[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Ortho Substitution Rearrangement and Certain Related Reactions in the Naphthalene Series Catalyzed by Sodium Amide[1]

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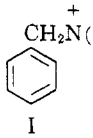
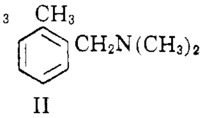
The 1- and 2-naphthylmethyltrimethylammonium ions underwent with sodium amide in liquid ammonia the ortho substitution rearrangement to form 1-methyl-2-dimethylaminomethyl- and 2-methyl-1-dimethylaminomethylnaphthalenes, respectively. The methiodide of the former tertiary amine failed to undergo with this reagent further rearrangement which would have involved the 3-position. The methiodide of 2-methyl-1-dimethylaminomethylnaphthalene underwent partly the first phase of the ortho substitution rearrangement to form an *exo*-methylenamine, and partly a Stevens type of 1,2-shift to give a β-arylethylamine. Mechanisms are considered.

The benzyltrimethylammonium ion (I) has previously[2] been rearranged by sodium amide in liquid ammonia to form tertiary amine II (96%), and the methiodide of this amine, further rearranged to give tertiary amine III (67%). Still further rearrangements around the aromatic ring have also been effected.[2]


I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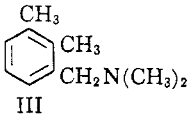
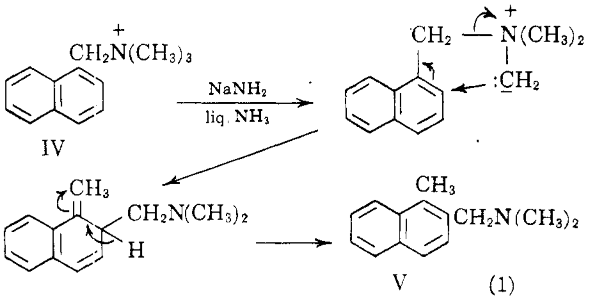

III

In the present investigation a study was made of this ortho substitution type of rearrangement in the naphthalene series. The 1-naphthylmethyltrimethylammonium ion (IV) underwent the rearrangement to form tertiary amine V in good yield. The mechanism for this reaction, which involves the β-position of the naphthalene nucleus, may be represented by equation 1.



(1)

Whereas the rearrangement of quaternary ion I was complete within a few minutes, that of IV proceeded much more slowly possibly because of the low solubility of the latter quaternary ammonium salt in the liquid ammonia. In Table I are summarized the yields of tertiary amine V obtained from IV on varying the time and equivalents of sodium amide. The maximum yield (75%) of V was realized after five hours employing two equivalents of sodium amide.

TABLE I

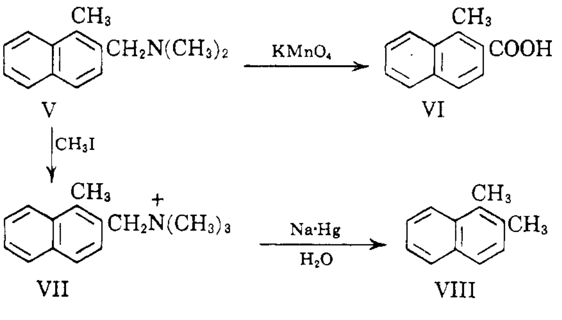
INFLUENCE OF TIME AND OF EQUIVALENTS OF SODIUM AMIDE ON YIELD OF AMINE V FROM QUATERNARY ION IV

$NaNH_2$, Equivalents[a]	Time, Hr.	Amine V, Yield, %	Recov. IV, %
2	1	29	61
2	3	68	27
2	5	75	17
2	8	71	6
1	3	53	31
1.3	3	62	27

[a] One equivalent of quaternary ion IV was 0.15 mole.

The structure of the rearranged amine was established as V by a permanganate oxidation to form 1-methyl-2-naphthoic acid (VI), and by an Emde reduction of the methiodide (VII) to give 1,2-dimethylnaphthalene (VIII) (Scheme A).

