124. *The Action of Heat on β-Naphthylisopropylamine Hydrochloride.*

By Tom Heap.

In an attempt to prepare 1-*iso*propyl-2-naphthylamine by the action of heat on β-naphthyl-*iso*propylamine hydrochloride, the anticipated migration of the *iso*propyl group did not occur, propylene was evolved, and β-naphthylamine was obtained. At 300—320° complete decomposition occurred in 6 hours; but at 200—220° the percentage of the primary amine in the product increased during 9 hours and decreased on longer heating, di-β-naphthylamine being obtained in increasing amounts. Klopsch (*Ber.*, 1885, **18**, 1585) noticed the ease of formation of di-β-naphthylamine when hydrogen chloride was passed into molten β-naphthylamine at 170—190°, and the compound has now been obtained by heating β-naphthylamine hydrochloride in a sealed tube at 200—220° or higher temperatures.

The study is being extended to other *N*-alkylnaphthylamines.

β-*Naphthyliso**propylamine***.—β-Naphthylamine (20 g.), *iso*propyl bromide (14·5 c.c.; 1·1 mols.), and *iso*propyl alcohol (20 c.c.) were heated in a sealed tube at 180° for 6 hr., the product decomposed with hot conc. NaOH aq., and the bases extracted with Et_2O, dried (K_2CO_3), and distilled. The fraction (22 g.), b. p. 160—165°/10 mm., was almost pure β-naphthyl*iso*propylamine, a colourless liquid, b. p. 307—310°/760 mm., which rapidly darkened in the air. The *benzoyl* derivative formed short colourless prisms (from EtOH), m. p. 96—98° (Found : C, 83·1; H, 6·7. $C_{20}H_{19}ON$ requires C, 83·0; H, 6·6%), and the p-*toluenesulphonamide* colourless needles (from EtOH), m. p. 119—120° (Found : C, 70·8; H, 6·3. $C_{20}H_{21}O_2NS$ requires C, 70·8; H, 6·2%). The *hydrochloride*, obtained by cooling a solution of the base in boiling dil. HCl, formed pale pinkish needles, m. p. 209—210° (Found : C, 70·3; H, 7·0; Cl, 15·9. $C_{13}H_{15}N,HCl$ requires C, 70·4; H, 7·2; Cl, 16·0%); after two recrystns., it gave no reaction for primary amine and was used in the following expts.

Action of Heat on β-*Naphthyliso**propylamine Hydrochloride***.—In each expt. the hydrochloride (5 g.) was heated in a sealed tube during 1·5 hr. to the required temp., which was maintained for a definite time. The press. developed was greater the higher the temp. and the longer the time of heating. The gas produced smelled of propylene and burned with a smoky flame. The contents of the tube were extracted with boiling dil. HCl, the solution filtered into a tared dish and evaporated, and the residue dried to const. wt. at 110°. The primary amine in the product was determined by diazotisation, coupling with an excess of *N*/20-R-salt, and titration of the excess with *N*/20-diazobenzene. The results obtained at 200—220° were :

Hrs. of heating	4	6	9	13	16	24	37
Yield (sol. in HCl aq.), g.	4·4	4·6	4·7	2·7	2·3	2·0	2·4
% Primary amine in product (as $C_{10}H_7{\cdot}NH_2,HCl$)	13·5	20·0	34·3	31·2	29·4	10·9	8·0

Erratic yields were often obtained, probably owing to the formation of tar, which rendered extraction difficult, but the results obtained for the percentage of primary amine in the product were reproducible.

Identification of the Primary Amine in the Product.—The combined products from a number of expts. (10·3 g.; primary amine content, as $C_{10}H_7{\cdot}NH_2,HCl$, 15·9%) were treated with *p*-toluenesulphonyl chloride (10 g.) and pyridine (10 c.c.). The product pptd. by H_2O (15 g.) was boiled with dil. HCl to remove tertiary amine—only a trace of tarry matter was removed—and then with dil. NaOH aq. to dissolve the *p*-toluenesulphonyl derivatives of primary amines. On acidification the alkaline extract gave a pinkish solid (2·1 g.), m. p. 130—131°, unchanged on admixture with *p*-toluenesulphon-β-naphthalide, m. p. 133°. Fractional crystn. did not separate any other product. The residue insol. in NaOH aq. was *p*-toluenesulphon*iso*propyl-β-naphthalide, m. p. 119—120°, unchanged on admixture with an authentic specimen.

*Di-*β*-naphthylamine*.—The product insol. in dil. HCl, on recrystn. from C_6H_6, gave leaflets, m. p. 167° (Ris, *Ber.*, 1887, **20**, 2618, gives m. p. 171° for di-β-naphthylamine). The picrate formed red-brown hair-like crystals (from C_6H_6), m. p. 165° (Benz, *Ber.*, 1883, **16**, 17, gives m. p. 164—165°).

β-Naphthylamine hydrochloride, heated for 6 hr. in a sealed tube at 200—220° or higher temps., gave a product which crystallised from C_6H_6 in leaflets, m. p. 167° (picrate, m. p. 165°). These two compounds were identical with those described above.

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