80.5°, obtained on recrystallization of this solid, were identified as 3,3′-biisoxazole.

Anal. Calcd. for $C_6H_4N_2O_2$: C, 53.0; H, 2.9; N, 20.6. Found: C, 53.8; H, 3.2; N, 20.7.

Bands in the infrared are at 3.17 μ (for =CH), 6.0 and 6.4 μ (for conjugated C=C and/or C=N), 7.15, 9.09, 9.64, 10.72, 10.93, and 12.71 μ (probably associated with isoxazole ring), 7.26 μ, 7.36 μ, 8.59 μ, 11.57 μ, and 12.87 μ (unassigned). The H^1 magnetic resonance spectrum for a 40% solution of I in $CDCl_3$ shows two kinds of hydrogen in a 1:1 intensity ratio. Each peak is split into a doublet. The chemical shifts from a benzene reference are −1.92 p.p.m. (H on C_4) and +0.20 p.p.m. (H on C_5). The J value is 2.0 ± 0.3 c.p.s. Oxidation of 3,3′-biisoxazole with acidic potassium permanganate by the method described by Quilico[3] gave an acid which melts at 149° and has a distribution ratio, ether/water, of 0.52. Quilico[3] reports 149° as the melting point of 3-isoxazolecarboxylic acid.

Anal. Calcd. for $C_4H_3NO_3$: N, 12.4; C, 42.5; H, 2.7; neut. equiv., 113. Found: N, 12.4; C, 42.3; H, 2.7; neut. equiv. 115.

The acid was converted to an amide by reaction with thionyl chloride and alcoholic ammonia. After recrystallization from ethanol, the product melted at 134–135° as compared with melting points of 143.5–144° (amide of 3-osoxazolecarboxylic acid) and 173–174° (amide of 5-isoxazolecarboxylic acid) reported by Quilico.[3]

The viscous, black distillation residue (4.3 g.) changed to a brittle resin on cooling. It was noted that a resin was obtained on redistillation of 3-cyanoisoxazole. In the redistillation there was a strong odor of hydrogen cyanide at the vacuum pump exhaust, and the amount of resinous product obtained corresponded to 10–12% of the original 3-cyanoisoxazole.

Acknowledgment. Helpful suggestions in connection with this work made by B. W. Howk are gratefully acknowledged.

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Notes A department for short papers of immediate interest.

ortho-Substitution Rearrangement of Benzyltrimethylammonium-benzyl-C^{14} Iodide

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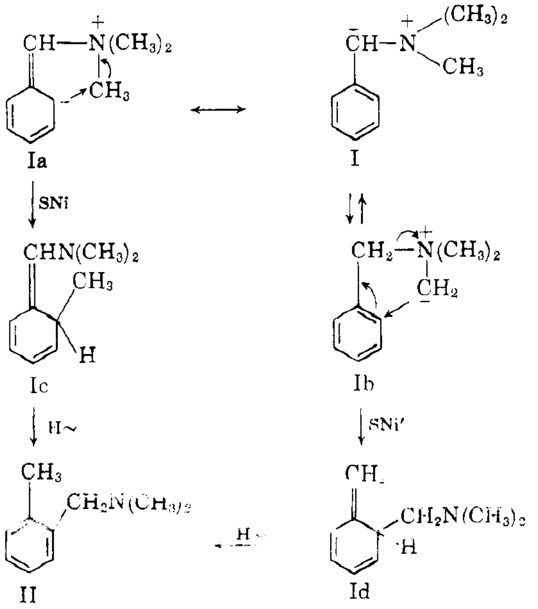
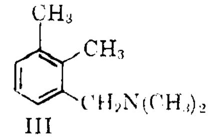
In the original paper[2] on the *ortho*-substitution rearrangement of benzyltrimethylammonium ion by amide ion in liquid ammonia, two mechanisms were considered (Scheme A). One involved an SNi displacement within resonance form Ia of the more predominant carbanion I, and the other SNi′ displacement within the less predominant carbanion Ib. The initial product in each mechanism underwent a prototropic shift to form the rearranged amine II.

Although these two mechanisms were not distinguished for the parent benzyltrimethylammonium ion, the SNi′ but not the SNi mechanism would account for the further rearrangement of the methiodide of amine II to form amine III, not IV[2]. Furthermore, rearrangement of the 2,4,6-trimethylbenzyltrimethyl ammonium ion[3] gave *exo*-methyleneamine V, corresponding to intermediate Id in Scheme A.