Scheme A



Whereas the methiodide of amine II in the benzene series was further rearranged to amine III, the methiodide of amine V (formula VII) apparently failed to undergo with sodium amide in liquid ammonia further rearrangement around the naphthalene ring. Instead of another distillable tertiary amine, only tarry material was obtained. This is not surprising in view of the well known

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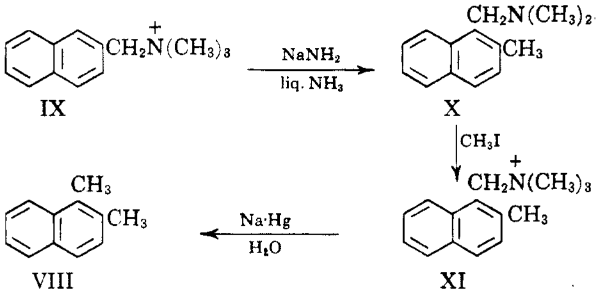
[1] Supported by the Office of Ordnance Research, U. S. Army and by Eli Lilly and Co.

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

deficiency in double bond character at the 2,3-position of the naphthalene nucleus.[3]

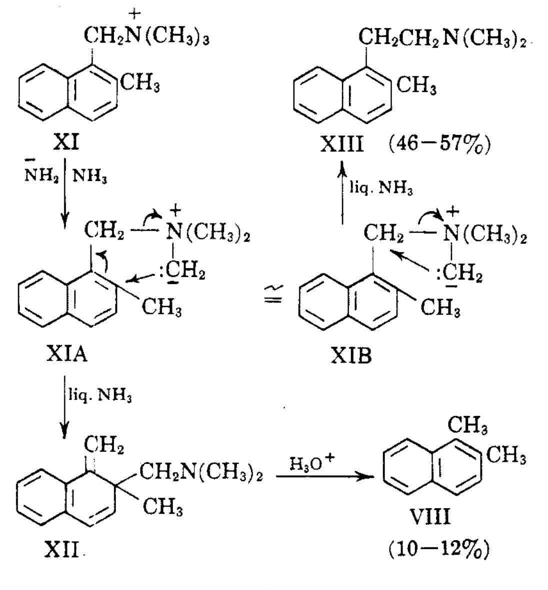
The 2-naphthylmethyltrimethylammonium ion (IX) underwent the *ortho* substitution rearrangement to form tertiary amine X in 84% yield. This rearrangement into the α-position of the naphthalene nucleus was anticipitated. The structure of the product was established by an Emde reduction of the methiodide (XI) to give 1,2-dimethylnaphthalene (VIII) (Scheme B).

Scheme B

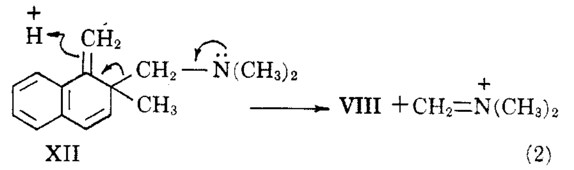


The methiodide of rearranged tertiary amine X (formula XI) underwent two courses of reaction with sodium amide in liquid ammonia, both courses involving the same intermediate carbanion XIA-B (Scheme C).

Scheme C

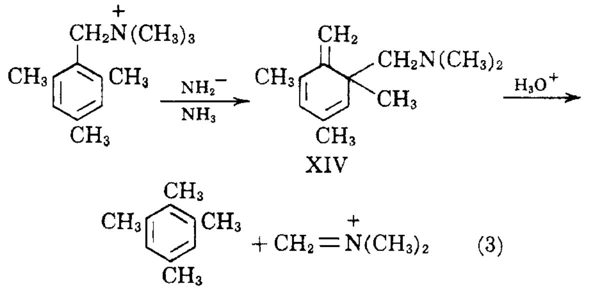


It can be seen from Scheme C that the intermediate carbanion rearranged partly to *exo*-methylenamine XII but mainly to β-arylethylamine XIII. The former product arose from a first-phase *ortho* substitution rearrangement (indicated in XIA) and the latter, from a Stevens type of 1,2-shift (indicated in XIB). The *exo*-methylenamine (XII) was identified by decomposition with hydrochloric acid to form 1,2-dimethylnaphthalene (VIII), the dimethylmethyleniminium ion being eliminated (Equation 2).



