

ture, the reaction mixture was decomposed with water and 6*N* hydrochloric acid. There was obtained 14.0 g. (50%) of 2-methyl-1-( $\beta$ -hydroxyethyl)naphthalene, b.p. 122–124° at 0.3 mm.,  $n_D^{25}$  1.5967, as a pale yellow, viscous liquid.

*Anal.* Calcd. for  $C_{13}H_{14}O$ : C, 83.83; H, 7.58. Found: C, 83.90; H, 7.59.

The *picrate*, after two recrystallizations from 95% ethanol, melted at 126.5–127.5°.

*Anal.* Calcd. for  $C_{19}H_{17}N_3O_8$ : C, 54.94; H, 4.13; N, 10.12. Found: C, 55.14; H, 4.14; N, 9.98.

To a solution of 13.0 g. (0.07 mole) of this alcohol in 30 ml. of dry chloroform was added dropwise a solution of 13.5 g. (0.05 mole) of phosphorus tribromide in 10 ml. of dry chloroform.<sup>16</sup> After refluxing 1.5 hr., the solvent was removed, and 100 g. of ice added. The resulting product was taken up in ether, and the ethereal solution washed three times with saturated sodium bicarbonate solution and dried over magnesium sulfate. The solvent was removed, and the residue distilled to give 7.8 g. (45%) of 2-methyl-

1-( $\beta$ -bromoethyl)naphthalene, b.p. 119–121° at 0.5 mm.,  $n_D^{25}$  1.6014.

*Anal.* Calcd. for  $C_{13}H_{13}Br$ : C, 62.66; H, 5.26. Found: C, 62.89; H, 5.34.

This bromide (7.0 g., 0.028 mole) and 20 ml. of absolute methanol were placed in a 125-ml., amber-colored, screw-cap bottle, and 13.5 g. (0.30 mole) of liquid anhydrous dimethylamine added with stirring. The bottle was closed, and allowed to stand in the dark at room temperature for one week. The solvents were evaporated, and the residue made strongly alkaline with 50% sodium hydroxide. The product was taken up in ether, and the ethereal solution washed with water and dried. The solvent was removed, and the residue distilled to give 4.25 g. (72%) of 2-methyl-1-( $\beta$ -dimethylaminoethyl)naphthalene (XIII), b.p. 165–168° at 10 mm.,  $n_D^{25}$  1.5806. After two recrystallizations from 95% ethanol, the *picrate* of this amine melted at 174–175°. This melting point was not depressed on admixture with the *picrate* of the tertiary aromatic amine obtained from the rearrangement of XI.

DURHAM, N. C.

(16) See P. Cagniant, C. Mentzer, and N. P. Buu-Hoi, *Bull. soc. chim. France*, [5], 10, 145 (1943).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

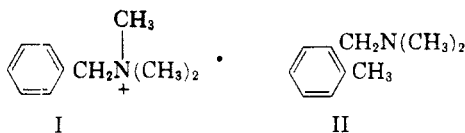
## Rearrangement of the Methiodide of *N,N*-Dimethylaminomethylferrocene by Potassium Amide in Liquid Ammonia<sup>1</sup>

CHARLES R. HAUSER, JACQUE K. LINDSAY, AND DANIEL LEDNICER

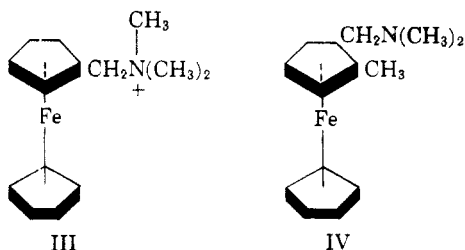
Received August 27, 1957

The methiodide of *N,N*-dimethylaminomethylferrocene was found to undergo with potassium amide in liquid ammonia a rather novel type of Stevens 1,2-shift involving the migration of the ferrocylmethylene group to form the  $\beta$ -ferrocylethylamine. The structure of the product was established by the conversion of its methiodide to vinylferrocene by further treatment with potassium amide and by two independent syntheses. Mechanisms are considered.

The benzyltrimethylammonium ion (I) has previously been shown to undergo with sodium amide or potassium amide in liquid ammonia the ortho substitution rearrangement to form tertiary amine II in 96% yield.<sup>2</sup>

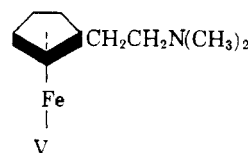


Since the ferrocene nucleus has been observed to possess certain aromatic properties,<sup>3</sup> the correspond-



ing quaternary ammonium ion (III) in the ferrocene series might be expected to exhibit this type of rearrangement to form tertiary amine IV.

