

Hofmann–Martius Rearrangement of *N*-Methylnaphthylinium Salts

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THE thermal rearrangement of *N*-alkylanilium salts into *C*-alkylated anilines has been extensively studied and is discussed in most texts covering aromatic rearrangements.¹ Interest in this Hofmann–Martius rearrangement continues^{2–4} but, in apparently the sole previous extension to naphthylamines, Heap⁵ reported that *N*-isopropyl-2-naphthylamine hydrochloride gave only propene and 2-naphthylamine on heating at 300° in a sealed tube. It might thus be wrongly inferred that nuclear alkylation does not occur with naphthylamines.

We have now prepared the hydrochlorides and

hydrobromides of both *N*-methyl-1- and *N*-methyl-2-naphthylamine. The parent amines were synthesised by reaction of methyl iodide with the sodium salts of the respective *N*-acetylnaphthylamines and subsequent removal of the acetyl group following a procedure⁶ used for related compounds. The benzoyl derivatives, hydrochlorides, and hydrobromides of the 1-isomer had melting points 121–122° (Lit.,⁷ 121°), 174–175°, and 188–189° respectively, and those of the 2-isomer, 84° (Lit.,⁸ 84°), 183–184° (Lit.,⁹ 182–183°) and 193–194°.

Decompositions were carried out by heating in

¹ See, for example, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N.Y., 1953, p. 615.

² H. Hart and J. R. Kosak, *J. Org. Chem.*, 1962, **27**, 116.

³ Y. Ogata, H. Tabuchi, and K. Yoshida, *Tetrahedron*, 1964, **20**, 2717.

⁴ M. J. Molera, J. M. Gaborra, and M. del Val Cob, *Anales Real Soc. Españ. Fis. Quím.*, 1959, **55**, B, 493; *ibid.*, 1961, **57**, B, 595; *ibid.*, 1963, **59**, B, 379.

⁵ T. Heap, *J. Chem. Soc.*, 1933, 495.

⁶ J. H. Billman and L. R. Caswell, *J. Org. Chem.*, 1951, **16**, 1041.

⁷ O. Hess, *Ber.*, 1885, **18**, 685.

⁸ G. T. Morgan and F. P. Evans, *J. Chem. Soc.*, 1919, **115**, 1140.

⁹ R. Pschorr and W. Karo, *Ber.*, 1906, **39**, 3140.

sealed tubes at 250° for 3 hours. The reaction mixtures were neutralised and, after chemical separation of the benzacridines formed, were distilled under reduced pressure and analysed by v.p.c. Components were identified by comparison of their retention times on two columns with authentic samples. Components present to more than 10%, based on the original amine, were separated by preparative v.p.c. and further characterised as their benzoyl derivatives.

It was found that nuclear-alkylated products could not be detected in the decompositions of either of the hydrochlorides. Thus, *N*-methyl-1-naphthylinium chloride gave 1-naphthylamine (18%), *N*-methyl-1-naphthylamine (30%), *NN*-dimethyl-1-naphthylamine (5%) and 1,2,8,9-dibenzacridine (27%); percentages are molar amounts based on the quantity of material decomposed. The 2-isomer gave 2-naphthylamine (19%),

N-methyl-2-naphthylamine (35%), and 3,4,6,7-dibenzacridine (20%). By contrast *N*-methyl-1-naphthylinium bromide gave 1-naphthylamine (23%), *NN*-dimethyl-1-naphthylamine (4%), *N*-methyl-1-naphthylamine (15%), 4-methyl-1-naphthylamine (7%), 2-methyl-1-naphthylamine (20%), and 1,2,8,9-dibenzacridine (8%) under identical conditions. The isomeric 2-derivative gave 2-naphthylamine (15%), *N*-methyl-2-naphthylamine (24%), 1-methyl-2-naphthylamine (31%), and 3,4,6,7-dibenzacridine (12%).

That only the hydrobromides should give *C*-alkylated products under these conditions is in accord with recent work³ on the rearrangement of *N*-methylanilinium salts. It was then suggested that the attacking intermediate was the alkyl halide which has been isolated in such systems.

(Received, September 23rd, 1965; Com. 605.)