[Contribution from the Research Division of Armour and Company]

THE PREPARATION OF SOME MIXED DIALKYLAMINES

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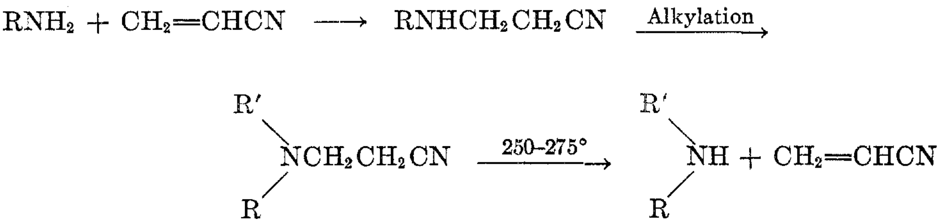
Received March 25, 1952

The method described herein permits preparation of certain mixed dialkylamines (*e.g.*, methyl, hydroxyethyl) from primary amines more conveniently or in better yields than other procedures (1–9). Addition of a primary amine to acrylonitrile yields the 2-cyanoethylalkylamine (10, 11, 12), which is alkylated (by the Wallach method or by ethylene oxide); the resulting 2-cyanoethyldialkylamine is cleaved thermally (2, 11, 13, 14) to yield the dialkylamine and acrylonitrile:



$$RNH_2 + CH_2{=}CHCN \longrightarrow RNHCH_2CH_2CN \xrightarrow{\text{Alkylation}}$$

$$(R')(R)NCH_2CH_2CN \xrightarrow{250\text{–}275^\circ} (R')(R)NH + CH_2{=}CHCN$$

The over-all yield is determined largely by the success of the alkylation step.

EXPERIMENTAL

2-Cyanoethyldodecylamine. To 92.5 g. (0.5 mole) of dodecylamine (N.E. 185) is slowly added 106 g. (1.0 mole) of acrylonitrile. The reaction temperature is maintained at abut 35° with a cold-water bath. The mixture is stirred for one-half hour, at 35°, after the final addition of the acrylonitrile, then refluxed at the boiling point for one hour, stripped under a vacuum, and the residue distilled. ("Pot" temperature should be kept below 160°). The 2-cyanoethyldodecylamine distills at 140° at 0.5 mm. in about 95% yield.

Methyldodecylamine. To a solution of 83.4 g. (0.35 mole) of 2-cyanoethyldodecylamine dissolved in a mixture of 50 cc. of methanol and 25 cc. of water, (containing 2 g. of sodium chloride) is slowly added 33.8 cc. of 85% formic acid solution. The temperature is now allowed to rise above 65°. Aqueous formaldehyde (29.8 cc. of a 36% aqueous solution) is added (the addition, and stirring, is stopped if the evolution of carbon dioxide becomes too vigorous) and the solution kept at about 50° for 3–4 hours. The solution is then cooled, neutralized with aqueous sodium hydroxide, and the upper amine layer separated and dried over K_2CO_3. The 2-cyanoethylmethyldodecylamine is pyrolyzed at 250–275° under slightly reduced pressure for 6 hours. Distillation gives 58.5 g. (84%) of N-methyldodecylamine of neutral equivalent 200 (theoretical is 199). Salicylaldehyde titration (15) shows no primary amine present. Infrared spectrophotometric analysis of the amine and the melting point of the acetate salt (53–54°) agree with those of a known sample of N-methyldodecylamine. The over-all yield is 80%.

2-Hydroxyethyldodecylamine. To 50 g. (0.21 mole) of 2-cyanoethyldodecylamine is added a solution of 11 cc. (0.22 mole) of ethylene oxide and 3.8 cc. (0.21 mole) of water in 150 cc. of methanol. The mixture is held at 40–45° for 4 hours and at 50° for 2½ hours. Removal of the solvent yields 58.3 g. (90%) of a product having a neutral equivalent of 283 (theoretical is 282). Pyrolysis of this intermediate and distillation of the product gives an 80% yield

