Tetrahedron Letters No.7, pp.613-616, 1971. Pergamon Press. Printed in Great Britain.

# PROTONATION AND DEUTERATION OF TROPONEIRON TRICARBONYL

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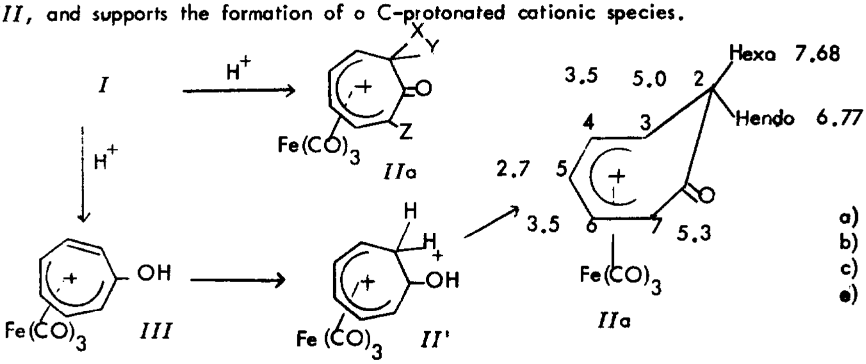
(Received in UK 21 December 1970; accepted for publication 13 January 1971)

The protonation of ketones and the observation of the corresponding cations by nmr, has recently received considerable attention[3,4]. Our interest in this area led us to investigate several metal complexes of ketones, among which were troponeiron tricarbonyl *I* and bicyclo [3.2.2] nonatrieneiron tricarbonyl[5], in strongly acidic media. *I* has been known since 1962 and was prepared in very poor yields, either from acetylene and $Fe_2(CO)_9$[6] or from tropone and $Fe_3(CO)_{12}$[7,8]. We obtained *I* in high yield from tropone and $Fe_2(CO)_9$.

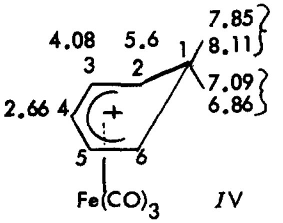
When a $CH_2Cl_2$ solution of *I* was extracted with concentrated $H_2SO_4$ (98%) at 0°, the ion *IIa* was formed and its nmr spectrum was measured at ambient temperature. A priori, one might expect protonation to take place at oxygen to form *III*[3,4]. However, the observed nmr spectrum is consistent only with the proposed structure *IIa* i.e., cycloheptadienyl-1-one iron tricarbonyl, and not with hydroxy tropylium iron tricarbonyl *III*, although the latter might constitute an intermediate species to *IIa* via *II'*. This constitutes, to the best of our knowledge, an unprecedented case of observed C-protonation in such systems. The high field AB pair at $\tau$6.77 and $\tau$7.68 (as part of an ABX pattern) is inconsistent with *III*, and supports the formation of a C-protonated cationic species.



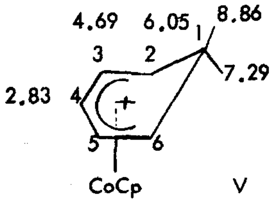
*II*

a) X=Y=Z=H;
b) X=Y=D; Z=H;
c) X=Y=Z=D;
e) X=D;Y=Z=H;

The chemical shifts and the coupling constants found for *IIa* were similar to those reported for the cations *IV*,[9] and V[10]. The cations resemble ours, especially in the nmr region due to the two methylene protons on $C_2$, where the signals appear as AB pairs.[9] In the spectrum of *IIa*, the lower field quartet at $\tau$6.67 is attributed to the absorption of Hendo, with two large coupling constants: $J_{endo,\,exo}$ = 16.5 Hz and $J_{endo,3}$=8.0 Hz. The upfield double doublet is assigned to Hexo, the very small coupling constant being due to the interaction of Hexo with $H_3$. Such a pattern was interpreted by Wilkinson[9] in terms of non-equivalence of the protons on $C_1$ and of the non-planarity of the cyclohexadienyl ring in IV.



