *exo* side of the ligand, *trans* to the metal–carbon bond. Theoretical calculations on these two pathways for the protonation of a simple three-centered, metal–olefin bond would be of interest.

To the best of our knowledge, the protonation of (XVIa), (XXV)[23] and the addition of hydrochloric acid to (butadiene)tricarbonyliron (I)[27]* in a nonpolar medium are the only examples in which electrophilic addition is postulated to occur from the *exo* side of a π-complexed organic ligand**. Evidence supporting selective attack from the *endo* side of a coordinated π-olefin ligand has been obtained for the protonation of cyclooctatetraene–$Mo(CO)_3$ (VIIId)[8], –$Mo(CO)_4$ (VIIIe)[9] and cyclohexadiene–$Fe(CO)_3$ [3,27].

In contrast to the situation in trifluoroacetic acid, deuteration of (XVIa) in sulfuric acid-d_2 occurs from both the *exo* and *endo* sides of the molecule and is, therefore, non-stereoselective. Also, in sulfuric acid-d_2 but not in trifluoroacetic acid-*d*, the protons at C(7) and C(2) in (XVIIIa) undergo exchange for deuterium and the rate of this exchange process is several times faster at C(7) than at C(2). In fluorosulfonic acid-*d* deuteration is also non-stereoselective but deuterium exchange does not occur below $-14°$ [11]. At room temperature, in fluorosulfonic acid-*d*, H(7) and H(2) undergo slow exchange and again the deuterium incorporation is found to be more rapid at C(7) than at C(2)[11]. Eisenstadt and Winstein estimate that the rate of exchange in fluorosulfonic acid-*d* to be 2×10^{-4} sec^{-1} at C(7) and 8×10^{-6} sec^{-1} at C(2)[11].

The above results are consistent with the postulate that the rate of exchange is a function of acid strength as well as the strength of the corresponding conjugate

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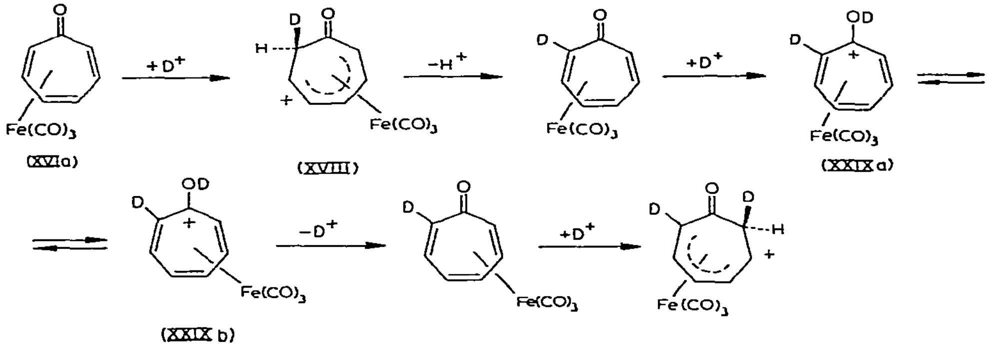
* Recently, Whitesides and Arhart[33] have obtained data which suggest that the mechanism proposed for this reaction[27] may not be correct. They have also demonstrated that cyclohexadiene–$Fe(CO)_3$ is protonated from the *endo* side of the organic ligand in CF_3COOH.