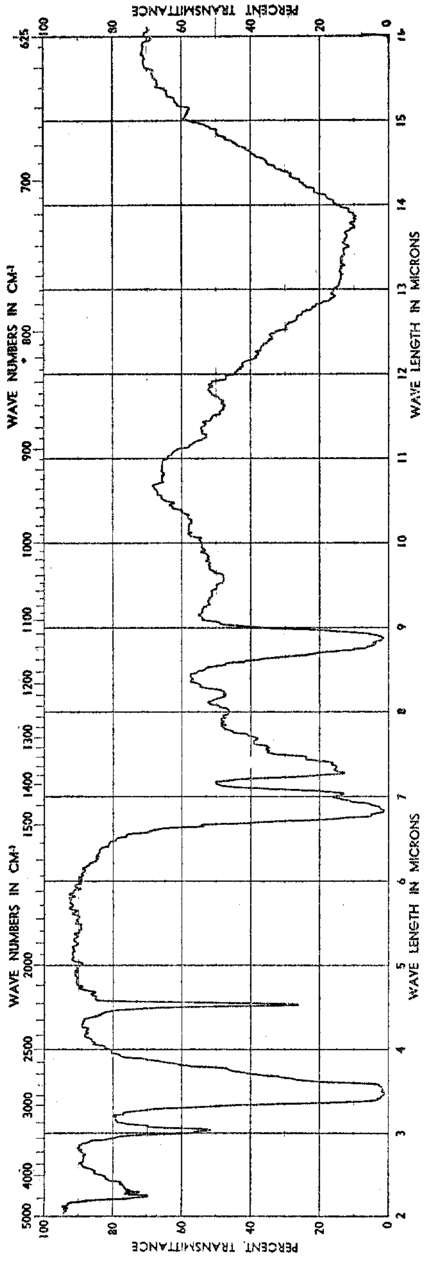


FIG. 1. INFRARED ABSORPTION SPECTRUM OF 2-CYANOETHYLDODECYLAMINE. Liquid in a 0.10-mm. cell.

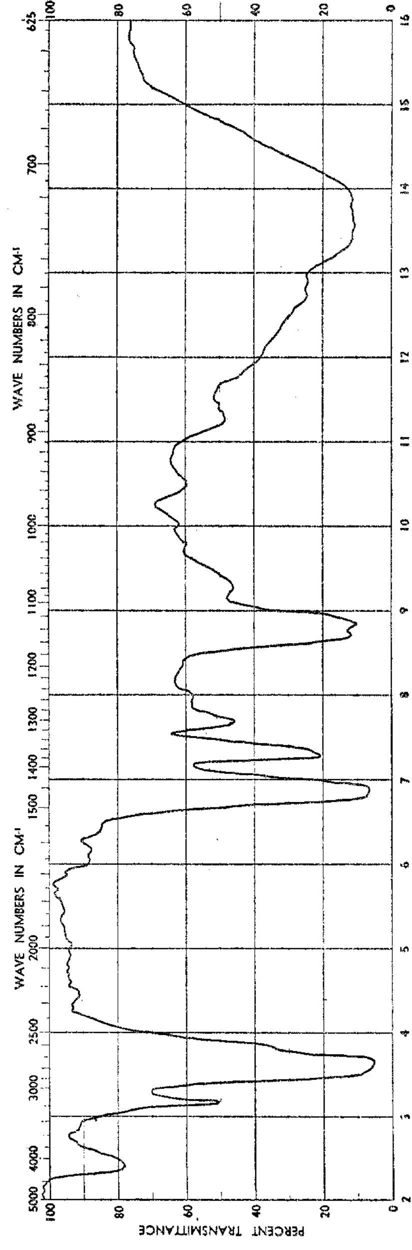


FIG. 2. INFRARED ABSORPTION SPECTRUM OF METHYLDODECYLAMINE. Liquid in a 0.10-mm. cell.

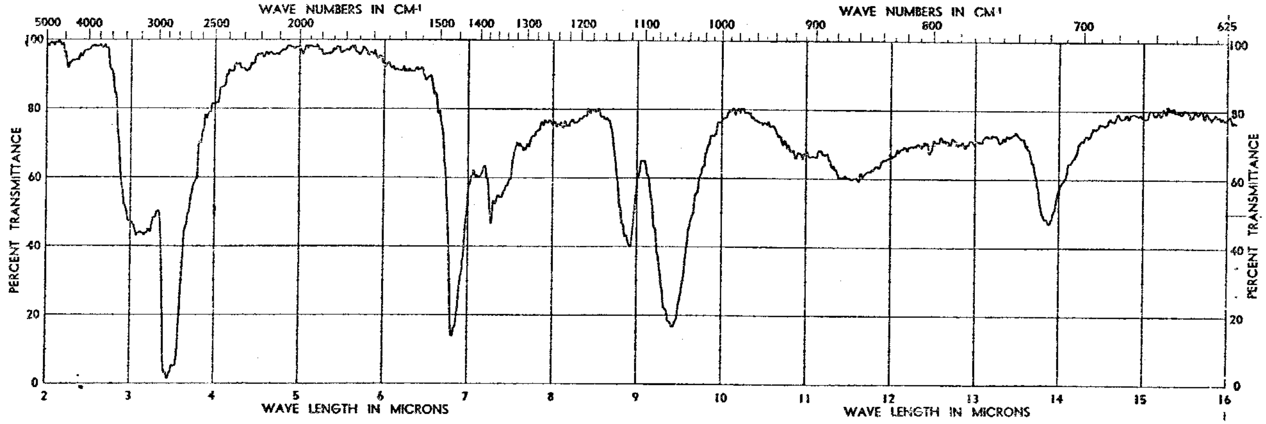


FIG. 3. INFRARED ABSORPTION SPECTRUM OF 2-HYDROXYETHYLDODECYLAMINE. Compound as a 10% chloroform solution in a 0.10-mm. cell.