However, it was found in the present investigation that quaternary ion III is rearranged by potassium amide in liquid ammonia to form the  $\beta$ -ferrocylethylamine (V) in yields of 40 to 50%.<sup>4</sup> This rearrangement was realized in lower yield with sodium amide.



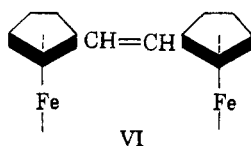
Also there was obtained a neutral by-product (10–20%) which is tentatively assigned structure VI. Such dimeric olefins have been produced as by-products in certain rearrangements of quaternary ammonium ions.<sup>2</sup>

(1) Supported by the Office of Ordnance Research, U. S. Army.

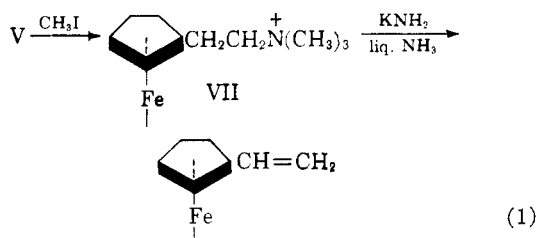
(2) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951).

(3) See P. L. Pauson, *Chem. Revs.*, **9**, 391 (1955).

(4) This rearrangement in which structure IV was assumed for the product was reported in a communication by C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **21**, 382 (1956). Preliminary evidence for structure V was reported in a later communication by C. R. Hauser, J. K. Lindsay, D. Lednicer, and C. E. Cain, *J. Org. Chem.*, **22**, 717 (1957).

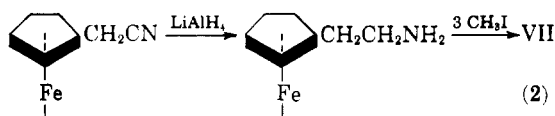


The structure of the rearranged tertiary amine was established as V by the further treatment of its methiodide (VII) with potassium amide, in which vinylferrocene was produced in good yield (Equation 1).

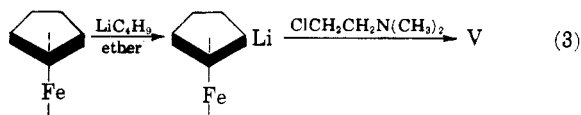


Incidentally this  $\beta$ -elimination of trimethylamine from methiodide VII to form vinylferrocene was observed in low yields with aqueous sodium hydroxide, sodium in ethanol, and sodium amalgam in water. These two last experiments were carried out in attempts to effect reduction to a nonnitrogenous compound.

The structure of the rearranged amine from quaternary ion III was confirmed as V by two independent syntheses. The first synthesis involved the reduction of ferrocylacetonitrile and the exhaustive methylation of the resulting primary amine as described elsewhere<sup>5</sup> (Equation 2). The over-all yield in this sequence was 43%.



The second independent synthesis involved the metalation of ferrocene with butyllithium and the alkylation of the resulting lithio derivative with  $\beta$ -dimethylaminoethyl chloride (Equation 3).



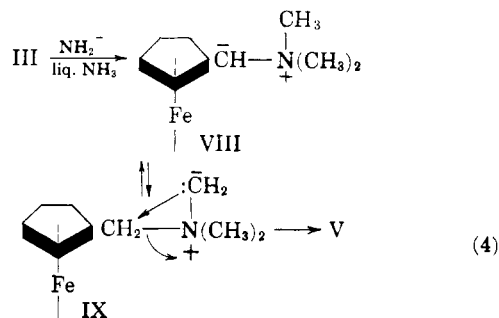
Although the yield was low (about 3%), tertiary amine V was the only isolable basic product. This is in line with the observation of earlier workers<sup>6</sup> who reported less than a 10% yield of a mixture of mono- and dibasic carboxylic acids on carbonation of the metalated intermediate.

The mechanism of formation of the  $\beta$ -ferrocylethylamine V from quaternary ion III is considered

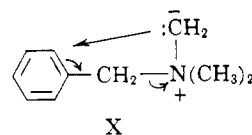
(5) D. Lednicer, J. K. Lindsay, and C. R. Hauser, *J. Org. Chem.*, in press.

(6) R. A. Benkeser, D. Goggin, and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954).

to involve the Stevens type of 1,2-shift of the methyleneferrocene group within carbanion IX, which presumably is in equilibrium with the predominant carbanion VIII (Equation 4).