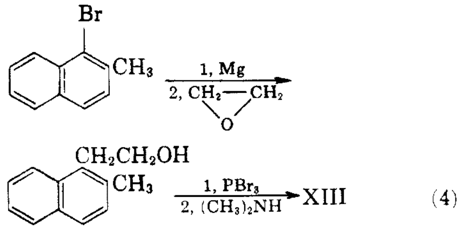
(2)

The formation of a similar *exo*-methylenamine (XIV) and its acid-induced decomposition has recently[4] been realized in high yields starting with the 2,4,6-trimethylbenzyltrimethylammonium ion (Equation 3).



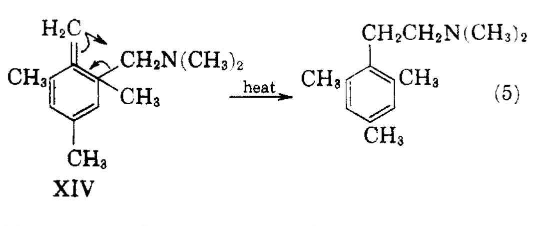
(3)

The β-arylethylamine (XIII), which was the main product from the rearrangement of quaternary ion XI (Scheme C), was identified by an independent synthesis from 2-methyl-1-bromonaphthalene (Equation 4).



(4)

It might appear that β-arylethylamine XIII arose from the thermal isomerization of *exo*-methylenamine XII during distillation, since such a thermal isomerization has been observed to occur readily with *exo*-methylenamine XIV (Equation 5).



(5)

However, whereas *exo*-methylenamine XIV underwent some thermal isomerization on distillation under reduced pressure even at 50°, *exo*-methylenamine XII appeared to undergo relatively little isomerization on distillation at 80–87° or at 137–145°. Moreover, the yield of β-arylethylamine XIII was not decreased when the ether solution of

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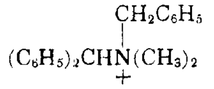
[3] See for example, R. C. Fuson, *Advanced Organic Chemistry*, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 600–603.

[4] C. R. Hauser and D. N. Van Eenam, *J. Am. Chem. Soc.*, **79**, 5512 (1957).

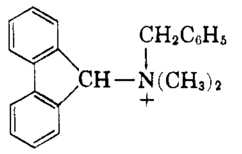
the reaction products from the rearrangement of quaternary ion XI was shaken with hydrochloric acid, and the products then distilled. In fact the best yield (57%) of XIII was obtained under these conditions, the yield of 1,2-dimethylnaphthalene (VIII) being only 12%. This treatment with acid undoubtedly converted all of *exo*-methylenamine XII to the latter product.

It should be pointed out that the Stevens type of 1,2-shift indicated in XIB predominates apparently because the first phase of the ortho substitution rearrangement is somewhat hindered. In fact 1,2-shifts have been observed[5] with sodium amide in liquid ammonia only with relatively complex quaternary ammonium ions such as XV and XVI; in these quaternary ions the benzhydryl and fluorenyl hydrogens are mainly ionized and the benzyl group is rearranged.



