

71. A New Method for the Preparation of p-Dialkylaminobenzaldehydes.

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After dimethylaniline, hexamethylenetetramine, acetic and formic acids have been heated together, *p*-dimethylaminobenzaldehyde can be separated in satisfactory yield by adding the mixture to dilute hydrochloric acid. The corresponding derivatives from other dialkyl- and from benzylalkyl-anilines have also been prepared by this method.

p-DIALKYLAMINO BENZALDEHYDES have already been prepared by the following methods: (1) Ullmann and Frey (*Ber.*, 1904, **37**, 855) used a reaction between a dialkylaniline, *p*-nitrosodimethylaniline, and formaldehyde. This method has been developed and recommended for preparing *p*-dimethylaminobenzaldehyde (*Org. Synth.*, Coll. Vol. 1, 1932, 208). (2) D.R.-P. 105,105 describes the preparation of *p*-dimethyl- and *p*-diethyl-aminobenzaldehydes from interaction of the dialkylaniline, formaldehyde, and *m*-nitrobenzenesulphonic acid in the presence of iron and hydrochloric acid. (3) D.R.-P. 118,567 describes a modification of method (2), using an amino-sulphonic acid instead of the corresponding nitro-acid. (4) In D.R.-P. 103,578 use is made of a reaction between a dialkylaniline, formaldehyde, and a hydroxylaminotoluenesulphonic acid. (5) Vilsmeier and Haack (*Ber.*, 1927, **60**, 119) used a reaction between *N*-formylmethylaniline, phosphorus oxychloride, and a dialkylaniline, obtaining very good yields of *p*-aldehydes from dimethyl-, diethyl-, and benzylmethyl-aniline.

For methods (2), (3), and (4) yields are not recorded. Dippy, Hogarth, Watson, and Williams (*J. Soc. Chem. Ind.*, 1937, **56**, 346r) investigated the first three methods and concluded that (1) was satisfactory, (2) unsatisfactory, and (3) had to be modified to give good yields of *p*-dimethyl- and *p*-diethyl-aminobenzaldehydes. Methods (4) and (5) are the only recorded methods for preparing *p*-benzylalkylaminobenzaldehydes.

The author (*J.*, 1941, 547) has already described a method for the preparation of *o*-hydroxy-aldehydes from the reaction between phenols and hexamethylenetetramine in glyceroboric acid. It was decided then to investigate the possibility of introducing an aldehyde group into dialkylanilines by a similar method. Glyceroboric acid was found unsuitable as an acid medium for the reaction, but acetic acid, which was not a success with phenols, was found to be suitable for use with the tertiary amines, especially when formic acid also was present.

Formic acid alone gave only poor yields of the aldehydes; acetic acid alone gave satisfactory yields, but the aldehydes were slightly discoloured. After several hours' heating of the dialkylaniline and hexamethylenetetramine in a mixture of acetic and formic acids the resulting solution was poured into 0.5*N*-hydrochloric acid, and the aldehyde separated in almost pure condition. The yields compare favourably with those recorded for other general methods. This new method has been applied successfully to dimethyl-, diethyl-, and methyl-ethyl-aniline, and to dimethyl-*m*-toluidine, but failed, as expected, with dimethyl-*o*- and -*p*-toluidines. A modified procedure was necessary for the purification of the *p*-aldehydes obtained from benzylmethyl- and benzylethyl-anilines. The mechanism of the reaction could not be established by the separation of any intermediate compound. It probably proceeds in the same way as that suggested for the formation of phenolic aldehydes (*loc. cit.*) and may therefore be as follows:



followed by isomerisation and hydrolysis:



The dilute hydrochloric acid used in the separation of the aldehyde hastened the hydrolysis and served to retain in solution the more basic by-products.

EXPERIMENTAL.

Preliminary experiments showed that a mixture of glacial acetic acid and 90% formic acid was more effective than when either acid was used alone. Anhydrous formic acid was less useful than the 90% acid in the mixture. This mixed acid had to be added in portions during the reaction, apparently because the formic acid had a reducing effect, indicated by the evolution of carbon dioxide. Alcohol was used in the process merely to assist in bringing more of the hexamethylenetetramine into solution initially.

All the aldehydes now prepared have been made by other methods, and, except *p*-methylethylaminobenzaldehyde, they agree with the recorded descriptions of their properties. They all give bright yellow condensation products with aniline, reduce Tollens's reagent, and form phenylhydrazones and/or *p*-nitrophenylhydrazones.