** Data in the literature also suggest that (cyclooctatetraene)tricarbonyliron (XVIIIa) is protonated from the *endo* side of the organic ligand[6]. We believe, however, that the literature assignments for protons H(8A) and H(8B) in (Xa)[5,6b,8] are in error and should be reversed. Signals for the two H(8) protons in (Xa) are observed at τ 8.47, $J(1.8)$ 4.5 Hz and τ 8.65, $J(1,8)$ 8 Hz. For adjacent protons on a cyclopropane ring, $J(cis)\approx 8$ Hz and $J(trans)\approx 4.5$[28]. Therefore, H(8A) should be assigned to the signal at τ 8.47 and H(8B) to the signal at τ 8.65. In the NMR spectrum of the monodeuterio derivative, obtained by treating (VIIIa) with sulfuric acid-d_2, the signal corresponding to the single proton at C(8) occurs at τ 8.59, $J(1,8)$ 7.9 Hz[6]. Thus, the proton derived from the acid becomes H(8A) in the (Xa) and, therefore, enters from the *exo* side of the cyclooctatetraene ligand.

base. The slow incorporation of deuterium in fluorosulfonic acid-*d* is probably due to the inability of the weak conjugate base, FSO_3^-, to deprotonate (XVIIIb) efficiently[11].

Several explanations can be offered to account for the effect of acid strength on the protonation and exchange reactions. Only two of these, however, are consistent with the observation that the low-energy pathway for protonation in trifluoroacetic acid involves addition of a proton to the coordinated double bond from the *exo* side of C(2). One possibility is that in sulfuric acid-d_2, but not in the weaker trifluoroacetic acid-*d*, deuteration occurs from both the *exo* and the *endo* sides of the coordinated double bond and also to a small extent at the oxygen atom of the ketone group. Rapid incorporation of deuterium at C(7) of (XVIIIa) would result from the first of these paths and slow deuteration of 2-d_1-(XVIa) at oxygen followed by isomerization of (XXIXa) to its valence tautomer (XXIXb) would facilitate incorporation of deuterium at C(2) of (XVIIIa) (Scheme 3)*. NMR experiments in FSO_3H/SO_2 and $FSO_3H/SO_2/SbF_5$ down to −70° failed to detect any (XXIX). Thus if (XXIX) is an intermediate in the exchange reaction, it must be present in low concentration.

SCHEME 3



An alternate explanation of the above results assumes that in the strong acid, sulfuric acid-d_2, deuteration occurs from the *exo* and the *endo* sides of the ring at both the coordinated and the uncoordinated double bonds. According to this mechanism, deuterium is incorporated more slowly at C(2) than at C(7) in (XVIII) because the energy of activation for deuteration (dedeuteration) from the least favorable side of the uncoordinated olefin linkage is higher than that for deuteration (dedeuteration) from the *endo* side of C(2) (Scheme 4)**.

In summary, NMR data indicate that the three acids, CF_3COOD, D_2SO_4, and FSO_3D, all affect the complete conversion of (XVIa) to its conjugate acid (XVIII). Furthermore, the rate of incorporation of deuterium into positions in (XVIII) other than that favored in the initial attack of D^+ increases as the rate of deprotonation (rate determining step) increases and increases as the regio- and stereoselectivity of the

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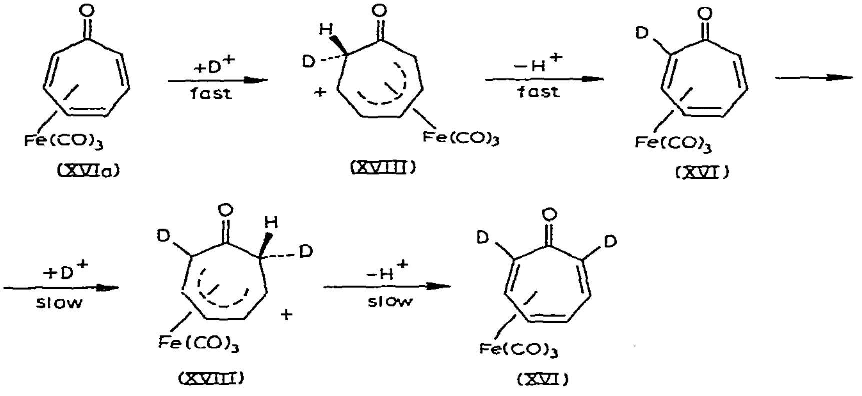
* Rapid valence tautomerism has also been postulated for the unsubstituted tropylium-$Fe(CO)_3$ cation in order to explain why only a single peak is observed in the NMR spectrum of this species[22].

