81. *The Nuclear Alkylation of Aromatic Bases. Part IV. The Action of* n-*Dodecyl Alcohol on the Hydrochlorides of α- and β-Naphthylamine.*

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The action of *n*-dodecyl alcohol on β-naphthylamine hydrochloride at elevated temperatures gave didodecylamine, didodecyl ether, dodecene, N-*dodecyl*-β-*naphthylamine*, β-naphthol, and di-β-naphthylamine. In the corresponding reaction with α-naphthylamine hydrochloride only didodecylamine, didodecyl ether, dodecene, and α-naphthol were isolated. In neither case was any evidence of nuclear alkylation detected. It is suggested that the relative ease with which the higher aliphatic alcohols lose water renders them unsuitable for use in the Hofmann–Martius reaction.

The action of methyl alcohol at elevated temperatures on the hydrochlorides of bases of the benzene (Part I, J., 1931, 1581), diphenyl (Part II, J., 1934, 645), and naphthalene series (Part III, J., 1936, 1783) has already been investigated. The action of a long-chain alcohol, *n*-dodecyl alcohol, on the hydrochlorides of α- and β-naphthylamine is now described. Alcohols other than methyl alcohol have been used in this reaction with bases of the benzene series, *e.g.*, ethyl alcohol (Hodgkinson and Limpach, J., 1892, **61**, 420) and *iso*butyl alcohol (Effront, *Ber.*, 1884, **17**, 419, 2317). In reactions with a primary aromatic amine in presence of zinc chloride, ethyl alcohol (Benz, *Ber.*, 1882, **15**, 1646), *n*- and *sec.*-butyl alcohol (Reilly and Hickinbottom, J., 1920, **117**, 103), and amyl alcohol (Calm, *Ber.*, 1882, **15**, 1642) have been used (of. Hofmann, *Ber.*, 1874, **7**, 526). In the closely related reaction in which nuclear alkylation is effected by the action of heat on a monoalkylaniline in presence of certain metallic halides Hickinbottom and his collaborators have successfully employed alkylanilines derived from many alcohols from ethyl to *n*-octyl, including also *n*-dodecyl and cetyl alcohols (J., 1927, 64; 1930, 1558, 1566; 1931, 1281; 1932, 2396; 1937, 404, 1119). Nuclear alkylation of bases of the benzene series with long-chain alcohols has been described in B.P. 468,226 (Coffey, Haddock, and Imperial Chemical Industries Ltd., *Brit. Chem. Abstracts*, 1937, *B*, 1023).

In the reactions between *n*-dodecyl alcohol and the hydrochloride of both α- and β-naphthylamine no evidence was obtained of the entry of a dodecyl group into the naphthalene nucleus. With three molecular proportions of *n*-dodecyl alcohol and β-naphthylamine hydrochloride at 220° in an open vessel, or at 240—260° in an autoclave, the product consisted of a mixture from which didodecylamine, didodecyl ether, dodecene, N-*dodecyl*-β-*naphthylamine*, β-naphthol, and di-β-naphthylamine were isolated; in the former experiment more *N*-dodecyl-β-naphthylamine was formed than didodecylamine, but in the latter the reverse was the case. In the corresponding reaction with α-naphthylamine hydrochloride carried out in the autoclave at 240—260°, the product contained a high proportion of tarry matter: didodecylamine, didodecyl ether, dodecene and α-naphthol were isolated, but neither *N*-dodecyl-α-naphthylamine nor di-α-naphthylamine was detected (cf. Part III, *loc. cit.*).

The formation in these reactions of dodecene and didodecyl ether by elimination of one molecular proportion of water from one and two molecular proportions of *n*-dodecyl alcohol respectively takes place when the alcohol alone is heated at 250° in presence of hydrogen chloride, but it is possible that the dodecene may also be produced in part by the action of heat on *N*-dodecylnaphthylamine hydrochloride, since Heap (J., 1933, 495) has shown that the action of heat on *N*-*iso*propyl-β-naphthylamine hydrochloride gives propylene. The failure to detect nuclear alkylation in these reactions in the naphthalene series may be due in part to the relative ease with which water is lost by the long-chain alcohol. It is thus probable that the Hofmann–Martius reaction, in which nuclear alkylation is effected by heating the salt of an aromatic amine with an aliphatic alcohol, is less suitable for long-chain alcohols than the alternative reaction effected by the action of heat on an alkylarylamine in presence of a metallic salt (Hickinbottom and co-workers, *locc. cit.*). Even in the case of the relatively simple *iso*propyl group, however, Heap (*loc. cit.*) was unable to detect any migration due to the action of heat on *N*-*iso*propyl-β-naphthylamine hydrochloride.

