81. *Condensation of Benzanilides and* p-*Dialkylanilines with Phosphorus Oxychloride as Condensing Agent, and the Mechanism of the Reaction.*

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Whereas symmetrical *pp'*-tetra-alkyldiaminobenzophenones can be readily prepared, *viz.*, by the action of carbonyl chloride on dialkylanilines, no such simple method is available for the preparation of *p*-dialkylaminobenzophenones.

The action of benzoyl chloride on dimethylaniline at 150—180° gives, not dibenzoyldimethylaniline (Michler and Dupertius, *Ber.*, 1876, **9**, 1901), but *N*-benzoylmethylaniline (Hesse, *Ber.*, 1885, **18**, 685), formed by the elimination of methyl chloride. The action of benzoic acid on dimethylaniline in the presence of phosphoric oxide at 180—200° is stated by O. Fischer (*Ber.*, 1877, **10**, 958) to give *p*-dimethylaminobenzophenone, but was later shown by Neundlinger (*Annalen*, 1915, **409**, 182) to give a mixture of this ketone, *N*-benzoylmethylaniline, and tetramethyldiaminodiphenylmethane.

The only convenient method for preparing a *p*-dialkylaminobenzophenone is the condensation of a benzanilide with a dialkylaniline by means of phosphorus oxychloride (D.R.-P. 41,751; Friedländer, " Fortschritte," I, 44, 47). The reaction has been but little studied, and its mechanism has not been elucidated. By means of it, Meisenheimer, Budkewicz, and Kananow (*Annalen*, 1921, **423**, 75) prepared *p*-dimethylamino-, *p*-diethylamino-, and *p*-dimethylamino-*p'*-diethylamino-benzophenone. Noelting (*Ber.*, 1897, **30**, 2588), however, showed that the anilides of salicylic, *o*-cresotic, and *o*-hydroxynaphthoic acids behaved exceptionally with dimethylaniline, giving dyes of malachite-green type.

The reaction has now been more fully studied with the object of examining the influence of substituents in the acid residue of the anilide on the course of the reaction. Dimethylaniline has been condensed with the anilides of *o*-, *m*-, and *p*-nitro-, *o*-chloro-, *p*-bromo-, *o*-acetoxy-, *o*-, *m*-, and *p*-methoxy-, and *m*- and *p*-methylcarbonato-benzoic acids and of α- and β-naphthoic acids, and diethylaniline with the anilides of *m*- and *p*-nitro-, *o*-chloro-, and *p*-methoxy-benzoic acids.

In all cases except the *o*-acetoxy- and *o*-nitro-benzanilides, the main reaction is ketone formation, but small amounts of green byproducts are almost always formed. *o*-Nitrobenzanilide gives, in addition to a small yield of orange-coloured ketone, a colourless crystalline product in relatively larger amount, the constitution of which is being investigated. The product obtained from *o*-acetoxybenzanilide consists largely of a green colouring matter, no ketone being isolated. In contrast to *o*-hydroxy- and *o*-acetoxybenzanilides, *o*-methoxybenzanilide gives a good yield of ketone.

The mechanism of the reaction has hitherto been regarded as consisting in the conversion of the benzanilide by the phosphorus oxychloride into an imido-chloride, which undergoes nuclear condensation with the dialkylaniline with formation of a ketone-anil, this on hydrolysis giving the ketone; *e.g.*,

$$\mathrm{Ph{\cdot}CO{\cdot}NHPh} \xrightarrow{\mathrm{POCl_3}} \mathrm{Ph{\cdot}CCl_2{\cdot}NHPh} \xrightarrow{-\mathrm{HCl}} \mathrm{Ph{\cdot}CCl{:}NPh} \xrightarrow{\mathrm{PhNMe_2}}$$
$$\mathrm{Ph{\cdot}C({:}NPh){\cdot}C_6H_4{\cdot}NMe_2} \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}C_6H_4{\cdot}NMe_2}$$

(see D.R.-P. 41,751; Friedländer, "Fortschritte," I, 44; Dimroth and Zoeppritz, *Ber.*, 1902, **35**, 993; Lassar-Cohn, "Arbeit-methoden der organische Chemie" (English translation), p. 117; Meisenheimer, Budkewicz, and Kananow, *loc. cit.*; Chapman, J., 1922, **121**, 1676; Hewitt, Thorpe's "Dictionary of Applied Chemistry," vol. VII, 1922 ed., p. 714).

