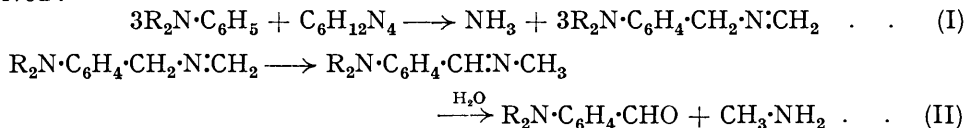


### 204. Reactions between Dialkylanilines and Hexamine in Acetic Acid and in Formic Acid.

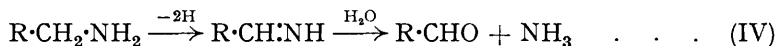
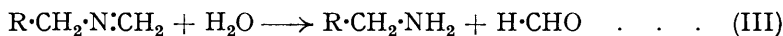
By J. C. DUFF and (MISS) V. I. FURNESS.

The formation of *p*-dialkylaminobenzaldehydes from dialkylanilines and hexamine in glacial acetic acid is shown to proceed by the stages shown in (I) and (II), below. When formic acid is used as the medium for the reactions, ditertiary amines of general formula *p*-R<sub>2</sub>N·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·NMe<sub>2</sub> are formed in addition to the aldehydes.

A GENERAL method for the preparation of *p*-dialkylaminobenzaldehydes from dialkylanilines and hexamine heated in a mixture of acetic and formic acids has been described by one of us (Duff, *J.*, 1945, 276), who suggested that the following expressed the reactions involved :



This mechanism corresponded to that originally put forward to explain the Sommelet reaction. Angyal and Rassack (*J.*, 1949, 2700), however, have since shown that the following steps explain the latter reaction :



the hexamine acting as the dehydrogenating agent. The present authors (*J.*, 1951, 1512) found that dehydrogenation by hexamine was an essential step in the formation of *o*-hydroxyaldehydes from phenols and hexamine in a non-aqueous medium. Phenols were found to form first secondary amines of the type HO·X·CH<sub>2</sub>·NH·CH<sub>2</sub>·X·OH (H·X·OH = a phenol) followed by dehydrogenation to the Schiff's bases HO·X·CH:N·CH<sub>2</sub>·X·OH, which are then hydrolysed by aqueous acid.

With the above observations in mind the reactions between dialkylanilines and hexamine have been re-examined. Preliminary experiments having shown that formic acid

differs from acetic acid in yielding additional products, the reactions in both these acids have been investigated separately. In neither case has it been possible to isolate any intermediate compounds which would account for the formation of the *p*-dialkylaminobenzaldehydes, but we have found a probable example of an intermediate compound in the methylene derivative of *p*-dimethylaminobenzylamine and have been able to show that this derivative can be converted into the related aldehyde and also into the ditertiary amine,  $\text{Me}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NMe}_2$ .

*Reactions in Acetic Acid.*—Satisfactory yields of *p*-dialkylaminobenzaldehydes were obtained by heating the dialkylanilines with hexamine in glacial acetic acid. Alcohol and aqueous formic acid, which were used in addition in the method described by Duff (*loc. cit.*), were omitted to eliminate the possibility of hydrolysis before the final treatment with dilute hydrochloric acid. No formaldehyde could be detected in the vapour arising when air was drawn through the heated reaction mixture. The absence of formaldehyde indicates that the mechanism of the reaction is not analogous to that given by Angyal and Rassack (*loc. cit.*) in scheme (III) for the Sommelet reaction.

Since the aldehyde must be formed by hydrolysis, the reaction mixture was examined for the presence of the other hydrolysis product, which could be either a primary amine or ammonia. The only primary amine detected was methylamine. Under different experimental conditions the molecular ratio of methylamine to *p*-dialkylaminobenzaldehyde was found to be always 1 : 1. The yields of the two products are shown in the table. The

*Yields (in moles) from 1 mole of dialkylaniline \**

Dialkylaniline	A		B		C	
	Aldehyde	Me·NH <sub>2</sub>	Aldehyde	Me·NH <sub>2</sub>	Aldehyde	Me·NH <sub>2</sub>
NMe <sub>2</sub> Ph .....	0·18	0·185	0·305	0·305	0·145	0·145
NMeEtPh .....	0·26	0·26	0·23	0·23	0·05	0·05
NEt <sub>2</sub> Ph .....	0·22	0·215	0·16	0·16	0·05	0·05
NPr <sub>2</sub> Ph .....	0·47	0·47	0·18	0·18	0·21	0·21
NBu <sub>2</sub> Ph .....	0·62	0·62	0·75	0·75	0·38	0·38
NMePh·CH <sub>2</sub> Ph .....	0·42	0·43	0·25	0·255	0·36	0·36
NEtPh·CH <sub>2</sub> Ph .....	0·61	0·62	0·46	0·46	0·355	0·355