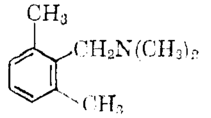
Evidence is now presented to show that the SNi′

SCHEME A

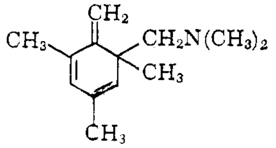




III



IV



V

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[1] National Science Foundation Co-operative Fellow, 1960–1961.

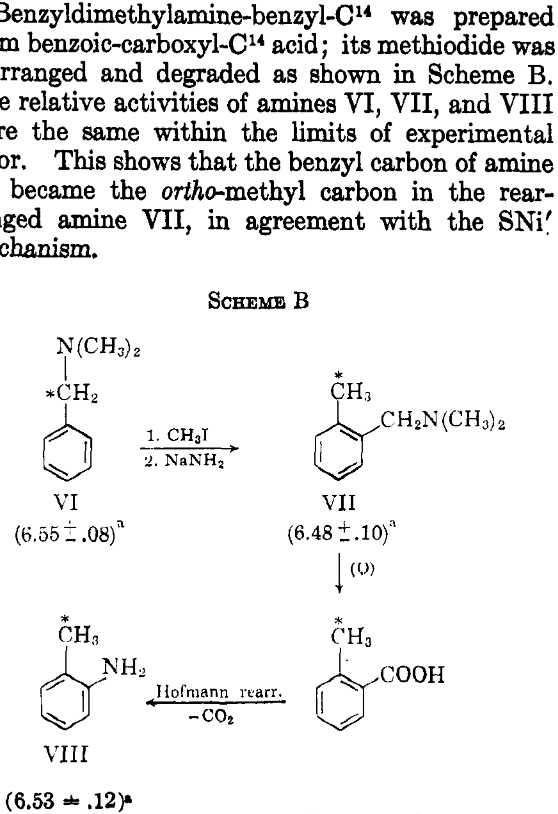
[2] S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, 73, 4122 (1951).

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

mechanism applies also to the rearrangement of the parent quaternary ion.

Benzyldimethylamine-benzyl-C^{14} was prepared from benzoic-carboxyl-C^{14} acid; its methiodide was rearranged and degraded as shown in Scheme B. The relative activities of amines VI, VII, and VIII were the same within the limits of experimental error. This shows that the benzyl carbon of amine VI became the *ortho*-methyl carbon in the rearranged amine VII, in agreement with the SNi′ mechanism.

SCHEME B



[a] Relative activities in counts min.$^{-1}$ mmole.$^{-1}$ × 10^{-4}.

While certain details of the mechanism of this rearrangement may still remain to be established, this result does confirm that the benzyl-carbon to nitrogen bond is broken, as in the SNi′ mechanism.

EXPERIMENTAL

Benzyltrimethylamine-benzyl-C^{14} (VI). This amine was prepared from 98.4 g. (0.82 mole) of benzoic-carboxyl-C^{14} acid (61 microcuries per mole) by reduction with lithium aluminum hydride, reaction with thionyl chloride, and reaction of the resulting benzyl chloride with excess dimethylamine in ether solution. The yield of VI, b.p. 178–179°, was 63.8 g. (58%).

The methiodide was obtained by treatment of 55.8 g. (0.41 mole) of VI with excess methyl iodide in 300 ml. of acetonitrile at room temperature for 12 hr. Slow addition of anhydrous ether precipitated 113 g. (99%) of the salt, m.p. 178–179°; lit.[5] m.p. 179°.

Rearrangement of the methiodide of VI *to form amine* VII. This salt (83.8 g., 0.30 mole) was added to a stirred slurry of sodium amide (0.35 mole) in 300 ml. of commercial anhydrous liquid ammonia. After 3 hr., the reaction mixture was neutralized with ammonium chloride and worked up as previously described.[3] Distillation gave 41.4 g. (93%) of VII, b.p. 73–74° at 9.5 mm.; lit.,[3] b.p. 80–80.2° at 14 mm.