As the explanation did not appear probable to the authors, it was tested experimentally.

A mixture of benzanilide and phosphorus oxychloride (excess), protected from access of moisture, melted to a homogeneous liquid at about 120° and hydrogen chloride was given off on further heating. The crude product after removal of the oxychloride at 130°/50 mm. was a viscous oil which decomposed on distillation under 20 mm. pressure, no benzanilide imidochloride being obtained. The substance, which was obviously a phosphorus compound, was easily hydrolysed to benzanilide and readily gave *p*-dimethylaminobenzophenone when heated with dimethylaniline on the steam-bath.

Scarcely any reaction took place between benzanilide imidochloride and dimethylaniline under the conditions (3–4 hours' heating on the steam-bath) under which a mixture of benzanilide, dimethylaniline, and phosphorus oxychloride gives a 70—80% yield of the ketone. Even at 120° and 140° there was very little reaction.

The reaction at higher temperatures, in which the ketone was only formed in negligible quantity as a by-product, was investigated with interesting results. The main product of the reaction between benzanilide imidochloride and dimethylaniline at 160—180° for 24 hours was a crystalline *base* (A), $C_{20}H_{18}N_2$, m. p. 148—150° (*hydrochloride*, m. p. 280—282°; picrate, m. p. 218°). The similar reaction with diethylaniline gave a crystalline *base* (B), $C_{21}H_{20}N_2$, m. p. 150° (*hydrochloride*, m. p. 289—290°).

As the analytical results indicated that an alkyl chloride was eliminated during the reaction (compare the analogous reactions of acid chlorides with dialkylanilines; Hesse, *Ber.*, 1885, **18**, 685; Bergel and Döring, *Ber.*, 1928, **61**, 844), the constitution (I; R = Me or Et) was assigned to the compounds (A) and (B), the reaction being assumed to be as follows :

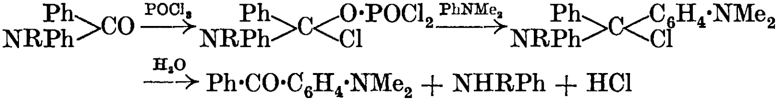
$$Ph\cdot CCl{:}NPh + PhNR_2 = Ph\cdot C({:}NPh)NRPh\ (I) + RCl.$$

The bases (A) and (B), however, were found not to be identical, respectively, with N-*methyldiphenylbenzamidine* (uncrystallisable oil; *hydrochloride*, m. p. 250°; *picrate*, m. p. 189—190°) and N-*ethyldiphenylbenzamidine* (crystalline solid, m. p. 81°; *hydrochloride*, m. p. 189—190°), which were prepared from the appropriate alkylaniline, phosphorus pentachloride, and benzanilide in benzene solution by the method of Hill and Cox (*J. Amer. Chem. Soc.*, 1926, **48**, 3214).

It is suggested that the compounds (A) and (B) may be geometrical isomerides of the two benzamidines, and in this connexion it may be mentioned that diphenyl-*p*-aminobenzamidine monohydrochloride can be obtained in two interconvertible forms, one colourless and the other yellow (Shah, *J. Indian Inst. Sci.*, 1925, **7**, 219), and that some diaryl-*p*-nitrobenzamidines and their salts also exist in two differently coloured modifications, one of which is stable and the other unstable (unpublished work).