$(C_6H_5)_2CH\overset{CH_2C_6H_5}{\underset{+}{N}}(CH_3)_2$

XV



XVI

The 1,2-shift indicated in XIB appears to be the first example brought about by sodium amide in liquid ammonia in which the carbanion of a methyl group is involved. This carbanion is presumably present in equilibrium with a predominant carbanion, that resulting from the ionization of a methylene hydrogen of quaternary ion XI. The latter type of carbanion has been observed to undergo the Stevens 1,2-shift of a methyl group only at relatively high temperatures.[5]

EXPERIMENTAL[6]

1-Naphthylmethyltrimethylammonium chloride (IV). To a solution of 216.0 g. (1.22 mole) of 1-chloromethylnaphthalene, b.p. 128–140° at 5 mm. (reported b.p. 128–133° at 5 mm.),[7] in 500 ml. of absolute ethanol there was added with swirling 100 g. (1.69 moles) of liquid anhydrous trimethylamine during 30 min. The flask was immersed in an ice bath occasionally to minimize loss of trimethylamine. After standing at room temperature for 5 hr., 1 liter of anhydrous ether was slowly added to precipitate the quaternary ammonium chloride (IV), which was collected on a funnel, washed with ether, and dried *in vacuo* in a desiccator. The somewhat hygroscopic salt melted at 226–227°; yield 93%. Its picrate, after three recrystallizations from water, melted at 161–162°.

Anal. Calcd. for $C_{20}H_{20}N_4O_7$: C, 56.07; H, 4.71; N, 13.08. Found: C, 56.09; H, 4.71; N, 12.99.

Rearrangement of IV to 1-methyl-2-dimethylaminomethylnaphthalene (V). This reaction was carried out in a 1-l. three-necked flask equipped with a Dry Ice reflux condenser and sealed stirrer, the quaternary salt (IV) being kept dry by adding it from a 250-ml. Erlenmeyer flask connected to the third neck of the flask through Gooch tubing. The yields of rearranged tertiary amine V and of recovered quaternary salt IV on varying the time and equivalents of sodium amide are summarized in Table I. A typical experiment is described below.

To a rapidly stirred suspension of 0.30 mole of sodium amide in 500 ml. of liquid ammonia there was added during approximately 5 min. 35.4 g. (0.15 mole) of finely powdered quaternary salt IV. The resulting bright red reaction mixture, which gradually became deep blue during 3.5 hr., was stirred for 5 hr. and then decomposed by the addition of excess solid ammonium chloride. The liquid ammonia was evaporated on the steam bath as 600 ml. of dry ether was added. The resulting ether suspension was filtered, and the solvent removed from the filtrate. The residual oil was distilled *in vacuo* to give 22.3 g. (75%) of 1-methyl-2-dimethylaminomethylnaphthalene (V), b.p. 157–159° at 10 mm., n_D^{25} 1.5928 (leaving 1.7 g. of residue).

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.35; H, 8.54; N, 7.08.

The picrate, after three recrystallizations from 95% ethanol, melted at 190–190.5°.

Anal. Calcd. for $C_{20}H_{20}N_4O_7$: C, 56.07; H, 4.71; N, 13.08. Found: C, 56.17; H, 4.98; N, 13.38.

The solid obtained by filtration of the ether suspension described above was extracted twice with minimum amounts of hot acetonitrile, and the extracts were combined. Dry ether was added, and the resulting precipitate was collected on a funnel, and dried *in vacuo*. There was recovered 6.0 g. (17%) of crude quaternary salt IV, m.p. 212–214°.

Oxidation of amine V to form 1-methyl-2-naphthoic acid (VI). This reaction was carried out essentially as described previously[2] for the oxidations of polyalkylbenzyldimethylamines.

To 0.5 g. of amine V suspended in 15 ml. of water and 1.0 ml. of 15% sodium hydroxide there was added in small portions during 3 hr. 1.0 g. of finely powdered potassium permanganate. After stirring 2 hr. longer at room temperature, the reaction mixture was filtered. The clear filtrate was acidified to give 0.2 g. of 1-methyl-2-naphthoic acid (VI), m.p. 176–177.5°. One recrystallization from benzene raised the melting point to 178–178.5° (reported m.p. 178°).[8]

Methiodide of tertiary amine V (VII). To a solution of 12.4 g. (0.062 mole) of tertiary amine V in 50 ml. of absolute ethanol there was added with swirling 14.2 g. (0.10 mole) of methyl iodide, the flask being cooled occasionally by immersion in an ice bath. After standing at room temperature for 1 hr. (some crystalline product separated), 200 ml. of ether was added to precipitate the quaternary ammonium salt, which was collected on a funnel washed with ether, and dried *in vacuo*. There was obtained 20.2 g. (95%) of 1-methyl-2-naphthyl methyltrimethylammonium iodide (VII), m.p. 237–238°, dec., with darkening at 200°.