\* A = Standard conditions (see p. 1161). B = Longer heating than for A. C = Reduced proportion of hexamine compared with A.

yields recorded under B show that, although prolonged heating in most cases reduces the yields, the ratio of aldehyde to amine remains unaltered. Although a first-stage reaction as represented by



can account for equivalent yields of aldehyde and methylamine, it is improbable that the 1 : 1 ratio of the two products would be maintained under conditions in which the yields are decreasing with increasing time of heating. Only hydrolysis of a single product to give both aldehyde and amine would account for the constant ratio. For this reason we consider that reactions (I) and (II) express the actual processes leading to formation of the requisite Schiff's base. These reactions include isomerisation of a methylene-azomethine type  $>\text{CH}\cdot\text{N}\cdot\text{C} < \rightleftharpoons >\text{C}\cdot\text{N}\cdot\text{CH} <$ .

Ingold and Shoppee (*J.*, 1929, 1199) examined this form of prototropy and in the case of  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{N}\cdot\text{CH}_2 \longrightarrow \text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{N}\cdot\text{CH}_3$  found that heating the methylene compound at 190° with alcoholic sodium ethoxide or at 300° with potassium hydroxide produced only about a 10% yield of benzaldehyde on subsequent hydrolysis. No reverse reaction was observed under the same conditions. Shoppee (*Nature*, 1948, **162**, 619) stated that since the isomerisation of  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{N}\cdot\text{CH}_2$  is only partial under drastic conditions, it is inherently improbable under mild conditions.

We have examined this isomerisation under other conditions. *N*-Methylenebenzylamine and *p*-dimethylamino-*N*-methylenebenzylamine were each heated with hexamine in acetic acid at 100° for two hours. Addition of water to the cold reaction mixtures then gave yields of 61% of benzaldehyde and 55% of *p*-dimethylaminobenzaldehyde, respectively, together with the equivalent amounts of methylamine.

When experiments were carried out with acetic acid containing 10% of water, the yield of benzaldehyde was 29%, and of *p*-dimethylaminobenzaldehyde 24%. Thus the reaction is retarded and not assisted when hydrolysis can occur, and the possibility that traces of water were favouring the reaction according to schemes (III) and (IV) is eliminated. To demonstrate that the reaction is a base-catalysed isomerisation and not a dehydrogenation, it has been examined by using other amines. With trimethylamine, yields of 40% of benzaldehyde and 46% of *p*-dimethylaminobenzaldehyde have been obtained with the formation of equivalent amounts of monomethylamine. The use of pyridine led to results of the same order.

Since isomerisation occurs readily under these conditions, it seems that a similar isomerisation could occur in the general method of preparation of the aldehydes, and that the mechanism originally suggested (*J.*, 1945, 276) and formulated in (I) and (II) is correct.

Although phenols yielded phenolic aldehydes (*J.*, 1951, 1512) *via* formation of secondary amines, it is probable that there was an initial formation of the *N*-methylenebenzylamine structure followed by further condensation with the phenol; *e.g.*



*Reactions in Formic Acid.*—After dialkylanilines had been heated with hexamine in a mixture of formic acid and ethyl alcohol, addition of aqueous sodium hydroxide liberated ether-soluble oils which on distillation yielded, besides the expected aldehydes, colourless mobile liquids which were identified as a new class of ditertiary amines, *p*-dialkylamino-benzyltrimethylamines,  $\text{R}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NMe}_3$ . They all reacted vigorously with methyl iodide to give monoquaternary salts,  $\text{R}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NMe}_3\text{I}$ . This structure was confirmed for the quaternary salts where  $\text{R} = \text{Me}$  and  $\text{R} = \text{Et}$  by thermal decomposition of the quaternary hydroxides, both of which yielded trimethylamine.