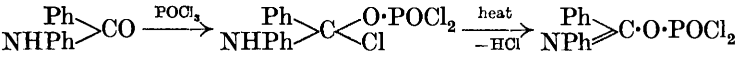
Light was thrown on the mechanism of the reaction whereby *p*-dimethylaminobenzophenone is produced from benzanilide, phosphorus oxychloride, and dimethylaniline when benzomethylanilide was substituted for benzanilide. The condensation took place readily with the formation of the same product, *p*-dimethylaminobenzophenone, and after hydrolysis of the reaction mixture and steam distillation, the distillate contained methylaniline but no aniline.

The course of both reactions may be represented as follows (R = H or Me) :



$$\genfrac{}{}{0pt}{}{Ph}{NRPh}\!>\!CO \xrightarrow{POCl_3} \genfrac{}{}{0pt}{}{Ph}{NRPh}\!>\!C\!<\!\genfrac{}{}{0pt}{}{O\cdot POCl_2}{Cl} \xrightarrow{PhNMe_2} \genfrac{}{}{0pt}{}{Ph}{NRPh}\!>\!C\!<\!\genfrac{}{}{0pt}{}{C_6H_4\cdot NMe_2}{Cl}$$
$$\xrightarrow{H_2O} Ph\cdot CO\cdot C_6H_4\cdot NMe_2 + NHRPh + HCl$$

The evolution of hydrogen chloride in the reaction between phosphorus oxychloride and benzanilide (see p. 643) may be explained as follows :



$$\genfrac{}{}{0pt}{}{Ph}{NHPh}\!>\!CO \xrightarrow{POCl_3} \genfrac{}{}{0pt}{}{Ph}{NHPh}\!>\!C\!<\!\genfrac{}{}{0pt}{}{O\cdot POCl_2}{Cl} \xrightarrow[-HCl]{heat} \genfrac{}{}{0pt}{}{Ph}{NPh}\!\geqslant\!C\cdot O\cdot POCl_2$$

An attempt will be made to study the compound formation between benzanilide and phosphorus oxychloride by physicochemical means.

EXPERIMENTAL.

Preparation of Anilides.—The acid was treated or warmed with the requisite quantity of phosphorus pentachloride until evolution of hydrogen chloride ceased. To the mixture of acid chloride and phosphorus oxychloride, dimethylaniline, diethylaniline, or pyridine (2—2·5 mols.) was added, with cooling. The whole was kept in a freezing mixture and stirred while aniline (1·2—1·5 mols.) was gradually added. The pasty mass was heated on a water-bath for ¼ hour, triturated with dilute hydrochloric acid, and washed successively with water, dilute sodium hydroxide solution, and water. The anilide obtained was fairly pure, and was further crystallised (yield, 70—80% in most cases).

Condensation of Anilides with Dialkylanilines.—General method. The anilide (1 mol.) and the dialkylaniline (2—2·5 mols.) were heated together on the water-bath until the mixture became liquid. Phosphorus oxychloride (1—2·5 mols.) was gradually added with external cooling. The mixture was heated until the reaction finished, a test portion then dissolving completely in dilute hydrochloric acid. The product was dissolved in hot (in some cases boiling) dilute hydrochloric acid, and the cooled filtered solution was made alkaline and steam-distilled to remove the excess of dialkylaniline and the aniline. The crude ketone was purified in a suitable manner.

The condensation in the following cases was brought about by heating on the water-bath for 3—4 hours. *p*-Diethylaminobenzophenone (yield, 70%) crystallised from hot alcohol in colourless prisms, m. p. 80—81° (Meisenheimer, *loc. cit.*, gives m. p. 79—81°). The *oxime*, prepared from hydroxylamine hydrochloride (2 g.) and the ketone (2 g.) in boiling aqueous alcohol, was crystallised from methyl alcohol; m. p. 143—144° (Found: N, 10·5. $C_{17}H_{20}ON_2$ requires N, 10·4%).

p-Dimethylaminobenzophenone (yield, 65%) crystallised from hot alcohol in needles, m. p. 92—93°. Döbner (*Annalen*, 1883, **217**, 257) gives m. p. 90°. The *oxime*, crystallised from methyl alcohol, had m. p. 152° (Found: N, 11·4. $C_{15}H_{16}ON_2$ requires N, 11·6%).

