82. *A New and Direct Synthesis of* p-*Dialkylaminobenzophenones.*

By RAMANLAL CHHAGANLAL SHAH and JAGANNATH SAKHARAM CHAUBAL.

ACID chlorides react with aromatic tertiary amines at a high temperature to give acyl derivatives of monoalkylanilines, alkyl halide being eliminated (Hesse, *Ber.*, 1885, **18**, 685; Bergel and Döring, *Ber.*, 1928, **61**, 844). It seemed that a direct synthesis of *p*-dimethylaminobenzophenone would be possible if the reaction between benzoyl chloride and dimethylaniline were carried out in the presence of anhydrous aluminium chloride, which would activate the nuclear *p*-hydrogen atom.

The condensation indeed gave *p*-dimethylaminobenzophenone, but the yield was poor, owing probably to further condensation of the ketone with dimethylaniline to form malachite-green.

When benzanilide imidochloride was substituted for benzoyl chloride, and the condensation was carried out in carbon disulphide

at the ordinary temperature, a high yield of *p*-dimethylaminobenzophenone was obtained after 24 hours.

$$Ph{\cdot}CCl{:}NPh \xrightarrow{PhNMe_2} Ph{\cdot}C(:NPh){\cdot}C_6H_4{\cdot}NMe_2 \xrightarrow{H_2O} Ph{\cdot}CO{\cdot}C_6H_4{\cdot}NMe_2 + NH_2Ph$$

A number of ketones have been prepared by this method, which proceeds smoothly and gives in comparable yields cleaner products than the phosphorus oxychloride method (preceding paper).

The work is being continued.

EXPERIMENTAL.

Condensation of Benzoyl Chloride with Dimethylaniline by Means of Anhydrous Aluminium Chloride.—To a solution of benzoyl chloride (10 g.) and dimethylaniline (19 g.) in carbon disulphide (125 c.c.), aluminium chloride (10 g.) was added in small portions with external cooling. The dark green mixture was refluxed for 3 hours, the solvent distilled off, and the product made alkaline and steam-distilled. Ether extracted from the residual oily liquid, a viscous mass, which solidified in a freezing mixture and gave, after two crystallisations from benzene, about 1 g. of *p*-dimethylaminobenzophenone, m. p. and mixed m. p. 89—90°.

Condensation of Benzanilide Imidochlorides with Dialkylanilines by Means of Aluminium Chloride.—Aluminium chloride (1·25 mols.) was added, with cooling, to a solution of the imidochloride (1 mol.) and the dialkylaniline (2·5 mols.) in dry carbon disulphide (or in dry benzene, for sparingly soluble imidochlorides), and the mixture, protected from moisture, was kept at room temperature for 24 hours. The solvent was then distilled off, the residue dissolved in hot dilute hydrochloric acid, and the cooled solution filtered from any benzanilide, made alkaline with sodium hydroxide (enough being used to dissolve the aluminium hydroxide), and steam-distilled. The non-volatile crude ketone was purified by crystallisation

Dimethylamino-, diethylamino-, 4′-nitro-4-dimethylamino-, 4′-nitro-4-diethylamino-, and 4′-bromo-4-dimethylamino-benzophenone were thus obtained in 80, 70, 50, 50, and 70% yield, respectively, the m. p.'s being practically identical with those of the same ketones prepared by the phosphorus oxychloride method (preceding paper).

p-*Nitrobenzanilide Imidochloride.*—*p*-Nitrobenzanilide (25 g.) and phosphorus pentachloride (23 g.) were heated together until the evolution of hydrogen chloride ceased. The viscous oil was poured into sodium-dried light petroleum (b. p. 89—100°); the precipitated *imidochloride* crystallised from petroleum in yellow plates, m. p. 120—121°. It was heated with sodium ethoxide in absolute-

alcoholic solution on the water-bath, water added, as much as possible of the alcohol evaporated, and the halogen in the cooled filtered solution estimated in the usual way (Found: Cl, 13·4. $C_{13}H_9O_2N_2Cl$ requires Cl, 13·6%). The imidochloride dissolves easily in cold benzene and in hot light petroleum. p-*Bromobenzanilide imidochloride*, similarly prepared from *p*-bromobenzanilide (10 g.) and phosphorus pentachloride (9 g.), crystallised from light petroleum in rectangular, pale yellow needles, m. p. 85—86° (Found: Cl, 11·9. $C_{13}H_9NClBr$ requires Cl, 12·1%).

4′-*Bromo*-4-*diethylaminobenzophenone* (yield, 60%), crystallised from alcohol, had m. p. 99—100° (Found: Br, 23·8. $C_{17}H_{18}ONBr$ requires Br, 24·1%). It is easily soluble in all the usual organic solvents except light petroleum.

2′-*Chloro*-4-*dimethylaminobenzophenone*. — o-*Chlorobenzanilide imidochloride*, prepared from *o*-chlorobenzanilide (10 g.) and phosphorus pentachloride (10 g.), distilled at 182—183°/10 mm. (Found: Cl, 28·1. $C_{13}H_9NCl_2$ requires Cl, 28·4%). The viscous *ketone* prepared from it in 60% yield was purified by solution in ether and subsequent crystallisation from alcohol; m. p. 68° (Found: Cl, 13·6. $C_{15}H_{14}ONCl$ requires Cl, 13·7%).

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ROYAL INSTITUTE OF SCIENCE,
BOMBAY.

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