The formation of trimethylamine from the hydroxide obtained from the methiodide of *p*-dimethylaminobenzyltrimethylamine suggests that the quaternary salt had been formed by addition of the methyl iodide to the aliphatic nitrogen atom, since Collie and Schryver (*J.*, 1890, 57, 777) have shown that thermal decomposition of trimethylphenylammonium hydroxide yields dimethylaniline and methyl alcohol. The formation of trimethylamine from the hydroxide obtained from the methiodide of *p*-diethylaminobenzyltrimethylamine confirms this view and proves that this hydroxide has the structure  $\text{Et}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{OH}$ .

The ditertiary bases probably result from the initially formed methylene compounds,  $\text{R}_2\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{N}\cdot\text{CH}_2$ , by reduction and methylation through the combined action of formaldehyde (from hydrolysis of hexamine) and formic acid (Eschweiler, *Ber.*, 1905, 38, 880; Clarke, Gillespie, and Weisshaus, *J. Amer. Chem. Soc.*, 1933, 55, 4571). In support of this suggestion we have found that *N*-methylenebenzylamine and *p*-dimethylamino-*N*-methylenebenzylamine when heated with hexamine in boiling alcoholic formic acid yielded respectively benzyltrimethylamine and *p*-dimethylaminobenzyltrimethylamine.

#### EXPERIMENTAL

Di-*n*-propylaniline was prepared by Slotta and Franke's method (*Ber.*, 1930, 63, 682). The other dialkylanilines were distilled from available supplies.

*Reactions in Acetic Acid.*—The following procedure gives the standard conditions for the results listed in Column A, of the table.

Hexamine (10 g., 0.07 mole) and glacial acetic acid (10 ml.) were heated on a boiling-water bath while a mixture of dimethylaniline (9 ml., 0.07 mole) and glacial acetic acid (20 ml.) was added dropwise during 1 hour. Heating was then continued for a further 2 hours. For the other dialkylanilines the weights used represented 0.07 mole for ethylmethyl- and diethylanilines, and 0.05 mole for di-*n*-propyl-, di-*n*-butyl-, benzylmethyl-, and benzylethylanilines. For the results given under B, of the table, the heating time was extended by approximately 2 hours. The results listed under C were obtained when the proportion of hexamine in the reactions was reduced by 20%, the heating time remaining the same as for the standard conditions.

*Treatment of the Reaction Mixtures to determine Yields of the Aldehydes and of Methylamine.*—

(a) *p*-Dimethyl- and *p*-diethyl-aminobenzaldehydes. The reaction mixtures were poured into aqueous hydrochloric acid (150 ml.; 0.5N) and set aside. The crystalline aldehydes which separated were collected and purified (see *J.*, 1945, 276). Methylamine was determined in one half of the filtrate (see below), and additional aldehyde was obtained from the other half by adding excess of sodium hydroxide solution, extracting with ether, and drying and distilling the extract. *p*-Dimethylaminobenzaldehyde (b. p. 170—175°/12 mm., m. p. and mixed m. p. 73°) and *p*-diethylaminobenzaldehyde (b. p. 168—170°/9 mm., m. p. and mixed m. p. 41°) were collected. The remainder of the extracted oils consisted mainly of unchanged dialkylaniline and the diarylmethane compounds  $R_2N \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot NR_2$  ( $R = Me$  or  $Et$ ).

(b) *p*-Ethylmethyl-, *p*-di-*n*-propyl-, and *p*-di-*n*-butyl-aminobenzaldehydes. The reaction mixtures were poured into aqueous 2.5N-hydrochloric acid (150 ml.). Methylamine was determined in one half of each clear solution (see below); the other half was made alkaline, and the liberated oils were extracted with ether, dried, and distilled. *p*-Ethylmethylaminobenzaldehyde was collected at 180—184°/10 mm. and solidified, m. p. and mixed m. p. 44°. *p*-Di-*n*-propylaminobenzaldehyde was obtained as a straw-coloured oil, b. p. 180—182°/4 mm.,  $n_D^{20}$  1.5684 (Found: C, 75.7; H, 9.3; N, 6.8.  $C_{13}H_{19}ON$  requires C, 76.1; H, 9.3; N, 6.8%). The *phenylhydrazone* was a fawn-coloured powder, m. p. 104° (Found: N, 14.25.  $C_{19}H_{25}N_3$  requires N, 14.2%), and the *p*-nitrophenylhydrazone was dark green crystals, m. p. 164° (Found: N, 16.6.  $C_{19}H_{24}O_2N_4$  requires N, 16.5%).