4-*Dimethylamino*-2′-*methoxybenzophenone* (yield, 55%). The crude ketone, a reddish pasty mass, was extracted with ether, the extract dried with anhydrous sodium sulphate, and the ether evaporated. The residue of prismatic crystals, recrystallised from alcohol, had m. p. 74° (Found: N, 5·4. $C_{16}H_{17}O_2N$ requires N, 5·5%). The ketone is easily soluble in all the usual organic solvents except light petroleum.

4′-*Bromo*-4-*dimethylaminobenzophenone* (yield, 75%) crystallised from hot alcohol in prisms, m. p. 128—129° (Found: Br, 26·2. $C_{15}H_{14}ONBr$ requires Br, 26·3%). The *oxime* melted at 185° (Found: Br, 24·7. $C_{15}H_{15}ON_2Br$ requires Br, 25·1%).

2′-*Chloro*-4-*diethylaminobenzophenone* (yield, 50%), crystallised from ether and then from alcohol, formed needles, m. p. 79° (Found: Cl, 12·1. $C_{17}H_{18}ONCl$ requires Cl, 12·3%).

4-Dimethylamino-3′-methoxybenzophenone (yield, 40%) crystallised from methyl alcohol in needles, m. p. 72—73° (Found: N, 5·6. Calc.: N, 5·5%). D.R.-P. 65,952 gives m. p. 67°. The *oxime* crystallised from alcohol in needles, m. p. 185° (Found: N, 9·9. $C_{16}H_{18}O_2N_2$ requires N, 10·4%).

4-Dimethylamino-4′-methoxybenzophenone (yield, 50%) crystallised from alcohol in rectangular plates, m. p. 132—134° (Found: N, 5·4. Calc.: N, 5·5%). D.R.-P. 295,495 gives m. p. 133°.

4-*Diethylamino*-4′-*methoxybenzophenone* (yield, 40%). The crude ketone, a reddish oil, was dissolved in ether, evaporation of which gave plates, m. p. 92° after recrystallisation from hot alcohol (Found: N, 5·0. $C_{18}H_{21}O_2N$ requires N, 4·9%).

4-*Dimethylamino*-3′-*hydroxybenzophenone* was prepared (yield, 50%) from *m*-methylcarbonatobenzanilide. The dirty grey solid obtained was the sodium salt of the hydroxy-ketone; this was treated with hydrochloric acid, and the free ketone crystallised from methyl alcohol, forming greenish needles, m. p. 185—187° (Found: N, 6·0. $C_{15}H_{15}O_2N$ requires N, 5·8%).

4-*Dimethylamino*-4′-*hydroxybenzophenone* was obtained (yield, 60%) from p-*methylcarbonatobenzanilide*, m. p. 179—181° (Found: N, 5·3. $C_{15}H_{13}O_4N$ requires N, 5·2%). The sticky product, after being washed with ether, gave pearly plates of the sodium salt of the hydroxy-ketone. Treatment with hydrochloric acid gave the free hydroxy-ketone, which crystallised from methyl alcohol in needles, m. p. 199—200° (Found: N, 5·9. $C_{15}H_{15}O_2N$ requires N, 5·8%).

The following four ketones were prepared by heating the reactants in an oil-bath at 110—115° for 2—3 hours.

3′-Nitro-4-dimethylaminobenzophenone (yield, 40%). The crude product was washed with cold alcohol and twice crystallised from hot toluene, yellow plates, m. p. 174—176°, being obtained (Found: N, 10·2. Calc.: N, 10·4%). D.R.-P. 42,853 gives m. p. 173°.

