CLXXXVIII.—2 : 4-*Dinitrobenzaldehyde as a Reagent.*

By GEORGE MACDONALD BENNETT and WALTER LAWRENCE C. PRATT.

THE use of 2 : 4-dinitrobenzaldehyde as a reagent for the characterisation of amines has been studied repeatedly (for example, by Lowy and his co-workers, *J. Amer. Chem. Soc.*, 1920, **42**, 849; 1921, **43**, 346; 1923, **45**, 1060). The exceptional ease with which this aldehyde condenses with the reactive methyl groups of heterocyclic bases was recently pointed out (Bennett and Willis, J., 1928, 1962). In the latter respect the dinitro- is more useful than the trinitrobenzaldehyde, which reacts more slowly, presumably owing to steric hindrance. We have therefore made further application of the dinitro-aldehyde in the two directions mentioned, and we describe below its condensation products with several new amines and heterocyclic bases.

The reagent differentiates sharply between the reactivities of the two methyl groups of 2 : 4-dimethylquinoline, since condensation in position 2 is rapidly completed, whereas prolonged boiling is necessary to effect the second stage of the reaction involving the 4-methyl group.

The dinitro-aldehyde also condensed with *p*-nitrophenylacetonitrile, but no reaction could be detected with dibenzyl sulphoxide or dibenzylsulphone.

An improvement in the method of preparation of the aldehyde is described.

EXPERIMENTAL.

Preparation of 2 : 4-*Dinitrobenzaldehyde.*—In the first stage of the preparation from 2 : 4-dinitrotoluene (Sachs and Kempf, *Ber.*, 1902, **35**, 1224) the sodium carbonate, which appears to function merely by removing traces of acid, may be much reduced in quantity. Dinitrotoluene (300 g.), *p*-nitrosodimethylaniline (265 g.), and sodium carbonate (30 g.) were condensed in boiling alcohol (1·5 l.) for 5 hours (yield of dinitrobenzylidene-*p*-aminodimethylaniline, m. p. 193°, 76%). The hydrolysis of this condensation product was simplified as follows : the crude washed material (100 g.) was covered with hydrochloric acid (125 c.c. of concentrated acid and 125 c.c. of water), and the mixture boiled, steam being introduced to ensure vigorous agitation. After 3—5 minutes at the boiling point the whole was cooled, the aqueous liquor removed, and the solid remelted as before under a fresh portion of the same acid. The solid product was finally washed with water and dried. This crude dinitrobenzaldehyde is best purified by crystallisation from light petroleum (b. p. 90—110°), the solvent being saturated at a temperature a little below the boiling point (yield of pale brown needles, m. p. 71°, 74% ; Sachs and Kempf claim 88% of the crude product). One further crystallisation raises the m. p. to 72°.

Condensation of Dinitrobenzaldehyde with Aromatic Amines.—The amine and the aldehyde (in slight excess) were mixed in hot alcoholic solution with the addition of a few drops of acetic acid. The products were usually analytically pure after one recrystallisation. *Dinitrobenzylidene*-m-*chloroaniline* separates from butyl alcohol in small orange pyramids, m. p. 137° (Found : N, 14·0. $C_{13}H_8O_4N_3Cl$ requires N, 13·75%). The corresponding derivatives of *o*-chloro- and *p*-chloro-aniline, prepared for comparison, melted at 164·5° and 158° respectively (Found : N, 13·7 and 13·8%). Downey and Lowy give these m. p.'s as 167·5° and 161·5° respectively. *Dinitrobenzylidene*-3 : 5-*dibromoaniline* crystallises from butyl alcohol in copper-red plates, m. p. 181° (Found : N, 10·1. $C_{13}H_7O_4N_3Br_2$ requires N, 9·8%). *Dinitrobenzylidene*-p-*iodoaniline* forms felted yellow needles, m. p. 163°, from amyl alcohol (Found : N, 10·5. $C_{13}H_8O_4N_3I$ requires N, 10·6%). *Dinitrobenzylidene*-p-*aminophenol* separates from ethyl alcohol in minute yellow polyhedra, m. p. 158° (Found : N, 14·5. $C_{13}H_9O_5N_3$ requires N, 14·6%). *Dinitrobenzylidene*-p-*aminoacetanilide* was obtained from ethyl alcohol in yellow monoclinic crystals, m. p. 199° (Found : N, 16·8. $C_{15}H_{12}O_5N_4$ requires N, 17·1%). *Bisdinitrobenzylidene*-o-*phenylenediamine* crystallises from aqueous alcohol in red-brown plates, m. p. 158° (Found : N, 18·2. $C_{20}H_{12}O_8N_6$ requires N, 18·1%). *Bisdinitrobenzylidene*-3 : 4-*tolylenediamine* crystallises from light petroleum in minute brown crystal aggregates, m. p. 153·5° (Found : N, 17·7. $C_{21}H_{14}O_8N_6$ requires N, 17·6%). *Bisdinitrobenzylidene*-4 : 4′-*diaminodiphenylamine* crystallises from nitrobenzene in purple pyramids with a green reflex, m. p. 263° (decomp.) (Found : N, 17·6. $C_{26}H_{17}O_8N_7$ requires N, 17·7%). *Dinitrobenzylidene*-6-*aminoquinoline* forms pale yellow needles, m. p. 206°, from butyl alcohol (Found : N, 17·7. $C_{16}H_{10}O_4N_4$ requires N, 17·3%).