** Another mechanism involving protonation at the oxygen of the ketone group as well as at carbon to give a dication has been suggested previously[11].

SCHEME 4



deuteration and dedeuteration reactions decrease.

When (XVIIIa), containing deuterium to the extent of 68%, 54% and 25% at C(7-*exo*), C(7-*endo*) and C(2) respectively was treated with an excess of triethylamine in methylene chloride, (XVI) containing deuterium to the extent of 52% at C(7) and 25% at C(2) was produced (Scheme 2). If deuterium abstraction had occurred by the reverse of the favored protonation pathway, the deuterium percentage at C(2) and C(7) in (XVI) should have been just the opposite, 25% at C(7) and 52% at C(2). That this is not the observed result provides additional support for the intermediacy of the π-allyl structure (XXVIII) in the protonation of (XVI). As long as the composition of an equilibrium mixture of (XVIIIa) and (XXVIII) strongly favors (XVIII), deuterium abstraction by triethylamine will only occur from (XVIII) and, therefore, afford the observed results.

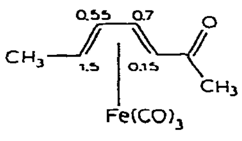
In addition to the protonation of (XVIa) in trifluoroacetic acid, we have also observed several other stereoselective reactions on compounds (XVI), (XVII) and (XVIII). On treatment with triethylsilane-*d*, (XVIIIb) is converted to the *cis*-d_2 derivative (XVIIe). Catalytic reduction of (XVIa) with D_2 at 167 atm also affords (XVIIe). Thus the reduction of (XVIa) by catalytic hydrogenation as well as by the protonation/hydride transfer sequence proceeds by *cis* addition of hydrogen from the *exo* side of the cycloheptatrienone ring. The two-step oxidation of (XVIIa) to (XVIa) using triphenylmethyl fluoroborate and potassium carbonate (Scheme 1) is also stereoselective and involves *cis* elimination of the two *exo* hydrogens at C(6) and C(7) respectively.

On prolonged treatment with sodium tert-butoxide in tert-butyl alcohol-*d*, (XVIIa) incorporates one deuterium at the C(7 *exo*) position. This result suggests that the structure of (XVIIa) has C(1), C(6) and C(7) located above the plane defined by the diene–$Fe(CO)_3$ group. Models show that in this conformation only the 7-*exo* hydrogen is coplanar with the π-orbital of the carbonyl group. As a consequence, continuous overlap of the developing carbanion with the π-orbital of the carbonyl group can occur only if the 7-*exo* and not the 7-*endo* hydrogen is abstracted by the tert-butoxide anion.

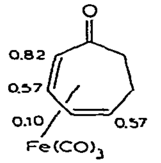
In trifluoroacetic and sulfuric acids, (XVII) is protonated at oxygen to give (XIX). Incorporation of deuterium does not occur when the corresponding deuterio

TABLE 1

$\Delta\tau$ VALUES FOR DIENONES[a]



(XIII)



(XVII)

[a] $\Delta\tau = \tau(CDCl_3) - \tau(H_2SO_4)$

acids are employed. Protonation of the acyclic dienone–$Fe(CO)_3$ complex (XIII) also takes place at oxygen and causes a large downfield shift of the signal corresponding to H(6) in (XIV) relative to the other protons on the organic ligand (Table 1). The chemical shift of H(3) is only slightly affected on protonation of (XIII). These observations are consistent with, but do not require, the postulate that the $Fe(CO)_3$ group moves toward the electron deficient center at C(2) in (XIV) and thus causes an increase in the shielding of H(3) and a decrease in the shielding of H(6)[10]. As might be expected for a cyclic system in which all carbon atoms of the pentadienyl cation can be bonded directly to the transition metal, no unusual changes in the chemical shift values ($\Delta\tau$) occur on conversion of (XVII) to (XIX). H(2) is deshielded somewhat more than expected but this is probably due to a change in the hybridization at C(2) (more sp^2 character) on going from (XVII) to (XIX). Otherwise, the $\Delta\tau$ values (Table 1) all show the alternation predicted by VB and MO theory.

