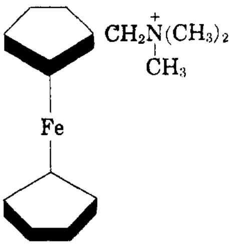
Communications TO THE EDITOR

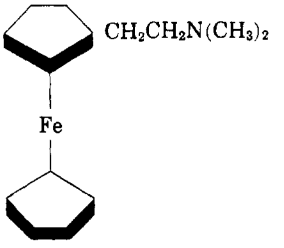
Some Reactions of the Methiodide of *N*,*N*-Dimethylaminomethylferrocene[1]

Sir:

Recently,[2] ferrocene was aminomethylated to form *N*,*N*-dimethylaminomethylferrocene, the methiodide of which (I) was rearranged by potassium amide in liquid ammonia to another tertiary amine. By analogy with the benzyltrimethylammonium ion, quaternary ion I was assumed to undergo the ortho substitution rearrangement. However, evidence has now been obtained that a rather unusual Stevens rearrangement occurs to form tertiary amine II, the methiodide of which was converted by potassium amide to vinylferrocene.[3] Amine II is being synthesized independently. The 1,2-shift of a methyl group does not occur as shown by synthesis of the product of such a reaction.

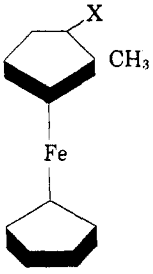


I



II

An unexpected ortho substitution type of reaction apparently occurs on treating quaternary ion I with aqueous sodium cyanide to form nitrile III (90%), m.p. 81–83° *Anal.*[4] Calcd. for $C_{12}H_{11}FeN$ C, 64.03; H, 4.93; N, 6.22; Fe, 24.81. Found: C, 64.00; H, 4.98; N, 6.05; Fe, 24.52. Reduction of this nitrile and dimethylation of the resulting primary amine produced in good yield a tertiary amine that was different from, but isomeric with, tertiary amine II obtained from the rearrangement. The tertiary amine prepared from the nitrile is presumably IV, b.p. 118–123° at 0.6 mm. *Anal.*[4] Calcd. for $C_{14}H_{19}FeN$: C, 65.38; H, 7.54; N, 5.45; Fe, 21.72. Found: C, 65.19; H, 7.32; N, 5.43; Fe, 21.37. *Methiodide,* m.p. 258° (dec.). *Anal.*[4] Calcd. for $C_{15}H_{22}FeIN$: C, 45.14; H, 5.56; N, 3.51; Fe, 13.99. Found: C, 45.34; H, 5.58; N, 3.51; Fe, 14.15. The methiodide of tertiary amine II melted at 248° (dec.); a mixed melting point with the methiodide of amine IV was 225–240°.



III (X = CN)
IV X = $CH_2N(CH_3)_2$
V (X = COOH)
VI (X = CH_2OH)

Nitrile III was hydrolyzed to acid V (94%), m.p. 154–156°. *Anal.*[4] Calcd. for $C_{12}H_2FeO_2$: C, 59.05; H, 4.96; 0, 13.11; Fe, 22.88. Found: C, 59.13; H, 5.07; Fe, 22.78. This acid was reduced to alcohol VI (86%) m.p. 41–41.5°. *Anal.*[4] Calcd. for $C_{12}H_{14}FeO$: C, 62.61; H, 6.13; Fe, 24.27. Found: C, 62.70; H, 6.04; Fe, 24.11. This alcohol was oxidized by "active" manganese dioxide[5] to the corresponding aldehyde (15%) which gave a strong carbonyl band in the infrared at 1680 cm.$^{-1}$ This band is also found in the spectrum of VIII. Such an oxidation is characteristic of benzyl type alcohols.[5] Attempts are being made to resolve such compounds as alcohol VI.

In contrast to sodium cyanide, sodium hydroxide has been shown[6] to react with quaternary ion I to form alcohol VII which on oxidation gives in good over-all yield aldehyde VIII. Several condensations of this aldehyde have been accomplished.[7] Recently,[8,9] aldehyde VIII was prepared by two other methods.

VII

VIII

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[1] Supported by the Office of Ordnance Research, U. S. Army.

[2] C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **21**, 382 (1956).

[3] We are indebted to Linde Air Products (Dr. R. L. Pruett) for an authentic sample of this compound.

[4] Analysis are by Galbraith Laboratories, Knoxville, Tenn.

[5] See R. J. Highet and W. C. Wildman, *J. Am. Chem. Soc.*, **77**, 4399 (1955).

[6] J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957). A redetermination of the infrared spectrum of aldehyde VIII has given a maximum at 1681 cm.$^{-1}$ instead of 1690 cm.$^{-1}$

[7] C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, in the hands of the editor.

[8] M. Rosenblum, *Chemistry and Industry*, 72 (1957).

[9] G. D. Broadhead, J. M. Osgerby and P. L. Pauson, *Chemistry and Industry*, 209 (1957).

Work in progress includes the conversion of alcohol VII to the dibenzyl type ether, and of aldehyde VII to an amphoteric acid (by air oxidation). Rather surprisingly, both the iron and the aldehyde group in VIII were found to be somewhat resistant to oxidation with certain reagents. Thus, although the iron was readily oxidized by cerric sulfate, aldehyde VIII was recovered unchanged after treatment with 2% potassium permanganate in aqueous alcoholic solution (acidic or basic) for 10 min. on the steam bath. Apparently the type of oxidizing agent is important.

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