3′-*Nitro*-4-*diethylaminobenzophenone* (yield, 20%). The impure ketone, a black mass, was twice crystallised (charcoal) from hot alcohol, yellowish-brown needles, m. p. 84°, being obtained (Found: N, 9·3. $C_{17}H_{18}O_3N_2$ requires N, 9·4%).

4′-*Nitro*-4-*dimethylaminobenzophenone* (yield, 45%), after being washed with cold alcohol, crystallised from toluene in orange-yellow plates, m. p. 206—207° (Found : N, 10·2. $C_{15}H_{14}O_3N_2$ requires N, 10·4%).

4′-*Nitro*-4-*diethylaminobenzophenone* (yield, 60%), crystallised from methyl alcohol in deep yellow plates, m. p. 116—117° (Found : N, 9·0. $C_{17}H_{18}O_3N_2$ requires N, 9·4%). The *oxime* crystallised from methyl alcohol in needles, m. p. 156° (Found : N, 13·1. $C_{17}H_{19}O_3N_3$ requires N, 13·4%).

2′-*Nitro*-4-*dimethylaminobenzophenone*. The reacting mixture was heated at 60° for 6 hours. The dark product was extracted with ether, a small quantity of black crystalline material remaining undissolved. The substance recovered from the extract was shaken with light petroleum (b. p. 60—80°). The petroleum extract on spontaneous evaporation gave a brown solid which, after being washed with light petroleum, separated from alcohol in colourless cubic crystals, m. p. 93°, turning violet in air. The ether-insoluble compound, which was the ketone, crystallised from boiling alcohol in deep orange, rectangular plates, m. p. 251—253° (Found : N, 10·7. $C_{15}H_{14}O_3N_2$ requires N, 10·4%). The compound is sparingly soluble in hot ethyl and methyl alcohol and acetone and easily in hot chloroform and benzene.

For the preparation of the two naphthyl ketones, 4—5 hours' heating on the water-bath was necessary.

p-Dimethylaminophenyl 1-naphthyl ketone (yield, 35%) crystallised from alcohol in pale yellow plates, m. p. 115—116° (Found : N, 4·8. Calc. : N, 5·1%), and the corresponding 2-naphthyl ketone (yield, 40%) in yellow needles, m. p. 128—129° (Found : N, 5·2%). D.R.-P. 42,853 gives m. p. 115° and 127° respectively.

Reaction of the Product from Benzanilide and Phosphorus Oxychloride with Dimethylaniline.—The crude oily product prepared as described on p. 643 from benzanilide (10 g.) and phosphorus oxychloride (12 g.) was heated on the water-bath with dimethylaniline (20 g.) for 4 hours. The viscous mass obtained dissolved almost completely in hot dilute hydrochloric acid. The acid extract was made alkaline and steam-distilled. The viscous residue on crystallisation from ether gave the ketone (3 g.), m. p. 90—91°, not depressed by admixture with authentic *p*-dimethylaminobenzophenone.

Interaction of Benzanilide Imidochloride and Dimethylaniline below 140°.—The imidochloride (10 g.) and dimethylaniline (20 g.) were heated together (calcium chloride guard-tube). The reaction mixture was extracted with hot dilute hydrochloric acid, and the filtered solution made alkaline and steam-distilled. The residual ketone was crystallised from alcohol. The following table shows the results obtained under different conditions.

Temp.	Time, hours.	Yield of ketone, g.	Benzanilide recovered, g.
Water-bath	4	Less than 0·1	9
,, (+ 5 g. $POCl_3$)	4	,,	9
115—120°	5	0·2	8—9
130—140°	6	0·5	7
,, (5 g. $POCl_3$)	6	(more impure product)	

Action of Benzanilide Imidochloride upon Dimethylaniline at Higher Temperatures.—The imidochloride (10 g.) and dimethylaniline (20 g.) were heated together (calcium chloride guard-tube) in an oil-bath at 160—180° for 24 hours. A crystalline hydrochloride separated on cooling. It was washed with dry benzene, recrystallised from hot alcohol, and dissolved in alcohol, and concentrated aqueous ammonia added. The crystalline *base* obtained was recrystallised from hot alcohol, forming needles, m. p. 148—150° (Found: C, 83·5; H, 6·6; N, 9·7. $C_{20}H_{18}N_2$ requires C, 83·9; H, 6·3; N, 9·8%), easily soluble in cold benzene and chloroform and in hot methyl and ethyl alcohol.