Anal. Calcd. for $C_{15}H_{20}NI$: C, 52.81; H, 5.92; N, 4.11. Found: C, 52.68; H, 5.99; N, 4.41.

Reduction of methiodide VII to form 1,2-dimethylnaphthalene (VIII). The general procedure of Emde[9] for the reduction of benzyl-type quaternary ammonium salts to hydrocarbons was followed.

To a stirred solution of 17.1 g. (0.05 mole) of 1-methyl-2-naphthylmethyltrimethylammonium iodide (VII) in 400 ml. of water heated on the steam bath, was added gradually (10 minutes) 200 g. of 5% sodium amalgam, and the stirring continued until all the sodium had reacted (*ca.* 12 hr.). After cooling, the oily reaction mixture was extracted with ether, dried, and the product distilled *in vacuo* to afford 7.5 g. (96%) of 1,2-dimethylnaphthalene (VIII), b.p. 138–

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

(6) Melting and boiling points are uncorrected. Microanalyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(7) O. Grummitt and A. Buck, *Org. Syntheses*, **24**, 30 (1944).

(8) F. Mayer and O. Schnecko, *Ber.*, **56**, 1408 (1923).

(9) H. Emde, *Ber.*, 42, 2590 (1909).

138.5° at 15 mm., n_D^{25} 1.6127 (reported b.p. 135–136° at 14 mm., n_D^{20} 1.6135).[10]

The picrate of this hydrocarbon, after crystallization from 95% ethanol, melted at 130.5–131° (reported m.p. 131°).[11]

2-Naphthylmethyltrimethylammonium chloride (IX). This salt was prepared in three steps in 71% over all yield from 2-naphthoic acid.

This acid (0.58 mole) was reduced with 0.725 mole of lithium aluminum hydride in 2 l. of ether employing the Soxhlet extractor as described by Nystrom and Brown.[12] After 6 hr., the reaction mixture was decomposed with water, followed by 20% sulfuric acid. One recrystallization of the product from ligroin (b.p. 60–90°) gave a 99% yield of 2-hydroxymethylnaphthalene, m.p. 80.5–81° (reported m.p. 80°).[13]

This carbinol (0.57 mole) was treated with 0.76 mole of thionyl chloride in 400 ml. of dry toluene (refluxed 3 hr.) to give a 73% yield of 2-chloromethylnaphthalene, b.p. 125–132° at 2 mm., m.p. 47–48° (reported b.p. 170° at 20 mm., m.p. 47°).[13]

A solution of 73.1 g. (0.41 mole) of this chloride in 750 ml. of absolute ethanol was treated with 75 g. (1.25 mole) of trimethylamine during 20 min., and the product precipitated with 1 l. of ether after several hours at room temperature, as described in the preparation of isomeric quaternary ammonium salt IV. There was obtained 94.3 g. (98%) of 2-naphthylmethyltrimethylammonium chloride (IX), m.p. 205–206°. The picrate of this somewhat hygroscopic salt, after three recrystallizations from water, melted at 160–161°.

Anal. Calcd. for $C_{20}H_{20}N_4O_7$: C, 56.07; H, 4.71; N, 13.08. Found: C, 56.03; H, 4.89; N, 13.10.

Rearrangement of IX to 2-methyl-1-dimethylaminomethylnaphthalene (X). This reaction was carried out with 94.3 g. (0.40 mole) of 2-naphthylmethyltrimethylammonium chloride (IX) and 0.80 mole of sodium amide in 1200 ml. of liquid ammonia (addition period, 20 min.) as described above for the rearrangement of IV. The resulting deep red reaction mixture, which gradually became blue-green, was decomposed with ammonium chloride after 2 hr. There was obtained 66.5 g. (84%) of 2-methyl-1-dimethylaminomethylnaphthalene (X), b.p. 152–153° at 10 mm., n_D^{25} 1.5927 (leaving 4.0 g. of residue).