Condensation of Dinitrobenzaldehyde with Substances having a Reactive Methyl or Methylene Group.—The reactions in general proceed rapidly in boiling acetic anhydride, the products crystallising from the reaction mixture.

From α-picoline α-*dinitrostyrylpyridine* was obtained which separated from butyl alcohol in yellow plates, m. p. 159° (Found : N, 15·6. $C_{13}H_9O_4N_3$ requires N, 15·5%). 2:6-Dimethylquinoline yielded 2-*dinitrostyryl*-6-*methylquinoline* crystallising from butyl alcohol in minute yellow needles, m. p. 213° (Found : N, 12·6. $C_{18}H_{13}O_4N_3$ requires N, 12·5%). The product from 2 : 4-dimethylquinoline after 0·5—1 hour was 2-*dinitrostyryl*-4-*methylquinoline,* which formed spherical aggregates of yellow crystals, m. p. 163·5°, from butyl alcohol, being moderately easily soluble in hot butyl alcohol and readily soluble in boiling xylene but sparingly soluble in the cold solvents (Found : N, 12·5%). When this monostyryl base or the original dimethylquinoline were heated in boiling acetic anhydride with an excess of dinitrobenzaldehyde for 6—8 hours, *tetranitro*-2 : 4-*distyrylquinoline* was produced. It was freed from the monostyryl compound by extraction with hot xylene and was obtained after crystallisation successively from *cyclo*hexanol and nitrobenzene as a deep yellow, microcrystalline powder, m. p. 270° (decomp.) (Found : N, 13·8. $C_{25}H_{15}O_8N_5$ requires N, 13·6%). The di- and tri-chloro-derivatives of 2 : 4-dimethylquinoline reacted equally rapidly to yield 5 : 8-*dichloro*-2-*dinitrostyryl*-4-*methylquinoline*, crystallising from toluene in orange needles, m. p. 198·5° (Found : N, 10·9. $C_{18}H_{11}O_4N_3Cl_2$ requires N, 10·4%), and 5 : 6 : 8-*trichloro*-2-*dinitrostyryl*-4-*methylquinoline*, which separated from butyl alcohol in bright yellow needles, m. p. 225·5° (Found: N, 9·7. $C_{18}H_{10}O_4N_3Cl_3$ requires N, 9·6%). 2 : 4 : 6-Trimethylquinoline condensed rapidly to give 2-*dinitrostyryl*-4 : 6-*dimethylquinoline*, which after crystallisation from butyl alcohol formed a microcrystalline yellow powder, m. p. 195° (Found : N, 12·4. $C_{19}H_{15}O_4N_3$ requires N, 12·0%). 2-Methylbenziminazole also reacted rapidly to yield 2-*dinitrostyrylbenziminazole*, which crystallised from ethyl alcohol in minute orange-yellow needles, m. p. 215° (Found : N, 17·6. $C_{15}H_{10}O_4N_4$ requires N, 18·1%).

p-Nitrophenylacetonitrile was converted under similar conditions into 2 : 4 : 4′-*trinitro*-α-*cyanostilbene*, which crystallised from butyl alcohol in aggregates of pale brown plates, m. p. 149° (Found : N, 16·3. $C_{15}H_8O_6N_4$ requires N, 16·5%).

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THE UNIVERSITY,
SHEFFIELD.

THE SECONDARY SCHOOL,
WATH-ON-DEARNE.

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