The *hydrochloride*, m. p. 282° (decomp.), was crystallised from alcoholic hydrochloric acid (Found: Cl, 10·9. $C_{20}H_{18}N_2$,HCl requires Cl, 11·0%). The picrate, prepared in benzene solution, had m. p. 218°.

Action of Benzanilide Imidochloride upon Diethylaniline.—This reaction (imidochloride, 15 g.; diethylaniline, 21 g.) proceeded as in the foregoing case. The *base* obtained separated from hot alcohol in needles, m. p. 150° (Found: C, 83·4; H, 6·1; N, 9·5. $C_{21}H_{20}N_2$ requires C, 84·0; H, 6·7; N, 9·3%), and resembled the preceding base in solubility.

The *hydrochloride*, m. p. 289—290° (decomp.), is sparingly soluble in water and easily in methyl alcohol (Found: Cl, 11·0. $C_{21}H_{20}N_2$,HCl requires Cl, 10·5%).

N-*Methyldiphenylbenzamidine.*—(1) Benzanilide imidochloride (15 g.) was gradually added to a cooled mixture of monomethylaniline (7 g.) and diethylaniline (compare Shah, *loc. cit.*). The mixture was finally heated for ¼ hour on the water-bath, allowed to cool, and triturated with dilute hydrochloric acid. The insoluble amidine hydrochloride was crystallised from glacial acetic acid and dissolved in alcohol, concentrated aqueous ammonia added, and the mixture diluted with water. The *base*, isolated by means of ether, was an oil. It was left for several days in a desiccator under reduced pressure (Found: C, 83·7; H, 6·9; N, 10·2. $C_{20}H_{18}N_2$ requires C, 83·9; H, 6·3; N, 9·8%).

The *hydrochloride* formed colourless prisms, m. p. 250°, from glacial acetic acid (Found: Cl, 10·9. $C_{20}H_{18}N_2$,HCl requires Cl, 11·0%). The *picrate*, crystallised from alcohol, melted at 189—190° (Found: N, 13·7. $C_{20}H_{18}N_2$, $C_6H_3O_7N_3$ requires N, 13·6%).

(2) The same substance was also obtained by the method of Hill and Cox (*loc. cit.*).

N-*Ethyldiphenylbenzamidine.*—Phosphorus pentachloride (6 g.), followed by monoethylaniline (6 g.), was added to a solution of benzanilide (5 g.) in dry benzene (25 c.c.), and the mixture refluxed for 3 hours. The benzene was evaporated, the residue dissolved in boiling dilute hydrochloric acid, and the filtered solution basified and steam-distilled. The residue (4·5 g.) crystallised from alcohol in needles, m. p. 81° (Found : C, 83·7; H, 6·5; N, 9·2. $C_{21}H_{20}N_2$ requires C, 84·0; H, 6·7; N, 9·3%).

The *hydrochloride* formed colourless prisms, m. p. 189—190°, from hot dilute hydrochloric acid (Found : Cl, 10·9. $C_{21}H_{20}N_2,HCl$ requires Cl, 10·5%).

N-*Alkyldiarylbenzamidines.*—The following amidines also were prepared by the method of Hill and Cox.