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.59; H, 8.79; N, 6.92.

The *picrate*, recrystallized three times from 95% ethanol, melted at 204–205°.

Anal. Calcd. for $C_{20}H_{20}N_4O_7$: C, 56.07; H, 4.71; N, 13.08. Found: C, 56.23; H, 4.71; N, 13.09.

Also, there was recovered by means of acetonitrile extraction (see above) 7.8 g. (8%) of crude IX, m.p. 193–197°.

Methiodide of tertiary amine X (XI). This salt (m.p. 184–185°, dec., with darkening at about 150°) was obtained in 98% yield from 66.5 g. (0.334 mole) of 2-methyl-1-dimethylaminomethylnaphthalene (X) and 95 g. (0.67 mole) of methyl iodide in 200 ml. of absolute ethanol as described for VII. The melting point of the white, crystalline product was not raised by recrystallization from absolute ethanol-ether.

Anal. Calcd. for $C_{15}H_{20}NI$: C, 52.81; H, 5.92; N, 4.11. Found: C, 52.62; H, 6.16; N, 4.06.

Reduction of methiodide XI to form 1,2-dimethylnaphthalene (VIII). This reaction was carried out with 20.5 g. (0.06 mole) of methiodide XI and 250 g. of 5% sodium amalgam in 450 ml. of water as described for the reduction of methiodide VII. There was obtained 8.9 g. (95%) of 1,2-dimethylnaphthalene (VIII), b.p. 139–140° at 15 mm., n_D^{25} 1.6127. The picrate melted at 129.5–130.5°. This melting point was not depressed on admixture with the picrate of 1,2-dimethylnaphthalene obtained as described above.

Two courses of reaction of methiodide XI with sodium amide. Finely powdered quaternary ammonium salt XI (51.2 g., 0.15 mole) was rapidly added to a suspension of 0.30 mole of sodium amide in 700 ml. of liquid ammonia as described for the rearrangement of IV. The reaction mixture, which at first was grey-violet but soon changed to bright green, was decomposed after one hour with ammonium chloride and the ammonia replaced by absolute ether. The mixture was filtered, and the solvent removed from the filtrate. The residual oil was distilled through a 7-cm. Vigreux column to give 20.2 g. of distillate, b.p. 80–104° at 0.4 mm., leaving 8.7 g. of tarry residue. Fractionation of this distillate through a 40-cm. Podbielniak type column gave (*1*) 3.1 g., b.p. 137–145° at 10 mm., 80–87° at 0.4 mm., and (*2*) 14.8 g., b.p. 168–169° at 10 mm., n_D^{25} 1.5808. Fraction (2) was identified as 2-methyl-1-(β-dimethylaminoethyl)naphthalene (XIII); yield 46%.

Anal. Calcd. for $C_{15}H_{19}N$: C, 84.45; H, 8.98; N, 6.57. Found: C, 84.43; H, 9.16; N, 6.37.

The *picrate*, recrystallized three times from 95% ethanol, melted at 174.5–175.5°.

Anal. Calcd. for $C_{21}H_{22}N_4O_7$: C, 57.01; H, 5.01; N, 12.66. Found: C, 57.27; H, 5.17; N, 12.77.

Fraction (*1*) appeared to consist mostly of *exo*-methyleneamine XII (10%), since it gave with excess 12*N* hydrochloric acid during 12 hr. 2.0 g. (10%) of 1,2-dimethylnaphthalene (VIII), identified by its picrate, m.p. and mixed m.p. 129–130°. The acidified aqueous solution from the decomposition of XII evidently contained the dimethylmethyleniminium ion, since formaldehyde and dimethylamine were detected after hydrolysis with 50% sodium hydroxide.