EXPERIMENTAL.

In the following experiments, except where otherwise stated, an electrically heated Monel metal autoclave of 250 c.c. capacity was used, the reaction mixture being contained in an open close-fitting Pyrex vessel within the autoclave (cf. Parts I and II, *locc. cit.*).

Action of n-*Dodecyl Alcohol on* α-*Naphthylamine Hydrochloride.*—The hydrochloride (1 mol.; 32·2 g.) and *n*-dodecyl alcohol (m. p. 22°; 3 mols., 100 g.) were heated in the autoclave for 20 hours at 240—260°. The product was extracted with hot benzene (600 c.c.), which, on cooling, deposited a yellow solid (6 g.). This was removed, and the filtrate extracted with 10% aqueous sodium hydroxide (500 c.c.), then washed with water, and finally extracted with 15% hydrochloric acid (500 c.c.) (residual benzene solution = A_1). The yellow solid deposited from the benzene extract yielded on treatment with aqueous sodium hydroxide a base, which after several crystallisations from 95% alcohol gave didodecylamine, m. p. 55—56° (Found : C, 82·2; H, 14·1. Calc. for $C_{24}H_{51}N$: C, 81·6; H, 14·4%). Treatment with hydrochloric acid gave the hydrochloride, m. p. 204—205°. Wojcik and Adams (*J. Amer. Chem. Soc.*, 1934, **56**, 2419) record m. p. 55—56° and m. p. 207—208° respectively (cf. Wibaut, Heierman, and Wagtendonk, *Rec. Trav. chim.*, 1938, **57**, 456; D.R.-P. 648,088, *Chem. Zentr.*, 1936, I, 3216). Acidification of the alkaline extract precipitated α-naphthol (4 g.), which separated from light petroleum (b. p. 40—60°) in needles, m. p. and mixed m. p. 93—94°. The acid extract was made alkaline with aqueous sodium hydroxide, but no basic material was precipitated and extraction with ether yielded only a minute residue. The residual benzene solution (A_1) was washed with water and distilled, giving (a) b. p. 220—250° (5 g.), (b) b. p. 250—290° (7 g.), and (c) b. p. 290—360° (2 g.). Fraction (a) was devoid of nitrogen, was unsaturated and did not solidify at 0°. It was regarded therefore as consisting largely of Δ^{α}-dodecene, for which Krafft (*Ber.*, 1883, **16**, 3020) recorded b. p. 96°/15 mm. Fraction (b) solidified in the refrigerator and consisted of unchanged *n*-dodecyl alcohol (m. p. and mixed m. p. 20—22°). Fraction (c) partly solidified and on filtration gave didodecyl ether, which separated from aqueous alcohol in white plates, m. p. 32·5—33° (Found : C, 81·6; H, 14·0. Calc. for $C_{24}H_{50}O$: C, 81·4; H, 14·1%). Mannich and Nadelmann (*Ber.*, 1930, **63**, 796) recorded m. p. 32·5° The oily filtrate from (c) together with the residue from the distillation was distilled at 13 mm., giving (d) b. p. 240—300° (10·5 g.), and (e) b. p. 300—350° (4 g.). A considerable non-volatile tarry residue remained. Fraction (d) solidified on cooling and crystallisation from dilute alcohol gave didodecyl ether, m. p. 31—32°. Fraction (e) consisted of a dark neutral oil which remained unidentified.