*p*-Di-*n*-butylaminobenzaldehyde was obtained as a colourless oil, b. p. 198—200°/3 mm.,  $n_D^{20}$  1.5852 (Found: C, 77.5; H, 10.0; N, 5.95.  $C_{15}H_{23}ON$  requires C, 77.3; H, 9.9; N, 6.0%). It formed a *phenylhydrazone* as a fawn-coloured powder, m. p. 92° (Found: N, 13.1.  $C_{21}H_{29}N_3$  requires N, 13.0%), and a *p*-nitrophenylhydrazone as dark red crystals, m. p. 133° (Found: N, 15.4.  $C_{21}H_{28}O_2N_4$  requires N, 15.2%).

(c) *p*-Benzylmethyl- and *p*-benzylethyl-aminobenzaldehydes. The reaction mixture was poured into aqueous hydrochloric acid (100 ml.; approx. 5N). Methylamine was determined (see below) in one half of the clear solution; the other half was made alkaline and the liberated oil extracted with ether. After removal of the ether by distillation, the aldehyde in the oil was collected as the *p*-nitrophenylhydrazone; the derivative of *p*-benzylmethylaminobenzaldehyde had m. p. 179°, and that of *p*-benzylethylaminobenzaldehyde, m. p. 164°, in agreement with those given by Duff (*J.*, 1945, 276).

*Methylamine.* The reserved solution from each preparation was made alkaline with sodium hydroxide, and the liberated volatile amines were distilled and collected in excess of hydrochloric acid. This solution was evaporated to dryness, and the mixed hydrochlorides were extracted first with chloroform to remove di- and tri-methylamine salts and then with *n*-butyl alcohol at 100° to dissolve methylamine hydrochloride. The amines were then determined by distilling them into standard acid. In no case was more than 0.01 mole of mixed di- and tri-methylamines found, and in general the amount was much less.

*Reactions of N-Methylenebenzylamine and p-Dimethylamino-N-methylenebenzylamine.*—*N*-Methylenebenzylamine, m. p. 48°, was prepared from benzylamine and formaldehyde (Ingold and Shoppee, *J.*, 1929, 1199). *p*-Dimethylaminobenzylamine, b. p. 150°/14 mm., was prepared by reduction of *p*-dimethylaminobenzaldoxime with 3% sodium amalgam (Shoppee, *J.*, 1931, 1225) and then stirred with excess of 40% formaldehyde solution. The aqueous layer was removed from the lower viscous liquid, and the latter dried *in vacuo* over concentrated sulphuric acid and finally washed with ethyl alcohol. The product was *p*-dimethylamino-*N*-methylenebenzylamine, a white powder, m. p. 97° (Found: C, 74.3; H, 8.7; N, 17.2.  $C_{10}H_{14}N_2$  requires C, 74.1; H, 8.6; N, 17.3%). *N*-Methylenebenzylamine (1 g., 0.0084 mole) and hexamine (1 g.) were heated in glacial acetic acid (3 ml.) on a steam-bath for 2 hours. No formaldehyde could be detected in the vapour carried off by a current of dry air passing through the solution during the heating period. The reaction mixture was cooled, and water added. The odour of benzaldehyde was noticed immediately. Methylamine was determined in one half of the aqueous solution by the method described above, and benzaldehyde in the other half by formation of the 2:4-dinitrophenylhydrazone following Shoppee's method (*J.*, 1931, 1225). For the whole batch the amount of methylamine was 0.16 g. (0.0052 mole) and the amount of benzaldehyde was 0.54 g. (0.0051 mole). *p*-Dimethylamino-*N*-methylenebenzylamine (1 g., 0.0061 mole), submitted to the same treatment as for *N*-methylenebenzylamine, gave methylamine (0.105 g., 0.0034 mole) and *p*-dimethylaminobenzaldehyde (0.49 g., 0.0033 mole); determined as the *p*-nitrophenylhydrazone.

Use of trimethylamine in place of hexamine (in the same molar proportions) in the above isomerisation experiments resulted in yields of 0.0036 mole of benzaldehyde and 0.0028 mole

of *p*-dimethylaminobenzaldehyde. Use of pyridine similarly gave yields of 0.0034 mole of benzaldehyde and 0.0025 mole of *p*-dimethylaminobenzaldehyde.