Method of Preparation for p-Dialkylaminobenzaldehydes.—To the dialkylaniline (30 g.), hexamethylenetetramine (40 g.), and 95% ethyl alcohol (20 ml.), heated under reflux on a boiling water-bath, 30 ml. of a mixture of glacial acetic acid (45 ml.) and 90% formic acid (45 ml.) were added, and the remainder of the mixed acid was added in 10-ml. portions at 30-min. intervals. After a total of 5 hours' heating, the hot liquid mixture was poured with stirring into 600 ml. of approx. 0.5*N*-hydrochloric acid and left for several hours. The aldehyde separating was purified either by crystallisation from 30% alcohol or by distillation under reduced pressure. In the case of *p*-dimethylaminobenzaldehyde the acid filtrate obtained after removal of the aldehyde was examined for by-products by adding excess of sodium hydroxide solution. This produced about 20 g. of yellow oil, from which about 3 g. of bis-(*p*-dimethylaminophenyl)methane crystallised. Distillation of the remaining oil produced a further 4 g. of *p*-dimethylaminobenzaldehyde, distilling at 145°/10 mm. The remainder of the oil was not identified and could not be distilled. *p*-Dimethylaminobenzaldehyde (yield 14 g.) was obtained in colourless leaflets, m. p. and mixed m. p. 73°, b. p. 180°/20 mm. A phenylhydrazone, m. p. 148°, and an oxime, m. p. 144° (Found: N, 17.3. Calc. for C₉H₁₂ON₂: N, 17.1%), were prepared by the usual methods.

p-Diethylaminobenzaldehyde was purified by crystallisation from 30% alcohol, yield 14 g., m. p. 41°. The oxime had m. p. 93°, and the phenylhydrazone m. p. 121° (Found: N, 15.9. Calc. for C₁₁H₁₄N₂: N, 15.7%); Ullmann and Frey (*loc. cit.*) give m. p. 93° and 103°, respectively.

p-Methylethylaminobenzaldehyde separated as an oil. It distilled at 180—185°/20 mm. and solidified (12 g.); m. p. 44° (Found: N, 8.7. Calc. for C₁₀H₁₃ON: N, 8.6%). Ullmann and Frey (*loc. cit.*) record m. p. 14°. They found N, 9.14% and do not record the yield. The phenylhydrazone had m. p. 114°, in agreement with Ullmann and Frey.

4-Dimethylamino-2-methylbenzaldehyde from *N*-dimethyl-*m*-toluidine was purified by crystallisation from 30% alcohol; yield 6 g., m. p. 67° (Found: N, 8.8. Calc. for C₁₀H₁₃ON: N, 8.6%). Dimethyl-*o*- and *p*-toluidines did not yield an aldehyde, being recovered unchanged in each case.

For the preparation of *p*-benzylmethylaminobenzaldehyde the process was modified as follows: To benzylmethyl-aniline (40 g.), hexamethylenetetramine (40 g.), and ethyl alcohol (25 ml.), heated under reflux on a boiling water-bath, were added 30 ml. of a mixture of glacial acetic acid (75 ml.) and 90% formic acid (25 ml.), the remainder being added in 15-ml. portions at 40-min. intervals. After heating and treatment as in the general method (above), the separated oil was taken up in ether (150 ml.) and shaken with sodium bisulphite solution. The crystalline addition compound was collected, dissolved in hot 2*N*-hydrochloric acid, and the aldehyde precipitated by excess of sodium hydroxide solution; yield 20 g., m. p. 63° (Found: N, 6.3. Calc. for C₁₁H₁₅ON: N, 6.2%). The *p*-nitrophenylhydrazone, m. p. 179°, was obtained as dark red leaflets (Found: N, 15.7. C₁₁H₁₀O₂N₄ requires N, 15.5%).

By the same process benzylethylaniline (40 g.) yielded *p*-benzylethylaminobenzaldehyde, but no addition compound with sodium bisulphite could be formed. The aldehyde was purified by extraction of the dried oil with light petroleum (b. p. 60—80°) to remove unchanged amine, 16 g. being left as a thick yellow oil which set to a glassy mass at 0° (in agreement with D.R.-P. 103,578). The *p*-nitrophenylhydrazone, m. p. 164°, was obtained in dark red leaflets (Found: N, 15.2. C₁₁H₁₂O₂N₄ requires N, 15.0%).

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