Tetrahedron Letters No. 46, pp 4349 - 4352, 1971. Pergamon Press. **Printed in Great Britain.**

LOW TEMPERATURE PROTONATION OF METHYLCYCLOOCTATETRAENEIRON TRICARBONYL

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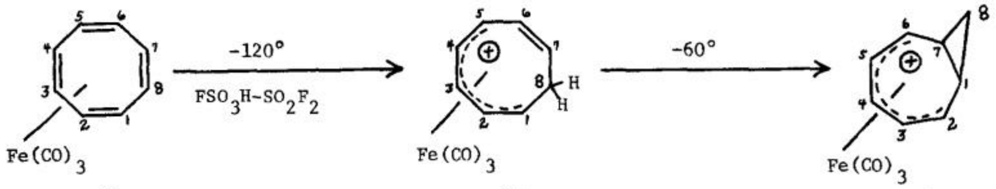
(Received in USA 7 September 1971; received in UK for publication 11 October 1971)

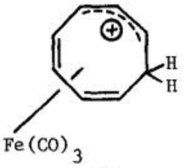
It has recently been reported[1] that low temperature protonation of the cyclooctatetraeneiron tricarbonyl complex, I, yields initially the cyclooctatrienyliron tricarbonyl complex, II, which undergoes electrocyclic ring closure at -60° to the bicyclo[5.1.0]octadienyliron tricarbonyl complex III. Earlier work by Davison[2] had shown that in D_2SO_4 the deuteration is stereospecific with the entering deuteron occupying the "inside" or endo position of the methylene group. This is in contrast to the stereospecificity observed for protonation of cyclooctatetraenemolybdenum tricarbonyl[3a] but similar to the protonation of cyclooctatetraene[3b] which is predominately endo.



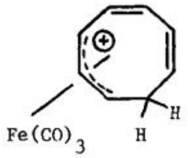
I

II

III



IV



V

The interesting question of the exact position and mechanism of protonation of I is still unanswered from the data presently available. Several plausible possibilities exist. Protonation at either C_6 or C_7, the internal positions of the uncomplexed diene moiety, would lead directly to the first observable ion, II. Viewing the C_5-C_6-C_7-C_8 unit as a free diene, protonation at a terminal position (C_5 or C_8) is reasonable and would yield ion IV which could rapidly give II. In analogy with simple dieneiron tricarbonyl complexes[4], protonation may occur at C_1 or C_4 to yield initially V which could then isomerize to II.[5] In view of the extensive work on the direct protonation of transition metals,[4b,6] another possible mechanism is one in which the iron atom is initially protonated followed by migration of the iron-bound proton to the ligand[7,8]; but this mechanistic scheme would not be in accord with the observed stereospecificity of protonation.

We report here the low temperature protonation of methylcyclooctatetraeneiron tricarbonyl, VI, which clearly establishes the position of protonation of both VI and I and yields interesting data concerning substituent effects on the formation of the monocyclic complexes and their relative rates of ring closure.

Anet[9] has shown that VI exists almost exclusively (>95%) as the isomer with the methyl group bound to one of the internal carbons of the bound diene unit as shown. In the following analysis the assumption is made (see below) that this is the isomer which is protonated.