*Reactions in Formic Acid.*—Hexamine (40 g.) and ethyl alcohol (40 ml.) were heated on a steam-bath while a mixture of dimethylaniline (30 ml., 0.24 mole) and formic acid (100 ml., 85%) was added dropwise during 3 hours. Heating was continued for a further 2 hours. The reaction mixture was then cooled, diluted with water (100 ml.), and made alkaline with sodium hydroxide solution. The oil which separated was extracted with ether, dried, and distilled. The fraction, b. p. 135—136°/10 mm., was *p*-dimethylaminobenzylidimethylamine (6.4 g.),  $n_D^{20}$  1.5422 (Found: C, 74.6; H, 9.9; N, 15.8.  $C_{11}H_{18}N_2$  requires C, 74.2; H, 10.1; N, 15.7%). A *methiodide*, formed immediately on addition of methyl iodide to an ethereal solution of the amine, was a microcrystalline powder, m. p. >250° (Found: N, 8.7; I, 39.6.  $C_{12}H_{21}N_2I$  requires N, 8.75; I, 39.7%). A *monopicate* of the ditertiary amine was obtained as orange-yellow crystals, m. p. 143° (Found, by use of titanous sulphate:  $NO_2$ , 34.0.  $C_{11}H_{18}N_2 \cdot C_6H_5O_7N_3$  requires  $NO_2$ , 33.9%), and a *dipicrate* as bright yellow crystals, m. p. 163° (Found:  $NO_2$ , 43.7.  $C_{11}H_{18}N_2 \cdot 2C_6H_5O_7N_3$  requires  $NO_2$ , 43.4%).

The same method and the same molal proportions being used, ethylmethylaniline yielded *p*-ethylmethylanilino-benzylidimethylamine (0.4 g.), b. p. 126—127°/5 mm.,  $n_D^{20}$  1.5399 (Found: C, 74.9; H, 10.6; N, 14.6.  $C_{12}H_{20}N_2$  requires C, 75.0; H, 10.4; N, 14.6%). This gave a *methiodide* as a crystalline powder, m. p. 139—140° (decomp.) (Found: N, 8.6; I, 38.0.  $C_{13}H_{23}N_2I$  requires N, 8.4; I, 38.0%). A *monopicate* was obtained as orange-yellow crystals, m. p. 93° (Found:  $NO_2$ , 32.9.  $C_{12}H_{20}N_2 \cdot C_6H_5O_7N_3$  requires  $NO_2$ , 32.8%), and a yellow crystalline *dipicrate*, m. p. 158° (Found:  $NO_2$ , 42.5.  $C_{12}H_{20}N_2 \cdot 2C_6H_5O_7N_3$  requires  $NO_2$ , 42.5%). Similarly, diethylaniline yielded *p*-diethylanilino-benzylidimethylamine (4.4 g.), b. p. 150—151°/8 mm.,  $n_D^{20}$  1.5425 (Found: C, 75.6; H, 10.7; N, 13.6.  $C_{13}H_{22}N_2$  requires C, 75.7; H, 10.7; N, 13.6%). This formed a *methiodide*, a microcrystalline powder, m. p. 146° (Found: N, 8.05; I, 36.5.  $C_{14}H_{25}N_2I$  requires N, 8.05; I, 36.5%), a *monopicate*, yellow crystals, m. p. 105° (Found:  $NO_2$ , 31.8.  $C_{13}H_{22}N_2 \cdot C_6H_5O_7N_3$  requires  $NO_2$ , 31.7%), and a *dipicrate*, yellow crystals, m. p. 151° (Found:  $NO_2$ , 42.1.  $C_{13}H_{22}N_2 \cdot 2C_6H_5O_7N_3$  requires  $NO_2$ , 41.6%).

For the remaining dialkylanilines the best yields of the ditertiary amines were obtained by reducing the proportion of the dialkylaniline in the above preparation method from 0.24 to 0.12 mole. Di-*n*-propylaniline yielded *p*-di-*n*-propylanilino-benzylidimethylamine (0.1 g.), b. p. 138—139°/4 mm.,  $n_D^{20}$  1.5130 (Found: C, 76.7; H, 10.9; N, 11.9.  $C_{15}H_{26}N_2$  requires C, 76.9; H, 11.1; N, 12.0%). It formed a *methiodide*, a microcrystalline powder, m. p. 147° (Found: N, 7.7; I, 33.9.  $C_{16}H_{29}N_2I$  requires N, 7.4; I, 33.8%), and a yellow crystalline *dipicrate*, m. p. 140° (Found:  $NO_2$ , 39.9.  $C_{15}H_{26}N_2 \cdot 2C_6H_5O_7N_3$  requires  $NO_2$ , 39.9%).