EXPERIMENTAL

General

NMR data were obtained on a Varian Associates HA-100 spectrometer using tetramethylsilane as the internal standard. NMR samples in deuteriochloroform were passed through a fine filter (Metricel Alpha 8, pore size 0.2μ or Millipore–Mitex (Teflon) pore size $5.0\,\mu$) in a Swinney adapter to remove paramagnetic particles. Mass spectra were obtained on Hitachi–Perkin–Elmer RMU-6E or AEI MS-902 spectrometers. The latter instrument is equipped with a dual electron impact/chemical ionization (EI/CI) source manufactured by Scientific Research Instruments Corporation, Baltimore, Md. Infrared spectra were recorded on a Perkin–Elmer 257 grating spectrophotometer and were calibrated against the 1601 cm^{-1} band of polystyrene. Melting points were determined on a Thomas–Hoover capillary-melting point apparatus and are uncorrected. Sulfuric acid-d_2 (98% in D_2O) was obtained from Diaprep Inc., Atlanta, Georgia. Trifluoroacetic acid was purchased from PCR, Inc., Gainesville, Florida. Silica Gel PF-254 (neutral) obtained from the EM Reagent Div. of Brinkman Instruments, Inc., was employed in all TLC experiments.

(2,3,4,5-*tetrahapto-Cycloheptatrienone*)*tricarbonyliron* (*XVIa*)*

A slurry of cycloheptatrienone[29] (0.9 g, 8.5 mmol) and diiron enneacarbonyl[30]

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* For a discussion of nomenclature see ref. 31.

(4.0 g, 11 mmol) in 30 ml of anhydrous diethyl ether was heated at reflux in the absence of light under nitrogen for 12 h. Filtration of the reaction mixture and evaporation of the solvent afforded an oily residue that was dissolved in hexane. Crude (XVIa) precipitated from the hexane solution at $-78°$. Sublimation of this material at 46°/0.2 mm gave 1.31 g (62%) of pure (XVIa) as an orange solid: m.p. 76.5–77.5° [lit. 63.5–64.5° and 83–84°]; IR (KBr) 2066, 2008, 1992 (C≡O) and 1637 (C=O) cm^{-1}; mass spectrum (70 eV) *m/e* (rel. intensity) 246 (1), 218 (8), 190 (12), 162 (18), 106 (42), 78 (100).

(2,3,4,5-*tetrahapto-Cycloheptadienone*)*tricarbonyliron* (*XVIIa*)

Triethylsilane (0.8 ml. 5.0 mmol) was added to a stirred solution of (XVI) (615 mg, 2.5 mmol) in 5 ml of trifluoroacetic acid[34a]. After 5 min the solution was diluted with 15 ml of methylene chloride and neutralized with solid potassium carbonate. Water (10 ml) was also added to facilitate complete neutralization of the reaction mixture. The methylene chloride layer was washed twice with a saturated solution of potassium carbonate, dried ($MgSO_4$) and filtered. Evaporation of the solvent at reduced pressure afforded a yellow solid which on TLC (diethyl ether/hexane, 2/1) and sublimation at 50°/0.2 mm gave 460 mg (75%) of (XVIIa): m.p. 105–106° [lit. 108–110°]; IR($CHCl_3$) 2060, 2000, 1990 (C≡O), 1653 (C=O) cm^{-1}; mass spectrum (70 eV) *m/e* 248 (13), 220 (35), 192 (45), 164 (100), 108 (30).

