119. *The Preparation of Chloromethylnaphthalenes and* 1 : 5-*Dimethylnaphthalene.*

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BLANC (*Bull. Soc. chim.*, 1923, **33**, 313) states that 1-chloromethylnaphthalene may be obtained in 54% yield by the interaction of paraform, naphthalene, and hydrogen chloride. We obtained only *ca.* 11% under his conditions, but 42% by a modification of the method. The conversion of 1-chloromethylnaphthalene into 1-naphthaldehyde, 1-methylnaphthalene, and di(chloromethyl)naphthalenes is now recorded. The dichloro-product is a mixture of isomerides containing 1 : 5-di(chloromethyl)naphthalene, since 1 : 5-dimethylnaphthalene may be obtained from it by reduction, and naphthalene-1 : 5-dicarboxylic acid by oxidation. This heteronuclear substitution in presence of an *o,p*-orienting group is probably due to partial deactivation of the adjacent nucleus by the chlorine atom.

1-*Chloromethylnaphthalene*.—Paraform (40 g.), $C_{10}H_8$ (300 g.), powdered $ZnCl_2$ (9 g.), and petroleum (b. p. *ca.* 100°; 250 g.) are stirred at 55—65° while dry HCl is passed in for 10—12 hr. The product is rapidly washed with H_2O and dried and the hydrocarbons are removed at 30—40 mm. 1-Chloromethylnaphthalene (100 g., m. p. 32° : picrate, yellow needles, m. p. 84°) distils at 130—132°/4 mm., followed by a small quantity of di(chloromethyl)naphthalenes, b. p. 180—185°/4 mm., and some 1 : 1′-dinaphthylmethane (m. p. 109°) at 245—250°/4 mm.

Sodium 1-naphthylmethanesulphonate, obtained in 60% yield by boiling 1-chloromethylnaphthalene (30 g.), sodium sulphite (42 g.), NaOH (4 g.), and H_2O (42 g.) for 3 hr., separates from EtOH in white flakes; on distillation with NaOH it gives a very small yield of 1-methylnaphthalene (b. p. 100—105°/10 mm. : picrate, m. p. 141°).

1-*Methylnaphthalene*.—Reduction of chloromethylnaphthalene with Na (4 atoms) and EtOH is incomplete and yields a mixture of methylnaphthalene and hydromethylnaphthalenes. The latter may be dehydrogenated by heating to 220° with S. A 68% yield of methylnaphthalene is obtained by adding Zn needles (10 g.) to a well-stirred solution of the chloro-compound (10 g.) in EtOH (50 c.c.) and passing dry HCl at 0° until the metal has dissolved.

(1-*Naphthylmethyl*)*aniline*.—Chloromethylnaphthalene (10 g.) and $PhNH_2$ (11 g.) at 100° furnish (1-naphthylmethyl)aniline (b. p. 210—215°/3 mm., m. p. 67°) in 77% yield. The nitrosoamine separates from ligroin in colourless plates, m. p. 57°. Oxidation of the amine with $KMnO_4$ in acetone at 0° gives naphthylideneaniline (m. p. 69°) in very small yield. The Schiff base is smoothly hydrolysed to naphthaldehyde.

1-*Naphthaldehyde*.—1-Chloromethylnaphthalene (10 g.), hexamine (8 g.), and 95% EtOH (100 c.c.) furnish 1-naphthaldehyde (b. p. 149—152°/13 mm. : semicarbazone, m. p. 224°) in 60% yield when heated to boiling for 4·5 hr.

Di(*chloromethyl*)*naphthalene*.—1-Chloromethylnaphthalene (36 g.), petroleum (b. p. 100—120°; 50 g.), paraform (8 g.), and powdered $ZnCl_2$ (2 g.) are maintained at 60—65° for 6 hr. during the passage of dry HCl. Most of the product separates on cooling and may be washed with H_2O and recrystallised from EtOH (yield, 57%). The material (Found : Cl, 30·8. $C_{12}H_{10}Cl_2$ requires Cl, 30·6%) melts indefinitely at 130—145° and the isomerides present cannot be separated by crystn. The crude picrate melts indefinitely and decomposes on recrystn. Oxidation with alkaline ferricyanide under the conditions employed by Weissgerber and Krüber (*Ber.*, 1919, **52**, 352) for the oxidation of dimethylnaphthalenes gives naphthalene-1 : 5-dicarboxylic acid (methyl ester, m. p. 113° either alone or after admixture with an authentic specimen). The dichloro-compound yields insol. amorphous products with hexamine in EtOH solution.

1 : 5-*Dimethylnaphthalene*.—Reduction of crude di(chloromethyl)naphthalene with Zn (3·3 atoms) and alc. HCl yields a mixture (b. p. 133—136°/15 mm. : picrate, orange-red needles, m. p. 139—140°) of dimethylnaphthalenes which partly solidifies at − 15°. The solid obtained, recryst. successively from 50% acetone and 85% EtOH, melts at 80—80·5° either alone or after admixture with a specimen of synthetic 1 : 5-dimethylnaphthalene kindly sent to us by Prof. V. Veselý (Veselý and Štursa, *Coll. Czech. Chem. Comm.*, 1931, **3**, 430). The light orange-yellow picrate melts at 138—139° (V. and S. give 137—138°). The liquid portion of the hydrocarbon gives an orange-red picrate, m. p. 139—140°, indistinguishable from that of the crude hydrocarbon mixture.

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