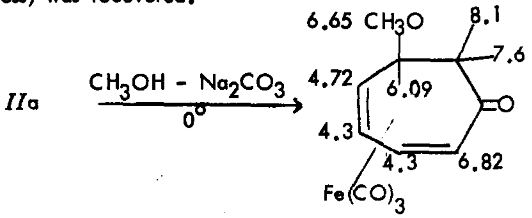
IV



V

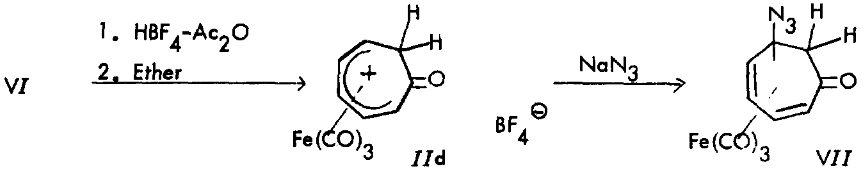
The cation *II*a is very stable in acidic solution ($H_2SO_4$) and does not noticeably decompose on standing at room temperature for five days. In addition, cation *II*a is unusual in exhibiting positive charge adjacent to the keto-group.

When a solution of *II*a was quenched in a rapidly stirred suspension of sodium carbonate in methanol at 0°, *VI*[11,12] in greater than 90% yield (based on troponeiron tricarbonyl used for the protonation process) was recovered.



*VI*

In addition to the direct observation of cation *II*a in strong acid, we were able to isolate it in quantitative yield as the stable solid crystalline tetrafluoroborate salt,[11,13] (decomp.140°) *II*d, by treating the methoxy-dienone complex *VI*, with $HBF_4$ in $Ac_2O$.



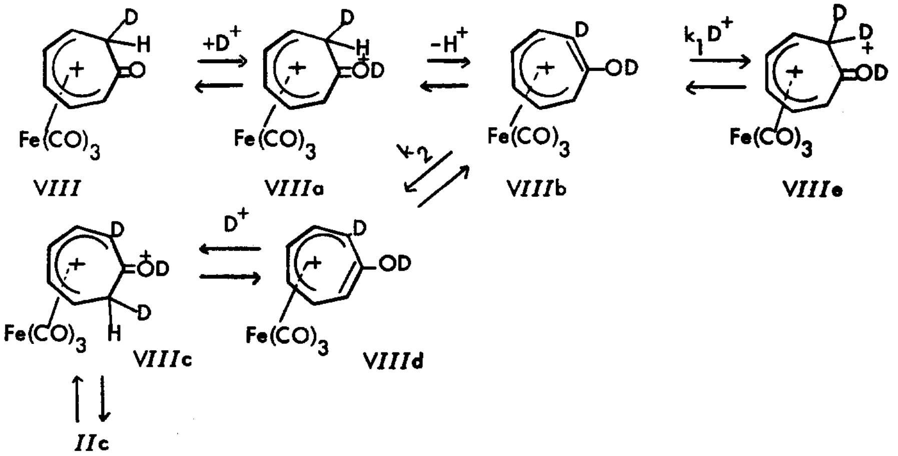
*II*d *VII*

Attack on the salt *II*d by a strong nucleophile such as $NaN_3$ in aqueous solution gave the corresponding azide, *VII*, with ir and nmr spectra very similar to those exhibited by *VI*.

When troponeiron tricarbonyl was dissolved in $D_2SO_4$ (99%) at 0° and the nmr spectrum of the solution observed, the absorptions which had been present for *II*a in $H_2SO_4$ at $\tau$6.7 and $\tau$7.6 had almost disappeared ( $>$ 95%) within 15 minutes and there were no peaks above $\tau$6.0. This suggests *transient formation of IIb on which we also observed the replacement of* $H_7$( $\tau$ 5.2) with deuterium, but at a slower rate disappearance after about 2.5 hr; to yield eventually *II*c[16]. Replacement of $H_7$ with D at ambient temperature (ca. 40° was followed as a function of time and gave a first order rate constant of ca. 4x10$^{-4}$ sec$^{-1}$ (half life of ca. 30 minutes).

$$I \xrightarrow{D_2SO_4} IIb \xrightarrow[\substack{\text{ca. } 35^\circ \\ k = 4.10^{-4}\text{sec}^{-1}}]{D^+} IIc$$

Initially, one might expect to find two deuterium atoms per cation *II*a at $C_2$ as a result of exchange via an enolic intermediate. However, to accommodate the incorporation of the third deuterium atom at $C_7$, we suggest a 1,2 shift of the pentadienyliron tricarbonyl system around the ring, as shown in the scheme below. The rate constant, $k_1$, of the enolic double bond deuteration is much faster than $k_2$ which represents the rate of fluxional isomerization of this double bond.



Thus, if the proposed mechanism is correct, the rate constant for incorporation of the third deuterium at $C_7$ in *II*b gives an estimate of the rate of ring fluxional isomerism of the $Fe(CO)_3$ moiety.