(2,3,4,5-*tetrahapto*-2,7-*Cycloheptatrienone*-d_2)*tricarbonyliron* (*XVIb*)

A solution of (XVIa) (200 mg, 0.8 mmol) in sulfuric acid-d_2 (1 ml) was stirred at room temperature for 15 h. The reaction mixture was diluted with methylene chloride (5 ml), neutralized with solid potassium carbonate, and filtered. Evaporation of the solvent at reduced pressure gave an orange solid which on TLC (diethyl ether/hexane, 2/1) and sublimation at 46°/0.2 mm afforded 50 mg (25%) of (XVIb). The isotopic purity of (XVIb) was found to be greater than 92% by mass spectrometry.

(2,3,4,5-*tetrahapto-6-exo-7-exo-Cycloheptadienone*-d_2)*tricarbonyliron* (*XVIIe*)

(*a*). The procedure was identical to that of (XVIIa) except that (XVIa) was dissolved in trifluroracetic acid-*d* and triethylsilane-*d* was employed as the reducing agent[34b].

(*b*). A mixture of (XVIa) (5.0 g, 20 mmol), hexane (75 ml), 10% Pd/C (1 g), and deuterium gas at 167 atm was heated at 40° for 66 h in a 150 ml autoclave. Filtration of the reaction mixture under N_2 followed by evaporation of solvent at reduced pressure gave an orange solid which was chromatographed under nitrogen on 100 g of Silica Gel (Brinkman Instruments, Inc., 70–325 mesh, ASTM) using benzene/diethyl ether (5/1) as the eluent. The compound contained in the first yellow band, presumably (3,4,5,6-*tetrahapto*-cycloheptadienone-d_2)tricarbonyliron, decomposed rapidly during evaporation of the solvent[12]. The second band afforded 3.27 g (66%) of (XVIa) on evaporation of the solvent. (Cycloheptadienone-d_2)tricarbonyliron (XVIIe) (1.5 g, 30%) was obtained from band three and purified further by sublimation at 50°/0.2 mm: m.p. 102–104°; mass spectrum (70 eV) *m/e* 250 (13), 222 (39), 194 (45), 166 (100), 110 (33). The isotopic purity of (XVIIe) was found to be greater than 96% by mass spectrometry.

(2,3,4,5-tetrahapto-2,-7exo, -7-endo-Cycloheptadienone-d_3)tricarbonyliron (XVIIf)

The procedure was identical to that described for the preparation of (XVIIa) except that (XVIa) (125 mg, 0.51 mmol) was dissolved in a mixture of trifluoroacetic acid-*d* (3.0 ml) and sulfuric acid-d_2 (0.5 ml).

(2,3,4,5-tetrahapto-6-exo-Cycloheptadienone-d_1)tricarbonyliron (XVIIc)

The procedure was identical to that of (XVIIa) except that triethylsilane-*d* was employed as the reducing agent.

(2,3,4,5-tetrahapto-2,-6-exo-7-exo,-7-endo-Cycloheptadienone-d_4)tricarbonyliron (XVIIh)

The procedure was identical to that of (XVIIf) except that triethylsilane-*d* was employed as the reducing agent.

Oxidation of (XVII) to (XVI)

A slurry of (XVIIa) (125 mg, 0.5 mmol) and triphenylmethyl fluoroborate[32] (490 mg, 1.5 mmol) in methylene chloride (5 ml) was stirred at room temperature for 24 h. Evaporation of the solvent at reduced pressure gave a solid residue which was dissolved in trifluoroacetic acid (3 ml). The resulting solution was diluted with methylene chloride (15 ml), neutralized with solid potassium carbonate and filtered. Evaporation of the solvent at reduced pressure afforded an orange solid that was purified by TLC (diethyl ether/hexane, 1/1) and sublimation at 46°/0.2 mm. The yield of (XVI) was 31 mg (25%).