Degradation of rearranged amine VII. Oxidation of this amine was effected under controlled conditions by a modification of the earlier procedure.[3]

To a stirred mixture of 29.9 g. (0.20 moles) of amine VII and 600 ml. of 0.50*N* sodium hydroxide immersed in an ice bath was added 121 g. of potassium permanganate in portions of 6 g. at 2-3-min. intervals. The exothermic reaction maintained a temperature of 15–20°. The mixture was stirred at 20° for 1 hr. After slow addition of 17 g. of sodium sulfite to destroy excess permanganate, the mixture was filtered through a mat of Hyflo Supercel to remove precipitated manganese dioxide. The filtrate was acidified to precipitate *o*-toluic acid, m.p. 85–88°. Recrystallization from 1:4 ethanol-water gave 15.8 g. (58%) of the acid, m.p. 104–105°; lit.,[6] m.p. 104°.

A solution of 15.7 g. (0.114 mole) of this acid in 40 ml. of thionyl chloride was refluxed for 8 hr., concentrated and distilled to give 17.0 g. (96%) *o*-toluyl chloride b.p. 101–102° at 20 mm.; lit.,[7] b.p. 110–111° at 29 mm.

A solution of 17.0 g. (0.110 mole) of this acid chloride in anhydrous ether was treated with excess gaseous ammonia to give, on evaporation and recrystallization of the residue from 150 ml. of water, 13.3 g. (89%) of *o*-toluamide, m.p. 140.5–141.5°; lit.,[8] m.p. 141–141.5°.

Hofmann rearrangement of this *o*-toluamide (13.3 g., 0.098 mole) by a standard procedure[9] gave 6.5 g. of *o*-toluidine (VIII), b.p. 90–95° at 17 mm. Careful redistillation gave 4.9 g. (47%) of colorless product, b.p. 95–97° at 23 mm.; lit.,[10] b.p. 121° at 80 mm.

Preparation of amine hydrochlorides for radioassay.[11] A 1.0-g. sample of each amine was dissolved in absolute ethanol, and excess ethanolic hydrogen chloride was added to each solution. The hydrochlorides were precipitated by slow addition of absolute ether.

Benzyldimethylamine hydrochloride, recrystallized four times from chloroform-hexane, melted at 174.5–175°; lit.[12]; m.p. 175°.

o-Methylbenzyldimethylamine hydrochloride, recrystallized four times from acetone-chloroform, melted at 206.5–207°.

o-Toluidine hydrochloride, recrystallized three times from chloroform, melted at 217–218°; lit.,[13] m.p. 215°.

Weighed samples of each amine hydrochloride were dissolved in 1.00 ml. of water, and each solution was dissolved in 10.0 ml. of a 6:1:1 dioxane–anisole–ethylene glycol dimethyl ether solution containing 6.0 g. per l. of a 40:1 mixture of 2,5-diphenyloxazole and 1,4-bis-2-(5-phenyloxazole) benzene. The activities of these solutions were determined, using a Packard "Tricarb" scintillation counter. Hydrochlorides of amines VI and VII were each assayed at four concentrations and that of amine VII at two. The results and standard deviations given in Scheme B were obtained.

Acknowledgment. We thank the Duke University Medical School Department of Biochemistry for the use of the scintillation counter, and Dr. E. A. Davidson for his assistance in making the determinations.

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[4] Melting points and boiling points are uncorrected.

[5] H. Emde, *Arch. Pharm.*, **247**, 351 (1909).

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(7) A. Klages and G. Lickroth, *Ber.*, **32**, 1549 (1899).

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(11) Accurate determinations of the activity of free *o*-toluidine and of salts containing iodide ion could not be obtained; these materials developed color in solution which partially quenched the internal scintillations. Pure *o*-toluidine hydrochloride developed color more slowly.

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Solid State Ultraviolet Spectra

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The ultraviolet spectra of organic solids can be obtained by studying single crystals,[2] by examining the powder sublimed or otherwise deposited onto quartz plates,[3] or absorbed onto silicic acid,[4] and by measuring the optical properties of a compacted sample in which the absorbing substance has been diluted with another material which is transparent in the spectral region being investigated.[5] This latter technique has been employed extensively in the infrared region but neglected in the ultraviolet, although it was proposed originally for both.

Recently we have found that the potassium bromide disk method is applicable to the study of organic compounds in the 220–400 mμ range. The spectra obtained from three widely divergent samples are shown in Figs. 1, 2, and 3, together with the corresponding solution spectra.