The experiment was repeated with 34.1 g. (0.10 mole) of 2-methyl-1-naphthylmethyltrimethylammonium iodide (XI) and 0.20 mole of sodium amide in 500 ml. of liquid ammonia. After the ammonia had been replaced by ether and the precipitated salts removed by filtration, the ethereal solution of products was shaken with 200 ml. of 12*N* hydrochloric acid for 1 hr. Water was added and the two layers separated. The ethereal layer was washed with water and dried over magnesium sulfate, and the solvent was removed. The residue was distilled giving 1.8 g. (12%) of 1,2-dimethylnaphthalene (VIII), b.p. 127–129° at 10 mm., n_D^{25} 1.6129, leaving 1.1 g. of residue. This aromatic hydrocarbon was identified through its picrate, m.p. and mixed m.p. 129–130°.

The aqueous acid layer (and washings) was cooled and made alkaline with cold 50% sodium hydroxide solution (odor of formaldehyde detected). The resulting oil was taken up in ether, and the ethereal solution was washed with water and dried over magnesium sulfate. The solvent was evaporated and the residual oil distilled to give 12.1 g. (57%) of 2-methyl-1-(β-dimethylaminoethyl)naphthalene (XIII), b.p. 167–168.5° at 10 mm., n_D^{25} 1.5807, leaving 4.2 g. of dark residue. The picrate melted at 174–175°.

Independent synthesis of β-arylethylamine XIII. This amine was synthesized in three steps from 2-methyl-1-bromonaphthalene.

This halide[14] (33.2 g., 0.15 mole) was converted to its Grignard reagent with 3.8 g. (0.156 g.-atom) of magnesium turnings in 50 ml. each of dry ether and benzene (refluxed 1.5 hr.), and this reagent treated at −10° with 13.2 g. (0.30 mole) of ethylene oxide in 40 ml. of dry ether, following the directions of Wilds[15] for the preparation of β-1-naphthylethanol. After standing for 2 hr. at room tempera-

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(10) O. Kruber and W. Schade, *Ber.*, **68**, 11 (1935).

(11) R. P. Linstead, A. F. Millidge, S. L. S. Thomas and A. L. Walpole, *J. Chem. Soc.*, 1146 (1937).

(12) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2549 (1947).

(13) N. Campbell, W. Anderson, and J. Gilmore, *J. Chem. Soc.*, 819 (1940).

(14) See R. Adams and L. O. Binder, *J. Am. Chem. Soc.*, **63**, 2773 (1941).

(15) A. L. Wilds, *J. Am. Chem. Soc.*, **64**, 1421 (1942).

ture, the reaction mixture was decomposed with water and 6N hydrochloric acid. There was obtained 14.0 g. (50%) of 2-methyl-1-(β-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.[16] 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-(β-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-(β-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.

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[16] See P. Cagniant, C. Mentzer, and N. P. Buu-Hoï, *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[1]

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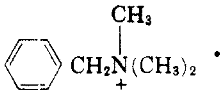
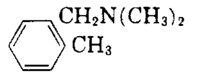
The methiodide of *N,N*-dimethylaminomethylferrocene was found to undergo with potassium amide in liquid ammonia a rather novel type of Stevens 1,2-shift involving the migration of the ferrocylmethylene group to form the β-ferrocylethylamine. The structure of the product was established by the conversion 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.[2]

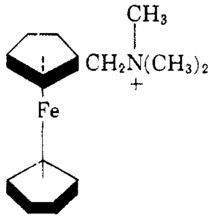


I

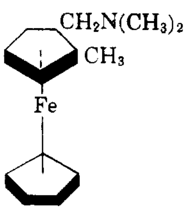


II

Since the ferrocene nucleus has been observed to possess certain aromatic properties,[3] the corresponding quaternary ammonium ion (III) in the ferrocene series might be expected to exhibit this type of rearrangement to form tertiary amine IV.

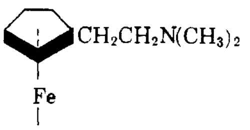


III



IV

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



V

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.[2]

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[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).