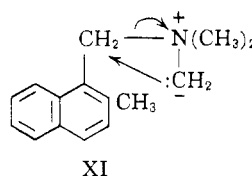


This rearrangement of carbanion IX is rather novel since corresponding methyl carbanions in the benzene series undergo the *ortho*-substitution rearrangement,<sup>2,7</sup> in which the benzene nucleus functions as an electron acceptor (aromatic nucleophilic substitution). For example, methyl carbanion X, which is structurally analogous to IX, rearranges exclusively to the *ortho*-substituted tertiary amine (II).<sup>2</sup>



This difference in the course of reaction of carbanions IX and X indicates that the ferrocene nucleus has less tendency to function as an electron acceptor than the benzene nucleus and/or that the methyleneferrocene group undergoes the 1,2-shift more easily than the benzyl group.

Only one other example of the Stevens 1,2-shift within a methyl carbanion to form a  $\beta$ -arylethyl-dimethylamine appears to have been observed. This involved carbanion XI in which there is an *o*-methyl substituent.<sup>8</sup>

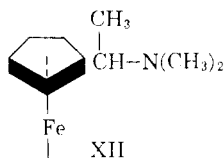


In connection with the present work it was shown that the product obtained from the rearrangement of quaternary ion III was not tertiary amine XII which might have arisen from the Stevens 1,2-shift of a methyl group within carbanion VIII. This tertiary amine was synthesized

(7) C. R. Hauser and A. J. Weinheimer, *J. Am. Chem. Soc.*, **76**, 1264 (1954).

(8) C. R. Hauser, D. N. Van Eenam, and P. L. Bayless, *J. Org. Chem.*, **23**, 354 (1958).

recently in another investigation.<sup>9</sup> Apparently the 1,2-shift of a methyl group, which is the more common Stevens rearrangement at higher temperatures, has not been observed in liquid ammonia.<sup>10</sup>



#### EXPERIMENTAL<sup>11</sup>

**Rearrangement of the methiodide III.** The quaternary salt III,<sup>12</sup> (38.5 g., 0.1 mole) was added to a well stirred solution of 0.2 mole of potassium amide in 500 ml. of liquid ammonia over the period of 1 hr. Each addition was followed by a transitory red color. At the end of an additional 3 hr. excess ammonium chloride was added to the brown reaction mixture and the ammonia was replaced by ether. The residue was removed by filtration and washed well with ether. The ether was evaporated from the combined filtrates to afford a clear amber oil. Distillation of this oil at 0.3 mm. gave a small forerun, b.p. 70–90°, of 4.0 g. and 10.5 g. (41%) of a fraction b.p. 101–103°. A sample of the latter was redistilled at 0.35 mm. to afford the tertiary amine V b.p. 103–104°,  $n_D^{25}$  1.5805.

*Anal.* Calcd. for  $C_{14}H_{19}NFe$ : C, 65.38; H, 7.45; N, 5.45; Fe, 21.72. Found: C, 65.16; H, 7.40; N, 5.74; Fe, 21.39.

In a number of runs, the yield of amine ranged from 40 to 50%.

The *picrate* of the amine was prepared in the usual way and recrystallized from ethanol to a constant m.p. of 179–180° (dec.).

*Anal.* Calcd. for  $C_{25}H_{22}O_7NFe$ : C, 49.40; H, 4.56; N, 11.52; Fe, 11.49. Found: C, 49.48; H, 4.55; N, 11.48; Fe, 11.62.

The forerun of the distillation in ether and the solution washed with *N* hydrochloric acid followed by saturated sodium bicarbonate and water. On removal of the solvent a brown solid remained. This was recrystallized from ethanol to give old gold colored plates m.p. 39–40° having a strong camphoric odor. This compound (VI) shows strong absorption at 1100  $cm^{-1}$  and 1000  $cm^{-1}$  and weak absorption at 1620  $cm^{-1}$ , suggesting mono substituted rings, and a double bond.

*Anal.* Calcd. for  $C_{22}H_{20}Fe_2$ : C, 66.71; H, 5.09; Fe, 28.20. Found: C, 66.81; H, 5.22; Fe, 28.46. Mol. wt. calcd. for  $C_{22}H_{20}Fe_2$ : 396. Found<sup>13</sup>: 425, 414, 392, 408.

**Methiodide VII of the rearrangement product.** To an ice cooled solution of 11.35 g. (0.045 mole) of the tertiary amine V in 15 ml. of methanol, there was added 10 ml. of methyl iodide. Heat was evolved and a crystalline solid gradually came out. At the end of 1 hr. ether was added and the solvent removed by filtration to afford 16.08 g. (91%) of methiodide VII m.p. 248–250° (dec.).<sup>14</sup>

(9) C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 906 (1957).