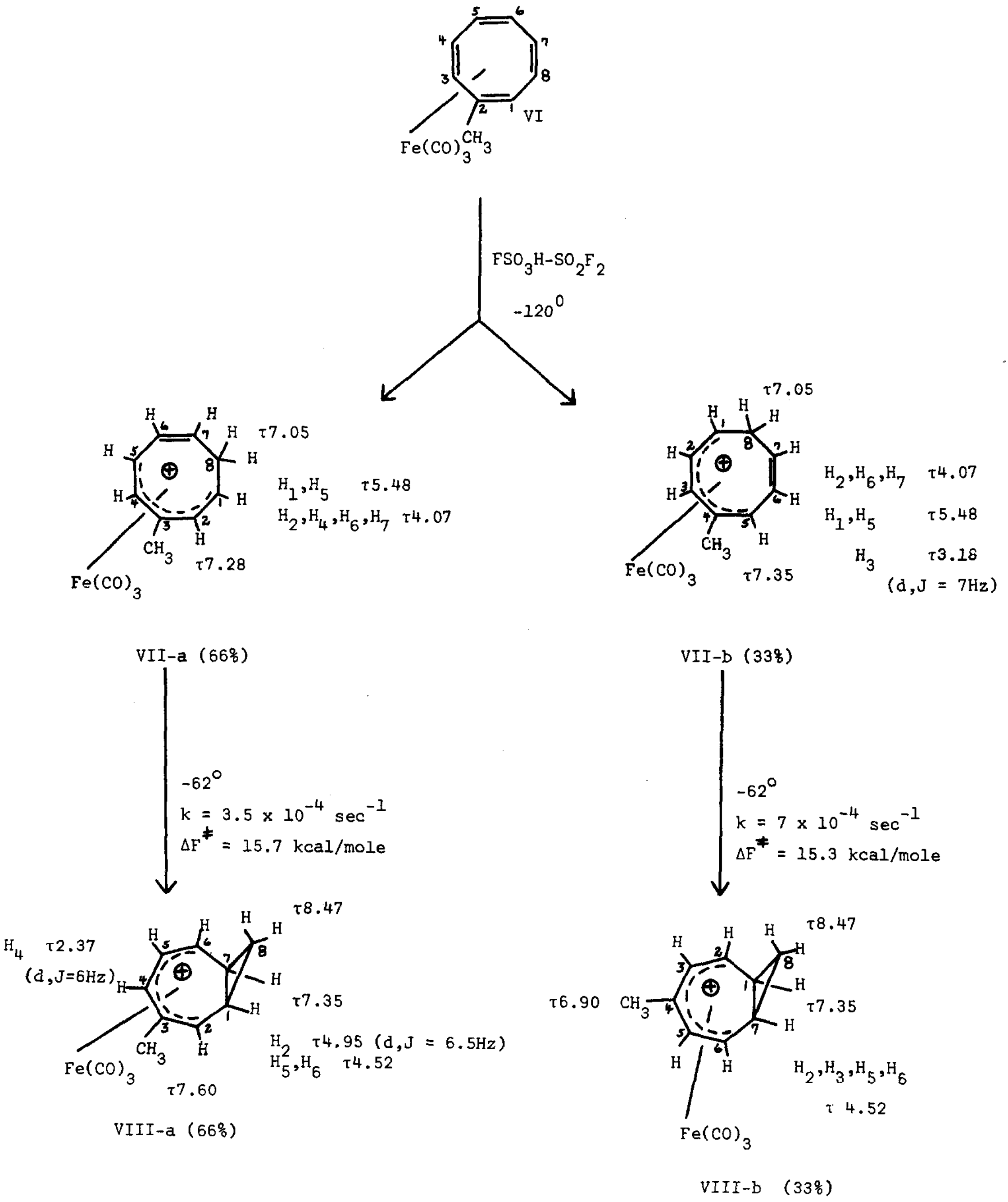
Protonation of VI at -120° in $FSO_3H-SO_2F_2$ (1:3 v/v) yields a clear yellow solution whose nmr spectrum[10] at -80° exhibits a doublet (J=7Hz) at τ3.18, and multiplets at τ4.07, 5.48, and 7.05. The integrated intensities of these bands are 0.33, 3.7, 2.0, and 2.0, respectively. Two methyl singlets appear at τ7.28 and 7.35 in the ratio of _ca._ 2:1 with a total integrated intensity of 3.0. This spectrum is readily interpreted as a 2:1 mixture of complexes VII-a and VII-b.[11]

The appearance of the two methyl singlets indicates the formation of two isomeric complexes in a _ca._ 2:1 ratio. In the region where the central proton H_3 of the pentadienyl system of the monocyclic complexes should appear (_ca._ τ3.2 in analogy with II[1]) the spectrum exhibits only a _single_ band of relative intensity 0.33. This clearly indicates that the major isomer (66%) must be VII-a having the methyl substituent at position 3. The appearance of the τ3.18 signal as a _doublet_ indicates the minor isomer (33%) must contain a methyl group adjacent to the C_3 position, otherwise the H_3 signal would appear as a triplet analogous to the H_3 signal for II. This minor isomer is assigned structure VII-b.[12] The positions and integrated intensities of the remaining signals (assignments shown) are in accord with and support these structural assignments.

When the $FSO_3H-SO_2F_2$ solution is warmed to _ca._ -60° both complexes VII-a and VII-b undergo ring closures to VIII-a and VIII-b. The nmr spectrum of this mixture of complexes exhibits a doublet (J=6Hz) at τ2.37, a multiplet at 4.52, a doublet (J=6.5Hz) at 4.95, multiplets at 7.35 and 8.47 and methyl singlets at 6.90 and 7.60. The relative integrated intensities of these signals are 0.63, 2.7, 0.64, 2.0, 2.0, 1.0, 2.0, respectively. These nmr data are in complete accord with the expected formation of complexes VIII-a (66%) and VIII-b (33%). The downfield region of the spectrum where the central proton (H_4) appears[1] exhibits only one signal, a doublet corresponding to 0.63 hydrogens which is as expected for the 2:1 mixture of isomers. The minor isomer VIII-b has no proton at position 4 while in VIII-a the adjacent methyl group causes the H_4 signal to appear as a doublet. The methyl signals are assigned on the basis of their integrated intensities, while the τ4.95 doublet is tentatively assigned to H_2 of VIII-a. Additional assignments are shown and are in accord with expected values based on assignments for III.[1,2]

The relative rates of ring closure of VII-a and VII-b were measured at -62° C. The first-order rate constant for closure of VII-a to VIII-a is 3.5×10^{-4} sec^{-1} corresponding to $\Delta F^{\ddagger} =$ 15.7 kcal/mole while the rate constant for closure of VII-b to VIII-b is 7.0×10^{-4}, $\Delta F^{\ddagger} = 15.3$ kcal/mole.