Di-*n*-butylaniline yielded *p*-di-*n*-butylanilino-benzylidimethylamine (0.4 g.), b. p. 160—161°/4 mm.,  $n_D^{20}$  1.5261 (Found: C, 78.1; H, 11.6; N, 10.4.  $C_{17}H_{30}N_2$  requires C, 77.9; H, 11.4; N, 10.7%). It yielded a *methiodide* as a microcrystalline powder, m. p. 135—136° (Found: N, 7.0; I, 31.6.  $C_{18}H_{33}N_2I$  requires N, 6.9; I, 31.4%), and a yellow crystalline *dipicrate*, m. p. 114° (decomp.) (Found:  $NO_2$ , 38.1.  $C_{17}H_{30}N_2 \cdot 2C_6H_5O_7N_3$  requires  $NO_2$ , 38.3%). Benzylmethylaniline yielded *p*-benzylmethylanilino-benzylidimethylamine (4.2 g.), b. p. 215—216°/8 mm.,  $n_D^{20}$  1.6015 (Found: C, 79.9; H, 8.5; N, 11.2.  $C_{17}H_{22}N_2$  requires C, 80.3; H, 8.7; N, 11.0%). It formed a *methiodide* as a microcrystalline powder, m. p. 140—144° (decomp.) (Found: N, 7.1; I, 31.8.  $C_{18}H_{25}N_2I$  requires N, 7.1; I, 32.1%), a yellow crystalline *monopicate*, m. p. 140° (Found:  $NO_2$ , 28.4.  $C_{17}H_{22}N_2 \cdot C_6H_5O_7N_3$  requires  $NO_2$ , 28.5%), and a yellow crystalline *dipicrate*, m. p. 163° (decomp.) (Found:  $NO_2$ , 38.6.  $C_{17}H_{22}N_2 \cdot 2C_6H_5O_7N_3$  requires  $NO_2$ , 38.7%). Benzylethylaniline yielded *p*-benzylethylanilino-benzylidimethylamine (2.9 g.), b. p. 210—211°/3 mm.,  $n_D^{20}$  1.5943 (Found: C, 80.6; H, 9.3; N, 10.2.  $C_{18}H_{24}N_2$  requires C, 80.6; H, 9.0; N, 10.4%). It formed a *methiodide* as a microcrystalline powder, m. p. 157° (decomp.) (Found: N, 6.9; I, 30.95.  $C_{19}H_{27}N_2I$  requires N, 6.8; I, 31.0%), and a yellow crystalline *monopicate*, m. p. 110° (Found:  $NO_2$ , 27.9.  $C_{18}H_{24}N_2 \cdot C_6H_5O_7N_3$  requires  $NO_2$ , 27.7%).

*Examination of the Quaternary Salts.*—The methiodides formed by *p*-dimethyl- and *p*-diethylanilino-benzylidimethylamine were shaken in water with precipitated silver oxide. The filtered solutions of the quaternary hydroxides were evaporated *in vacuo*, the crystalline bases remaining were decomposed by heating, and the alkaline vapours were absorbed in hydrochloric acid. Evaporation of the acid solutions in both cases yielded trimethylamine hydrochloride, m. p. 277—278° [platinichloride, m. p. 242° (Found: Pt, 37.2. Calc. for  $2C_3H_9N \cdot H_2PtCl_6$ : Pt, 37.1%)].

*Reactions of Methylenebenzylamine and Methylene-*p*-dimethylaminobenzylamine.*—*N*-Methyl-

enebenzylamine (2 g.), hexamine (2 g.), and ethyl alcohol (2 ml.) were heated on a steam-bath while formic acid (6 ml., 85%) was added dropwise during an hour. Heating was continued for 2 hours. The reaction mixture was diluted with water, made alkaline with sodium hydroxide solution, and extracted with ether. The dried ethereal solution was distilled. The oil collected at 72°/10 mm. was benzyldimethylamine but contained a small proportion of benzaldehyde. The amine was purified by dissolving it in hydrochloric acid and removing the aldehyde by ether extraction; 0.7 g. of benzyldimethylamine was recovered from the acid solution and identified as methiodide, m. p. 179—180° (Found: N, 5.1. Calc. for  $C_{10}H_{16}NI$ : N, 5.05%). *p*-Dimethylamino-*N*-methylenebenzylamine (1 g.) was subjected to the above treatment and yielded *p*-dimethylaminobenzyldimethylamine (0.62 g.), b. p. 130—132°/10 mm. It yielded the same derivatives as those already recorded in its preparation from dimethylaniline.

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