N-*Methyldiphenyl*-o-*nitrobenzamidine*, yellow prisms, m. p. 141° (Found : N, 12·6. $C_{20}H_{17}O_2N_3$ requires N, 12·7%); *hydrochloride*, m. p. 225—227° (Found : Cl, 9·4. $C_{20}H_{17}O_2N_3,HCl$ requires Cl, 9·7%). The corresponding *m*-nitro-compound is an oil (*hydrochloride*, m. p. 230°. Found : Cl, 9·7%). The p-*nitro*-compound, yellow prisms, m. p. 94° (Found : N, 12·6%); *hydrochloride*, m. p. 213° (Found : Cl, 9·8%).

N-*Ethyldiphenyl*-o-*nitrobenzamidine*, yellow prisms, m. p. 99—100° (Found : N, 12·1. $C_{21}H_{19}O_2N_3$ requires N, 12·2%); *hydrochloride*, m. p. 160—161° (Found : Cl, 9·4. $C_{21}H_{19}O_2N_3,HCl$ requires Cl, 9·3%). The m-*nitro*-compound, colourless needles, m. p. 174—175° (Found : N, 12·3%); *hydrochloride*, m. p. 247° (Found : Cl, 9·6%). The p-*nitro*-compound, pale yellow prisms, m. p. 112° (Found : N, 12·3%); *hydrochloride*, m. p. 179—180° (Found : Cl, 9·4%).

N-*Methyldiphenyl*-m-*methoxybenzamidine*, colourless needles, m. p. 83° (Found : N, 8·7. $C_{20}H_{20}ON_2$ requires N, 8·8%); *hydrochloride*, m. p. 214—215° (Found : Cl, 10·4. $C_{20}H_{20}ON_2,HCl$ requires Cl, 10·0%). N-*Ethyldiphenyl*-m-*methoxybenzamidine*, colourless prisms, m. p. 175° (Found : N, 8·6. $C_{21}H_{22}ON_2$ requires N, 8·4%); *hydrochloride*, m. p. 248° (Found : Cl, 10·0. $C_{21}H_{22}ON_2,HCl$ requires Cl, 9·6%).

N-*Methyldiphenyl*-o-*chlorobenzamidine*, colourless needles, m. p. 106° (Found : Cl, 11·0. $C_{20}H_{17}N_2Cl$ requires Cl, 11·1%); *hydrochloride*, m. p. 230—235° (Found : Cl′, 10·0. $C_{20}H_{17}N_2Cl,HCl$ requires Cl′, 9·9%). N-*Ethyldiphenyl*-o-*chlorobenzamidine*, colourless needles, m. p. 70—71° (Found : Cl, 11·1. $C_{21}H_{19}N_2Cl$ requires Cl, 10·6%); *hydrochloride*, m. p. 250° (Found : Cl′, 9·5. $C_{21}H_{19}N_2Cl,HCl$ requires Cl′, 9·6%). N-*Methyldiphenyl*-p-*bromo*-

benzamidine, stout colourless needles, m. p. 121—123° (Found: Br, 22·0. $C_{20}H_{17}N_2Br$ requires Br, 21·9%); *hydrochloride*, m. p. 290—295° (Found: Cl, 9·1. $C_{20}H_{17}N_2Br,HCl$ requires Cl, 8·8%).

Condensation of Benzomethylanilide with Dimethylaniline with the Aid of Phosphorus Oxychloride.—The methylanilide (10 g.), dimethylaniline (20 g.), and phosphorus oxychloride (10 g.) were heated together on the water-bath for 3 hours, the viscous reddish-brown product dissolved in boiling dilute hydrochloric acid, and the cooled filtered solution made alkaline and steam-distilled. The residual oil solidified to a cake, which was crystallised from alcohol (4·5 g., m. p. 92°) and proved to be dimethylaminobenzophenone by a mixed m. p. determination with an authentic specimen.

Ether extracted from the steam-distillate an oil which gave a negative test for aniline. The oil was heated on the water-bath with excess of acetic anhydride. After removal of acetic anhydride and dimethylaniline at 200—220°, the residue separated from alcohol in crystals, m. p. 101—102° (alone or mixed with authentic acetomethylanilide).

An extension of the work is contemplated.

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