The formation of complexes VII-a and VII-b is consistent only with protonation of VI at


VI
Fe(CO)$_3$ CH$_3$
FSO$_3$H-SO$_2$F$_2$
-120^0
τ7.05
H$_1$,H$_5$ τ5.48
H$_2$,H$_4$,H$_6$,H$_7$ τ4.07
τ7.28
Fe(CO)$_3$
VII-a (66%)
τ7.05
H$_2$,H$_6$,H$_7$ τ4.07
H$_1$,H$_5$ τ5.48
H$_3$ τ3.18
(d,J = 7Hz)
τ7.35
VII-b (33%)
-62^o
k = 3.5 x 10^{-4} sec^{-1}
ΔF‡ = 15.7 kcal/mole
-62^o
k = 7 x 10^{-4} sec^{-1}
ΔF‡ = 15.3 kcal/mole
τ8.47
H$_4$ τ2.37
(d,J=6Hz)
τ7.35
H$_2$ τ4.95 (d,J = 6.5Hz)
H$_5$,H$_6$ τ4.52
τ7.60
VIII-a (66%)
τ8.47
τ6.90 CH$_3$
τ7.35
H$_2$,H$_3$,H$_5$,H$_6$
τ 4.52
Fe(CO)$_3$
VIII-b (33%)

C_6 and C_7, the internal positions of the free diene moiety.[13] Regarding the methyl group as only a minor perturbation, the protonation of I clearly must also occur at C_6 and C_7. These results also suggest that for the electrophilic substitutions of I recently reported by Lewis[14] the attack of the electrophile probably also occurs at C_6 and C_7.

The effect of the methyl substituent upon relative rates of both formation and ring closure of VII-a and VII-b is also of interest. If it is assumed that the charge distribution in the iron-complexed pentadienyl ion is similar to that in the uncomplexed ion then VII-a would be expected to be more stable than VII-b. Such an assumption could explain the formation of VII-a as the major isomer and, applying Hammond's postulate, explain also why VII-b undergoes electrocyclic ring closure more rapidly than VII-a.

Acknowledgement: The authors are grateful to the National Science Foundation (Grant GP-29580), the Research Corporation and the University of North Carolina Research Council for support of this work.

References

1. (a) D.A.T. Young, Ph.D. Thesis, UCLA, 1969; (b) M. Brookhart and E. R. Davis, J. Am. Chem. Soc., 92, 7622 (1970).
2. A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, J. Chem. Soc., 4821, (1962).
3. (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, J. Am. Chem. Soc., 87 3267 (1965); (b) S. Winstein, C. G. Kreiter, and J. I. Brauman, ibid., 88, 2047 (1966).
4. (a) G. F. Emerson and R. Pettit, ibid., 84, 451 (1962); (b) D.A.T. Young, J. R. Holmes, and H. D. Kaesz, ibid., 91, 6968 (1969).
5. If protonation and iron migration were schyronous, neither ion IV nor V need be postulated as discreet intermediates.
6. (a) D. F. Shriver, Accounts Chem. Res., 3, 231 (1970); (b) J. C. Kotz and D. G. Pedrotti, Organometal. Chem. Rev., Sec. A, 4, 479 (1969).
7. For simple dieneiron tricarbonyl complexes, Young, Holmes, and Kaesz[1a,4b] have observed iron protonation and exchange of the iron-bound proton with the external protons of the diene.
8. The possibility that the electrophilic substitution of ferrocene proceeds by a mechanism in which the electrophile initially attacks at iron has been suggested by Rosenblum; M. Rosenblum and F. W. Abbate, Advan. Chem. Series, 62, 532 (1967).
9. F.A.L. Anet, J. Am. Chem. Soc., 89, 2491 (1967).
10. All chemical shifts are in τ relative to internal CH_2Cl_2 taken as $\tau 4.70$.
11. Each structure is numbered independently and therefore identical carbons do not retain the same number in comparing the neutral metal complexes with the cations.
12. Also consistent with the nmr data is the isomer containing the methyl substituent at C_2. This isomer is, however, ruled out by nmr data for the ring-closed ions.
13. The possibility that VII-a and VII-b arise from protonation of a minor isomer in equilibrium with VI is remote. For the case of either the 1- or 5- methyl isomer of VI, protonation would have to occur at two positions which are nonequivalent in I, while for the 6-methyl isomer protonation would have to occur at the unlikely 2 and 3 positions. In addition, protonation of VI would likely be more rapid than the maximum possible rate of conversion of VI to a minor isomer.[9]
14. (a) B.F.G. Johnson, J. Lewis, A. W. Parkins, and G.L.P. Randall, Chem. Comm., 595 (1969); (b) B.F.G. Johnson, J. Lewis, and G.L.P. Randall, J. Chem. Soc., Sect. A, 422 (1971).