202. *Imidochlorides. Part II. Condensation of Benzanilide Imidochloride with Substituted Dialkylanilines in Presence of Anhydrous Aluminium Chloride. Synthesis of Dialkylaminobenzophenones.*

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In extension of the work of Shah and Chaubal (J., 1932, 650, this paper is regarded as Part I of the series) we have condensed benzanilide imidochloride with dimethyl-*o*-, -*m*-, and -*p*-toluidine, diethyl-*o*-toluidine, dimethyl-α-naphthylamine, benzylmethylaniline, and benzylethylaniline. The substitution of dry ether, which readily dissolves aluminium chloride, for carbon disulphide as solvent is an improvement upon the original method. Condensation takes place in all cases with the production, after hydrolysis, of the corresponding ketones. 4-Dimethylamino-3-methylbenzophenone, easily obtainable by the present method, cannot be prepared by the older method from benzanilide, dimethyl-*o*-toluidine, and phosphoryl chloride (Meisenheimer, Budkewicz, and Kananow, *Annalen*, 1921, **423**, 75). Dimethyl-*p*-toluidine and dimethyl- and diethyl-*o*-toluidine react less readily than dimethyl-*m*-toluidine. The diminished reactivity of the two *o*-substituted dialkylanilines is in agreement with the observations of von Braun (*Ber.*, 1916, **49**, 1101; 1918, **51**, 1252).

The condensation is, as usual, assumed to take place in the *p*-position to the dimethylamino-group, except with dimethyl-*p*-toluidine, where *o*-condensation is assumed. This is supported by observations on the relative ease of formation of the oximes and the methiodides of the ketones. A substituent in the *o*-position to a dialkylamino-group hinders the formation of a quaternary halide (von Braun, *loc. cit.*); an *o*-substituent to a ketonic group likewise retards oxime formation. 4-*Dimethylamino*-2-*methylbenzophenone* readily affords the *methiodide*, and the *oxime* is obtained with difficulty; whereas 4-*dimethylamino*-3-*methylbenzophenone* gives the *oxime* with comparative ease, but the *methiodide* is difficultly formed. 2-*Dimethylamino*-5-*methylbenzophenone* gives neither the methiodide nor the oxime. The ketone obtained from dimethyl-α-naphthylamine forms an oxime and is regarded as 4-*benzoyldimethyl*-α-*naphthylamine*: the alternative formulation as 2-benzoyldimethyl-α-naphthylamine, which would not be expected to form an oxime by analogy with 2-dimethylamino-5-methylbenzophenone, is much less likely to be correct (the action of benzoyl chloride on α-naphthylamine in presence of zinc chloride gives 4-benzoyl-α-naphthylamine; Dziewoński and Sternbach, *Rocz. Chem.*, 1933, **13**, 704).

The constitution of 4-dimethylamino-3-methylbenzophenone has been confirmed by the identity of its methiodide with the methiodide prepared from 4-amino-3-methylbenzophenone (Chattaway and Lewis, J., 1904, **85**, 589) by methylation in two stages.

EXPERIMENTAL.

Condensation of Benzanilide Imidochloride with Substituted Dialkylanilines.—A solution of anhydrous aluminium chloride (1·25 mols.) in dry ether (about 50 c.c. for 10 g. of aluminium chloride) was gradually added to a solution of the imidochloride (1 mol.) and the dialkylaniline (2·5 mols.) in dry ether, cooled at intervals in ice-water. The mixture, which turned deep red and separated into two layers, was mechanically shaken in a stoppered bottle for about 24 hours at room temperature, the ether distilled off, and the residue treated with ice and then with hot dilute hydrochloride acid. The cooled filtered solution was basified, and the excess of tertiary amine removed by steam-distillation. From the non-volatile residue, ether extracted the ketone, which was distilled under reduced pressure. As dimethyl-α-naphthylamine, benzylmethylaniline, and benzylethylaniline could not conveniently be removed by steam-distillation, special methods of isolating the ketones were used in these three cases.

The replacement of a part of the tertiary amine (namely, the excess over 1 mol.) by pyridine, which did not react with benzanilide imidochloride under the experimental conditions, led to diminished yields of the ketone.

The ketones are viscous oils or low-melting solids, which distil undecomposed under reduced pressure. They dissolve readily in dilute hydrochloric acid (except *p*-benzylmethyl- and *p*-benzylethyl-aminobenzophenone, which are very feebly basic), form insoluble hydroferrocyanides, and give green dyes when heated with dialkylanilines and phosphoryl chloride.

4-*Dimethylamino*-2-*methylbenzophenone* (from dimethyl-*m*-toluidine) had b. p. 195—198°/2 mm. (Found: C, 79·8; H, 7·0; N, 6·1. $C_{16}H_{17}ON$ requires C, 80·3; H, 7·1; N, 5·9%). Yield, 10 g. from 27 g. of benzanilide imidochloride.

The *oxime*, prepared by the alkali method (cf. Lachman, *J. Amer. Chem. Soc.*, 1925, **47**, 260) by refluxing the ketone (1 g.), hydroxylamine hydrochloride (2 g.), and a concentrated aqueous-alcoholic solution of potassium hydroxide (1 g.) for at least 8 hours, separated on dilution with water, and crystallised from dilute alcohol in colourless needles, m. p. 158—160° (Found: N, 11·2. $C_{16}H_{18}ON_2$ requires N, 11·0%). It could not be prepared by the sodium acetate method.