Reaction of (XVIIa) with trifluoroacetic-d and sulfuric acid-d_2

A solution of (XVIIa) (60 mg, 0.26 mmol) in 0.4 ml of either trifluoroacetic-*d* or sulfuric acid-d_2 was monitored by NMR. Although deuteration of (XVIIa) occurred at oxygen in both of the above media, additional incorporation of deuterium was not observed over a 24 h period at room temperature.

Reaction of (XVIIa) with sodium tert-butoxide in tert-butyl alcohol-d

Cycloheptadienone–Fe(CO)$_3$ (XVIIa) (300 mg, 1.2 mmol) was added to a solution of sodium tert-butoxide in tert-butyl alcohol-*d* (prepared from sodium metal (33 mg, 1.5 mmol) in 8 ml of tert-butyl alcohol-*d*). The mixture was allowed to stand at room temperature for 3 h, acidified with dilute sulfuric acid-d_2, neutralized with solid potassium carbonate, filtered, and extracted with diethyl ether. The ether extracts were combined, dried ($MgSO_4$) and the solvent was then evaporated at reduced pressure. Sublimation of the residue afforded 246 mg (82%) of 7-*exo*-cycloheptadienone-d_1–Fe(CO)$_3$ (XVIIb) as a yellow solid. The isotopic purity of this material was found to be >92% by mass spectrometry.

(2,3,4,5-tetrahapto-6-Hydroxycycloheptadienone)tricarbonyliron (n.c.) (XX)

(Cycloheptatrienone)tricarbonyliron (910 mg, 3.7 mmol) was dissolved in 5 ml of CH_2Cl_2 and extracted into 3 ml of conc. sulfuric acid. After 15 min, the sulfuric acid solution was poured onto an excess of sodium carbonate (7.0 g, 60 mmol) and the resulting paste was diluted with CH_2Cl_2 (10 ml). Water (10 ml) was then added to the resulting mixture. When evolution of carbon dioxide ceased, 30 ml of CH_2Cl_2 was added to the mixture. The water layer was separated and extracted with CH_2Cl_2 (2 x 10 ml) and the combined CH_2Cl_2 extracts were washed with a saturated aqueous solution of sodium carbonate, dried ($MgSO_4$) and evaporated. The resulting yellow residue was triturated with 5 ml portions of CH_2Cl_2 until TLC indicated that all of the cycloheptatrienone–$Fe(CO)_3$ had been removed and only the desired product (XX) remained in the residue. Preparative TLC of the methylene chloride extracts afforded (XVIa) (60 mg) and (XX). This latter material (XX) was combined with the methylene-chloride-insoluble residue to give 700 mg (71 %) of (XX). Sublimation of this material at 120°/0.7 mm afforded an analytically pure sample: m.p. 165–167° (N_2); NMR ($CDCl_3$) τ 4.16 (t, 1), 4.41 (t, 1), 5.22 (s, 1, OH), 5.74 (m, 1), 6.68 (m, 2), 7.58 (m, 1), 7.82 (m, 1); mass spectrum (70 eV) *m/e* (rel. intensity) 264 (4), 236 (10), 218 (8), 208 (36), 190 (14), 180 (42), 162 (100). (Found: C, 46.01; H, 2.92. ($C_{10}H_8O_5Fe$ calcd.: C, 45.49; H, 3.05 %.)