(37.9 g.) of a white solid, 2-hydroxyethyldodecylamine, of neutral equivalent 233) theoretical is 229), f.p. 42.8°.

Methyl "tallow" amine.[1] 4-"Tallow" amine (200 g.; 0.72 mole) is treated with a 100% excess (76.5 g.) of acrylonitrile according to the procedure previously described. After removal of the excess acrylonitrile the residue is methylated without further purification, assuming quantitative conversion to the 2-cyanoethyl derivative, and pyrolyzed. Distillation of the pyrolysis product gives 167 g. of material, representing an 80% yield based on the primary amine. Salicylaldehyde titration indicates no primary amine. The neutral equivalent of the product is 289 (theoretical is 291) based on a N.E. of 277 for the primary amine.

Infrared absorption spectra have been used to determine the progress of the indicated reactions and the spectra of compounds prepared in this manner are shown in Figs. 1–3. These spectra were obtained[2] on a Baird Associates Model B spectrophotometer. Assignments of absorption bands are based upon published data (16).

In Fig. 1, the spectrum of 2-cyanoethyldodecylamine shows the C≡N band at 4.5 microns which together with the NH band at 3 microns and the C—N band at 8.9 microns characterizes this compound. Unreacted acrylonitrile may be detected at this stage by an additional band at 10.3 microns resulting from the C═C group.

In Fig. 2, the spectrogram for methyldodecylamine shows only the absorption bands characteristic of a long chain-methyl secondary amine. Successful pyrolysis of the intermediate tertiary amine is indicated by the absence of the 4.5 micron C≡N band.

The spectrum of 2-hydroxyethyldodecylamine, Fig. 3, shows the OH band at 3 microns, the C—N band at 8.9 microns, and the C—O of a primary OH at 9.4 microns. Polymerization of the ethylene oxide can be detected by a relative increase in the absorption at 8.9 microns where the C—O—C band overlies the C—N. Again the 4.5 micron band will determine the completeness of pyrolysis.

SUMMARY

A procedure has been described for the preparation of methyl- and 2-hydroxyethyl-alkylamines. This procedure involves the alkylation of 2-cyanoethyl-alkylamines followed by pyrolytic elimination of acrylonitrile.

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BIBLIOGRAPHY

(1) Hofmann, *Ber.*, **10**, 591 (1877).
(2) Schwoegler and Adkins, *J. Am. Chem. Soc.*, **61**, 3499 (1939).
(3) Hofmann, *Ann.*, **146**, 107 (1862).
(4) Nef, *Ann.*, **270**, 274 (1892).
(5) Baeyer and Caro, *Ber.*, **7**, 963 (1874).
(6) Mignonac, *Compt. rend.*, **172**, 275 (1921).
(7) Henze and Humphrey, *J. Am. Chem. Soc.*, **64**, 2878 (1942).
(8) Campbell, Sommers, and Campbell, *J. Am. Chem. Soc.*, **66**, 82 (1944).
(9) Buck and Baltzly, *J. Am. Chem. Soc.*, **63**, 1964 (1941).
(10) Holcomb and Hamilton, *J. Am. Chem. Soc.*, **64**, 1309 (1942).
(11) Hoffmann and Jacobi, U. S. Patent 1,992,615 (1935).
(12) Bruson, *Org. Reactions*, **5**, 79 (1949) Chapter 2, Cyanoethylation.
(13) Küng, U. S. Patent 2,401,429 (1946).
(14) Whitmore, Mosher, Adams, Taylor, Chapin, Weisel, and Yanko, *J. Am. Chem. Soc.*, **66**, 725 (1944).
(15) Wagner, Brown, and Peters, *J. Am. Chem. Soc.*, **69**, 2611 (1947).
(16) Colthup, *J. Optical Soc. Am.*, **40**, 397 (1950).

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[1] "Tallow" refers to the mixed alkyl groups derived from tallow fatty acids.

[2] The cooperation of Mr. A. E. Brake is gratefully acknowledged.