The *methiodide* was obtained by refluxing the ketone (0·5 g.), methyl alcohol (5 c.c.), and methyl iodide (3 g.) for 4 hours. It separated on cooling, and after being washed with benzene crystallised from dilute alcohol in pale yellow needles, which melted at 163° and then decomposed with effervescence, the ketone being regenerated (Found: I, 33·1. $C_{17}H_{20}ONI$ requires I, 33·3%).

4-*Dimethylamino*-3-*methylbenzophenone* (from dimethyl-*o*-toluidine).—From 25 g. of benzanilide imidochloride, 10 g. of the *ketone*, b. p. 205—214°/12 mm., were obtained after distillation. Redistillation gave the major portion at 208—210°/12 mm. as a yellow oil which gradually solidified. After being washed with light petroleum, the ketone was obtained in colourless hexagonal plates, m. p. 45°, easily soluble in the common organic solvents except light petroleum (Found: C, 81·0; H, 6·9; N, 6·1%).

The *oxime*, prepared by refluxing the ketone, hydroxylamine hydrochloride, and sodium acetate in aqueous-alcoholic solution for about 5 hours, crystallised from dilute alcohol in colourless needles, m. p. 119° (Found: N, 11·1%).

The *methiodide* was not formed by boiling a methyl-alcoholic solution of the reactants under reflux; but could be obtained by heating the ketone (0·5 g.) with methyl iodide (3 c.c.) in methyl-alcoholic solution in a sealed tube at 120°. The solution was diluted with water, and a little sodium thiosulphate added to discharge the colour of iodine. The separated methiodide, after being washed with benzene, crystallised from hot water in colourless needles, m. p. 184° (Found: I, 33·2%).

The same ketone was also obtained by refluxing 4-amino-3-methylbenzophenone (Chattaway and Lewis, *loc. cit.*) (1 g.), methyl iodide (3 g.), and a solution of sodium carbonate (1·5 g.) in water (25 c.c.) for 2 hours. The liquid was made alkaline with sodium hydroxide, and the separated 4-dimethylamino-3-methylbenzophenone (isolated by ether as a brown oil; 0·5 g.) was heated in methyl-alcoholic solution with methyl iodide (2 c.c.) in a sealed tube at 120° for 6 hours. The methiodide crystallised from hot water in colourless needles, m. p. 180—184° alone or mixed with the methiodide described above.

2-*Dimethylamino*-5-*methylbenzophenone* (from dimethyl-*p*-toluidine) had b. p. 176—178°/6 mm.; yield, 8 g. from 25 g. of benzanilide imidochloride (Found: C, 80·0; H, 7·5; N, 6·1%).

Nitro-derivative. Fuming nitric acid (5 c.c.) was added to the ketone (0·5 g.), cooled in a freezing mixture. After 12 hours, addition of water precipitated the *nitro*-compound, which was washed with dilute sodium carbonate solution and with water and crystallised from alcohol, forming fine yellow needles, m. p. 173—175° (Found: N, 18·7. $C_{15}H_{10}O_{11}N_6$ requires N, 18·7%).

4-*Diethylamino*-3-*methylbenzophenone* (from diethyl-*o*-toluidine) had b. p. 214—216°/15 mm.; yield, 6 g. from 15 g. of benzanilide imidochloride (Found: C, 80·3; H, 8·2; N, 5·4. $C_{18}H_{21}ON$ requires C, 80·9; H, 7·9; N, 5·2%).

4-*Benzoyldimethyl*-α-*naphthylamine* (from dimethyl-α-naphthylamine).—25 G. of benzanilide imidochloride were used. The oil obtained on basification of the filtered acidic solution was extracted with ether. The residue from the extract on distillation at 40 mm. yielded (1) mostly excess of the tertiary amine, b. p. 162—280°, (2) 7 g., b. p. 283—285°, (3) 0·5 g., b. p. 285—292°. The second fraction gradually solidified and the ketone then crystallised from light petroleum (b. p. 75—95°) in thick yellowish plates, m. p. 102—104° (Found: N, 5·3. $C_{19}H_{17}ON$ requires N, 5·1%).

The *oxime*, prepared by the alkali method, separated from alcohol in pale yellow crystals, m. p. 212—215° (Found: N, 10·0. $C_{19}H_{18}ON_2$ requires N, 9·7%).

4-*Benzylmethylaminobenzophenone* (from benzylmethylaniline).—The reaction mixture was treated with ice and then with hot dilute hydrochloric acid. The cooled mixture after a few hours deposited a greenish paste of benzanilide and the feebly basic ketone. The liquid was decanted, and the paste extracted with ether. On partial evaporation of the ether, some benzanilide separated. Complete evaporation then left an oil, which separated from light petroleum in slightly greenish crystals, m. p. 78—80° (Found: N, 4·8. Calc. for $C_{21}H_{19}ON$: N, 4·7%). D.R.-P. 41,751 gives m. p. 78—79°. Yield, 8 g. from 25 g. of benzanilide imidochloride.

4-*Benzylethylaminobenzophenone* (from benzylethylaniline).—The reaction mixture was worked up as in the preceding case. The oily residue from the ethereal extract yielded the *ketone* as the main fraction, b. p. 320—325°/40 mm., on distillation (Found: C, 83·2; H, 6·6; N, 4·6. $C_{22}H_{21}ON$ requires C, 83·8; H, 6·7; N, 4·4%). Yield, 12 g. from 20 g. of the imidochloride.

The *oxime* crystallised from alcohol in pale yellow plates, m. p. 140—142° (Found: N, 8·7. $C_{22}H_{22}ON_2$ requires N, 8·5%).

The authors thank Dr. T. S. Wheeler for his interest in the work.

ROYAL INSTITUTE OF SCIENCE, BOMBAY. [*Received, March 25th,* 1935.]