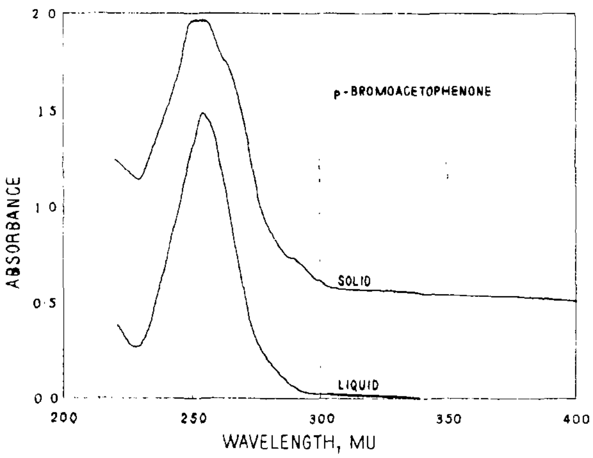

Figure 1

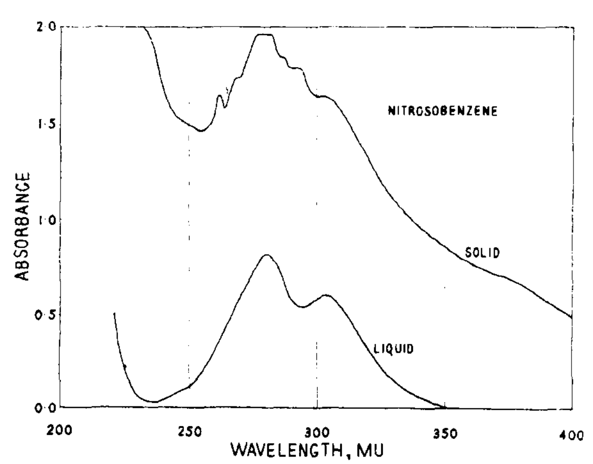

Figure 2

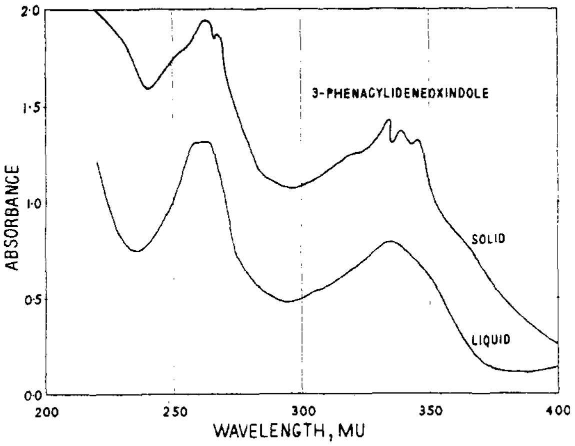

Figure 3

The principal advantages of this method are that (1) only extremely small quantities of sample are required; (2) sample preparation is easy and rapid; (3) sample disks can be filed for future reference; and (4) good quality spectra containing some fine structure are obtained. In addition, the spectra are free of solvent effects and should, therefore, be more amenable to theoretical interpretation.

EXPERIMENTAL

All melting points are uncorrected. Ultraviolet determinations were made with a Beckman DU quartz spectrophotometer.

p-Bromoacetophenone was obtained from Matheson, Coleman, and Bell, and was used without further treatment. It melted at 49–50° (lit.,[6] m.p. 49–50.5°).

Nitrosobenzene was prepared according to the directions of Vogel[7] and recrystallized three times from methanol to give an analytical sample, m.p. 67° (lit.,[8] m.p. 67.5–68°).

3-Phenacylideneoxindole was prepared by the method of Lindwall and Maclennan.[9] After recrystallization twice from ethanol, it melted at 193° (lit.,[9] m.p. 193–194°).

Sample preparation. A. Absolute ethanol solutions. Analytical solutions were prepared by standard volumetric techniques to give a final concentration of 0.02 mg. sample per ml. of absolute ethanol for all compounds examined. Absorption measurements on these solutions were made with 1 cm. silica cells using absolute ethanol as a blank.

B. Potassium bromide disks. Analytical grade potassium bromide and the sample compounds were separately ground in an agate mortar to approximately 200 mesh particle size. The appropriate weight of potassium bromide was taken and the desired weight of sample added directly, its weight being determined by difference from the weight of the mix-

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[1] (a) Present address: University of Tennessee, Knoxville, Tenn. (b) This paper is based on an M.S. dissertation by M.E.C., University of Georgia, 1959.

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