(10) See C. R. Hauser, R. M. Manyik, W. R. Brasen, and P. L. Bayless, *J. Org. Chem.*, **20**, 1119 (1955).

(11) Analyses are by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected.

(12) J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957).

(13) Molecular weight determination by Dr. C. Tiedcke, Teaneck, N. J.

(14) This melting point varies with the rate of heating.

*Anal.* Calcd. for  $C_{15}H_{22}NFe$ : C, 45.14; H, 5.56; N, 3.51; Fe, 13.99. Found: C, 45.18; H, 5.65; N, 3.29; Fe, 13.81.

The infrared spectrum of this salt (which shows the bands at 811, 1002, and 1108  $cm^{-1}$  characteristic of monosubstituted ferrocenes)<sup>3</sup> and that of an authentic sample prepared from ferrocylacetonitrile<sup>5</sup> are superimposable (as potassium bromide pellets).<sup>15</sup>

A sample of the methiodide was treated with saturated alcoholic picric acid to afford the quaternary picrate m.p. 150–152°. The mixed melting point of this with a freshly prepared sample of the authentic quaternary picrate<sup>5</sup> m.p. 150–152° was 150–152°.

**$\beta$ -Elimination of methiodide VII to vinylferrocene.** Over the period of 30 min. 20.0 g. (0.05 mole) of the yellow quaternary salt was added to a stirred solution of 0.1 mole of potassium amide in 250 ml. of liquid ammonia. After an additional 3 hr. stirring, excess ammonium chloride was cautiously added and the ammonia allowed to evaporate. The residue was washed several times with ether; the washes were combined and the solvent removed. The gummy orange solid, m.p. 45–52°, (10.1 g.), which remained was recrystallized from ethanol to afford vinylferrocene<sup>16</sup> m.p. 56°.

*Anal.* Calcd. for  $C_{12}H_{12}Fe$ : C, 67.96; H, 5.70; Fe, 26.34. Found: C, 68.10; H, 5.90; Fe, 26.13.

The infrared spectrum of this compound is superimposable upon one of authentic vinylferrocene<sup>17</sup> m.p. 52–53°.

**Tertiary amine V from ferrocene and  $\beta$ -dimethylaminoethyl chloride.** A solution of 0.75 mole of butyllithium (prepared from 102.8 g. of butyl bromide and 12.9 g. of lithium) in 500 ml. of ether was added to a vigorously stirred, ice-cooled, solution of 93 g. (0.5 mole) of ferrocene<sup>18</sup> in 1.5 l. of ether. The reaction mixture was slowly (1 hr.) brought to reflux temperature, heated for 5 hr., and then stirred at room temperature for 23 hr.<sup>8</sup> At the end of this time a solution of 81 g. (0.75 mole) of the freshly prepared<sup>19</sup> amino halide in 100 ml. of ether was added to the reaction mixture, at such a rate that gentle refluxing ensued. After heating for 3 hrs. the reaction was allowed to stand overnight. Water (500 ml.) was then cautiously added and the organic layer separated. The ethereal solution was subsequently extracted with three 100 ml. portions of *N* hydrochloric acid. The latter were combined, clarified by filtration, and made alkaline with 20% sodium hydroxide. Extraction of the alkaline suspension with ether followed by drying and finally evaporation of the solvent from the extracts afforded 20 g. of basic products as an oil. Distillation of this at 0.4 mm. afforded 4.0 g. of tertiary amine V b.p. 110–112°. No other readily distillable material was observed.

The picrate of this product, m.p. 177–179°, did not depress the m.p. of picrate of the rearrangement product (V).

A sample of the amine was converted to the methiodide in the manner described above. This salt formed a quaternary picrate, m.p. 150–152°, which when mixed with that of the rearrangement product melted at 150–152°.

#### DURHAM, N. C.

(15) When the spectra are run as Nujol mulls, samples of both the authentic salt and that obtained from rearranged amine exhibit spectra when both are crystallized from water which are different from those of samples crystallized from methanol-ether. In each case the absorptions of each pair are identical to each other.

(16) F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **77**, 6295 (1955).

(17) We are indebted to Dr. R. L. Pruett of Lindy Air Products Co. for a sample of this compound.

(18) We are indebted to Linde Air Products Co., Tonawanda, N. Y. (Dr. R. L. Pruett) for a generous sample of this compound.

(19) K. A. Slotta and R. Behnish, *Ber.*, **68**, 757 (1935).