The single band at τ4.2 observed in the tropyliumiron tricarbonyl *IX* was interpreted in terms of a rapid valence tautomerism of the $C_7H_7$ ring[14]. In the case of cation *II*a, the suggested intermediate which probably undergoes valence tautomerism is hydroxy-tropylium iron tricarbonyl, *III*, and it appears that the presence of the hydroxy substituent increases the energy barrier to the isomerization process, in the comparison to the parent cation *IX*.

We also attempted to measure the exchange rate of the methylene protons at $C_2$ by monitoring the rate of deuterium incorporation using $SO_2$-$FSO_3D$ (40 fold excess of the acid) at -78° and nmr spectra were recorded at -34 and -14[15], no exchange was detected after 2 hours at -14°. There was no exchange even after 2 days at -20°. (The first deuteration in $FSO_3D$ was found to be non-stereoselective). However, if the sample was allowed to warm up to room temperature (the $SO_2$ was evaporated) and stand for 24 hrs., the nmr spectrum showed almost full incorporation of two deuterium atoms at $C_2$, and, in contrast to the measurements in $D_2SO_4$, only ~ 20% D at $C_7$.

The exchange rate of the methylene proton at $C_2$ in $SO_2$-$FSO_3D$ at 16°C ($I \longrightarrow II$b), was ca. $2\times10^{-4}$ $sec^{-1}$ ( $\frac{1}{2}$ = 60 min). Moreover, the incorporation of the third D at $C_7$ was much slower in $FSO_3D$ than in $D_2SO_4$, ca. $8\times10^{-6}$ $sec^{-1}$. A rationale to the slower rate of D—exchange at all positions in $FSO_3D$ as compared to $D_2SO_4$ is possibly given by the increased acidity of the former, inhibiting the deportonation step in $FSO_3D$.

$$\begin{tikzcd} I \arrow[r, "SO_2\ -\ FSO_3D"] & IIe \arrow[r, "\begin{array}{c}-20^\circ/\ 2\ days\ \ X\\ +16^\circ/\ 2\times10^{-4}sec\end{array}", "r.t."'] & IIb \arrow[d, "ca.\ 8\times10^{-6}sec^{-1}"] \\ & & IIc \end{tikzcd}$$

## ACKNOWLEDGEMENT

We are grateful to Dr. P. Warner and Dr. D. Harris for helpful discussions and aid in the prepration of this manuscript.

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2. Deceased November 23rd 1969.

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8. The n.m.r. spectrum of *I* ($CDCl_3$, 100 MHz) displays signals at $\tau$ 3.42 (quartet $J_{3,4}$ = 8.0 Hz), $\tau$ 4,95 double double doublet ($J_{2,3}$ = 11.0 Hz, $J_{2,7}$ = 2.0 Hz, $J_{2,4}$ = 1.0 Hz), $\tau$ 3.61 (X part of $A_2X_2$ pattern) $\tau$ 6.81 (asym quintet), $\tau$ 7.25 complex triplet. Double resonance made possible unequivocal assignment to $H_3$, $H_2$, $H_{5,6}$, $H_7$ and $H_4$ respectively. Lit[7] (no signal assignments): $\tau$ 3.4 (complex), $\tau$ 5.09 ddd, $\tau$ 6.91 (asym. quintet), $\tau$ 7.29 triplet.

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11. All new compounds gave satisfactory C, H analyses and/or mass spectra.

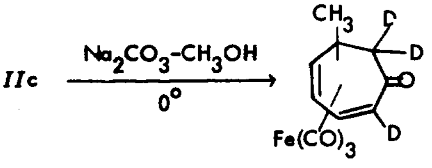
12. Crystallized from hexane, m.p. 78-80° Ir in the $M-C\equiv 0$ very similar to that of *I*: 2073, 2010 and 2002 $cm^{-1}$ in hexane.

13. Nmr spectrum of *IId* in $SO_2$ is the scme as that of *IIa* in $H_2SO_4$. Ir absorption of the ketonic carbonyl appears at 1625 $cm^{-1}$.

14. J.E. Mahler, D.A.K. Jones and R. Pettit, J. Amer.Chem.Soc. 86, 3589, (1964).

15. The nmr spectrum of *I* in $SO_2$-$FSO_3H$ at -34° and -14°, though largely similar to that found in $H_2SO_4$ at room temperature, shows some structural differences of $H_{4-6}$ and is currently under investigation. Quenching a solution of *I* in $SO_2$-$FSO_3H$ in cold $CH_3OH$-$Na_2CO_3$ gave more than a 90% recovery of methoxy-diene complex *VI*.

16. Cation *IIc* was also quenched in a suspension of methanol and sodium carbonate at 0° to give X as the only isolated product (as proved by proton nmr and mass spectral analyses.[11])



X