Action of n-*Dodecyl Alcohol on* β-*Naphthylamine Hydrochloride.*—(i) The procedure was the same as that described in the case of α-naphthylamine hydrochloride. During the extraction with 15% hydrochloric acid a yellow hydrochloride separated (3 g.); this was removed, the filtrate again extracted with hydrochloric acid, and the acid extracts combined (residual benzene solution = A_2). The yellow solid (7·5 g.) deposited from the original benzene extract was boiled with aqueous sodium hydroxide; the liberated didodecylamine, after several crystallisations from 95% alcohol, had m. p. 55—56° both alone and in admixture with the specimen obtained in the reaction with α-naphthylamine hydrochloride. The alkaline extract was acidified; extraction with ether then removed β-naphthol (0·5 g.), m. p. and mixed m. p. 119—120° (picrate, orange needles from aqueous alcohol, m. p. and mixed m. p. 155—156°). The hydrochloride which separated during the acid extraction of the benzene solution was boiled under reflux with aqueous sodium hydroxide. N-*Dodecyl*-β-*naphthylamine*, which separated on cooling, crystallised from 95% alcohol in plates, m. p. 41·5—43·5° (Found : C, 84·4; H, 10·5. $C_{22}H_{33}N$ requires C, 84·8; H, 10·6%). It could not be diazotised. The acid extract was made alkaline with aqueous sodium hydroxide; ether then extracted β-naphthylamine (0·2 g.), m. p. (after crystallisation from aqueous alcohol) and mixed m. p. 109—110°. The residual benzene solution (A_2) was washed with water, dried, and distilled, giving (a) b. p. 220—250° (8 g.), (b) b. p. 250—280° (7 g.), and (c) b. p. 280—360° (3 g.). Fraction (a) contained no nitrogen, was unsaturated, and would not solidify at 0°; it was regarded as Δ^{α}-dodecene. Fraction (b), which solidified, consisted of *n*-dodecyl alcohol, m. p. (after crystallisation from aqueous alcohol) and mixed m. p. 22°. Fraction (c), on cooling, deposited didodecyl ether, m. p. (after crystallisation from aqueous alcohol) and mixed m. p. 32·5—33°. The filtrate from fraction (c) together with the residue from the distillation was distilled at 13 mm., giving (d) b. p. 200—300° (10 g.) and (e) b. p. 300—340° (4 g.). Fraction (d), on cooling, deposited more didodecyl ether together with some di-β-naphthylamine m. p. (after crystallisation from benzene) and mixed m. p. 169° (picrate, m. p. 164°). Fraction (e) was not identified.

(ii) β-Naphthylamine hydrochloride (1 mol.; 13 g.) and *n*-dodecyl alcohol (3 mols.; 40 g.) were heated (air-condenser) in an oil-bath at 220° for 8 hours. The product was extracted with ether, during which didodecylamine (1·0 g.), m. p. 55—56°, separated, and the ethereal extract was washed successively with 10% aqueous sodium hydroxide and 15% hydrochloric acid (residual ethereal solution = A_3). During the acid washing a yellow hydrochloride (7·0 g.) again separated, from which *N*-dodecyl-β-naphthylamine, m. p. 41—43°, was obtained. Acidification of the alkaline extract liberated a small quantity of β-naphthol, but the acid extract contained only a negligible quantity of basic material. The residual ethereal solution (A_3) was dried and evaporated, and the residue distilled at 13 mm., giving (a) b. p. 145—165° (10 g.), (b) 245—270° (5·0 g.), and (c) 270—320° (4 g.). Fraction (a) consisted of a mixture of Δ^{α}-dodecene and *n*-dodecyl alcohol, (b) largely of didodecyl ether, and (c) of didodecyl ether and di-β-naphthylamine, all these products being isolated and identified as previously described. The tarry residue left after the distillation was not examined.

Didodecyl Ether.—*n*-Dodecyl alcohol (100 g.) containing dry hydrogen chloride (4 g.) was heated in the autoclave at 250° for 16 hours. The product was extracted with benzene, dried, and distilled, giving a mixture of Δ^{α}-dodecene and *n*-dodecyl alcohol (35 g.), b. p. 210—240°, *n*-dodecyl alcohol (30 g.), b. p. 250—260°, and a third fraction (12 g.), b. p. 260—340°, consisting largely of didodecyl ether. The residue on distillation at 11 mm. gave a fraction (8 g.), b. p. 200—280°, which yielded a further quantity of didodecyl ether. The total yield of the ether, obtained in white plates, m. p. 32°, from aqueous alcohol, was 16 g.

Thanks are due to Imperial Chemical Industries Ltd. (Dyestuffs Group) for the gift of *n*-dodecyl alcohol.

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[*Received, January 8th,* 1940.]