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REFERENCES

1 For recent reviews see: (a) E. W. Abel and S. Tyfield, *Advan. Organometal. Chem.*, 8 (1970) 117;
(b) M. A. Haas, *Organometal. Chem. Rev. A*, 4 (1969) 307.
2 G. F. Emerson and R. Pettit, *J. Amer, Chem. Soc.*, 84 (1962) 4591.
3 D. A. T. Young, J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, 91 (1969) 6968.
4 D. R. Falkowski, D. F. Hunt, C. P. Lillya and M. D. Rausch, *J. Amer. Chem. Soc.*, 89 (1967) 6387.
5 M. Brockhart and E. R. Davis, *J. Amer. Chem. Soc.*, 92 (1970) 7622.
6 (a) A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, *Chem. Ind.* (London), (1961) 553;
(b) *J. Chem. Soc.*, (1962) 4821.
7 M. Cooke, P. T. Draggett, M. Green, B. F. G. Johnson, J. Lewis and D. J. Yarrow, *Chem. Commun.*, (1971) 621.
8 S. Winstein, H. D. Kaesz, C. G. Kreiter and E. C. Friedrich, *J. Amer. Chem. Soc.*, 87 (1965) 3267.
9 H. D. Kaesz, S. Winstein and C. G. Kreiter, *J. Amer. Chem. Soc.*, 88 (1966) 1319.
10 N. A. Clinton and C. P. Lillya, *J. Amer. Chem. Soc.*, 92 (1970) 3065.
11 A. Eisenstadt and S. Winstein, *Tetrahedron Lett.*, (1971) 613.
12 W. Hübel and E. Weiss, *Chem. Ber.*, 95 (1962) 1179.
13 R. B. King, *Inorg. Chem.*, 2 (1963) 807.
14 (a) E. C. Freidrich, *J. Org. Chem.*, 33 (1968) 413;
(b) A. A. Bothner-By and E. Moser, *J. Amer. Chem. Soc.*, 90 (1968) 2347;
(c) L. Jackman and R. H. Wiley, *J. Chem. Soc.*, (1960) 2886.
15 M. L. Maddox, S. L. Stafford and H. D. Kaesz, *Advan. Organometal, Chem.*, 3 (1965) 1.
16 J. I. Musher and E. J. Corey, *Tetrahedron*, 18 (1962) 791.
17 R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*, John Wiley and Sons, New York, New York, 1967, p. 136.
18 M. L. H. Green, *Angew. Chem.*, 72, (1960) 719.
19 R. P. Dodge, *J. Amer. Chem. Soc.*, 86 (1964) 5429.
20 H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.*, 31 (1959) 1278.
21 H. J. Dauben Jr. and H. J. Ringold, *J. Amer. Chem. Soc.*, 73 (1951) 876.
22 J. E. Mahler, D. A. K. Jones and R. Pettit, *J. Amer. Chem. Soc.*, 86 (1964) 3589.
23 M. Brookhart and E. R. Davis, *Tetrahedron Lett.*, in press.
24 B. Dickens and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 83 (1961) 4862.

25 D. F. Hunt, C. P. Lillya and M. D. Rausch, *J. Amer. Chem. Soc.*, 90 (1968) 2561.
26 G. E. Coates, M. L. H. Green and K. Wade, *Organometallic Compounds*, Methuen and Co, London, 1968, p. 70.
27 G. F. Emerson, J. E. Mahler and R. Pettit, *Chem. Ind. (London)*, (1964) 836.
28 J. D. Graham and M. T. Rogers, *J. Amer. Chem. Soc.*, 84 (1962) 2249.
29 (a) A. P. Ter Borg, R. Van Helden and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, 81 (1962) 177; (b) K. Conrow, *Org. Synthesis*, 43 (1963) 101.
30 E. H. Braye and W. Hübel, *Inorg. Synthesis*, 8 (1966) 178.
31 F. A. Cotton, *J. Amer. Chem. Soc.*, 90 (1968) 6230.
32 H. J. Dauben, L. R. Honnen and K. M. Harmon, *J. Org. Chem.*, 25 (1960) 1442.
33 T. H. Whitesides and R. W. Arhart, *J. Amer. Chem. Soc.*, 93 (1971) 5296.
34 (a) F. A. Carey and H. S. Tremper, *J. Amer. Chem. Soc.*, 90 (1968) 2578; (b) F. A. Carey and C. W. Hsu, *J. Organometal. Chem.*, 19 (1969) 29.