CCXLVIII.—*Some Reactions of* mm'-*Dinitrobenzil.*

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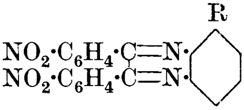
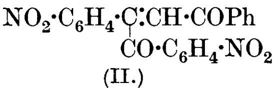
THE *mm'*-dinitrobenzil used in this research was prepared by direct nitration of benzil (Barrett and Kay, *Chem. News*, 1922, **125**, 57) and was separated from the accompanying *om'*- and *oo'*-isomerides by fractional crystallisation from acetone (compare Chattaway and Coulson, J., 1926, 1071), or by isolating the molecular *compound* with benzidine and decomposing that with dilute acid (see below).

mm'-Dinitrobenzil readily responds to the usual reactions for *o*-diketones : when treated in hot alcoholic solution with *o*-diamines it yields the corresponding quinoxalines, *e.g.*, 2 : 3-*di*-m-*nitrophenylquinoxaline* (I; R = H) and 5-*methylquinoxaline* (I; R = Me) with *o*-phenylene- and *o*-tolylene-diamine, respectively.

(I.)





$$\begin{array}{l} NO_2\cdot C_6H_4\cdot C{:}CH\cdot COPh \\ \qquad\quad CO\cdot C_6H_4\cdot NO_2 \end{array}$$

(II.)

Ferriss and Turner (J., 1920, **117**, 1143) and Le Fèvre and Turner (J., 1926, 2480) have disproved Cain and Micklethwait's work on the condensation of benzil with benzidine (J., 1914, **105**, 1437), and have shown that in glacial acetic acid solution 1 mol. of benzidine unites with 2 mols. of benzil, with the elimination of 2 mols. of water. *mm'*-Dinitrobenzil does not condense with benzidine in glacial acetic acid solution, but in hot alcoholic solution equimolecular proportions unite to form a compound which is quantitatively decomposed into its components by acetic acid or dilute mineral acid. A similar molecular *compound* is formed with *o*-tolidine.

mm'-Dinitrobenzil condenses with a molecular proportion of acetophenone under the influence of alcoholic caustic soda to give *dehydroacetophenone*-mm'-*dinitrobenzil* (α-m-*nitrobenzoyl*-β-*benzoyl*-m-*nitrostyrene*) (II). A compound with 2 mols. of acetophenone could not be isolated, nor could any crystalline product be obtained in many attempts to condense *mm'*-dinitrobenzil with acetone.

EXPERIMENTAL.

Preparation of Quinoxalines.—Equimolecular quantities of *mm'*-dinitrobenzil and the corresponding diamine were dissolved in alcohol, and the solution was boiled for about twenty minutes. The quinoxalines which separated were filtered off and recrystallised from a large quantity of alcohol. 2 : 3-*Di*-m-*nitrophenylquinoxaline* formed white needles, almost insoluble in alcohol, m. p. 208° (Found : C, 64·2; H, 3·3; N, 15·0. $C_{20}H_{12}O_4N_4$ requires C, 64·5; H, 3·2; N, 15·1%); and 2 : 3-*di*-m-*nitrophenyl*-5-*methylquinoxaline* formed pale yellow needles, slightly soluble in ether, and soluble in warm acetone or benzene, m. p. 208—210° (Found: C, 64·1; H, 3·6; N, 14·4. $C_{21}H_{14}O_4N_4$ requires C, 65·3; H, 3·7; N, 14·5%).

Molecular Compound of mm'*-Dinitrobenzil and Benzidine.*—When equimolecular quantities of *mm'*-dinitrobenzil and benzidine, dissolved in absolute alcohol, were boiled for a few minutes, a crystalline compound was formed; it recrystallised from alcohol as chocolate-brown plates, m. p. 163·5°, yield almost theoretical [Found: C, 64·3, 64·3; H, 4·5, 4·5; N, 11·4; NO_2 (by $TiCl_3$), 19·0. $C_{26}H_{20}O_6N_4$ requires C, 64·5; H, 4·5; N, 11·6; NO_2, 19·0%]. This *compound* is readily decomposed into its constituents by acetic acid or dilute mineral acids, and when decomposition was effected by dilute hydrochloric acid, the *mm'*-dinitrobenzil, after being washed with water and dried, corresponded to 59·0% of the initial material (Calc.: 60·2%). Cryoscopic measurements in 2 : 4-dinitrotoluene (Auwers, *Z. physikal. Chem.*, 1899, **30**, 310) gave $M = 258$, showing that the molecular compound is almost completely dissociated in that solvent.

Isolation of mm'*-dinitrobenzil by means of its benzidine compound.* Benzil was nitrated by Barrett and Kay's method (*loc. cit*), and the mixed nitro-compounds were boiled with a solution of sodium carbonate to remove nitro-acids; 25 g. of the resulting mixture were dissolved in 400 c.c. of boiling alcohol, and 18 g. of pure benzidine added. The chocolate-brown crystalline deposit formed after a few minutes' boiling was filtered from the hot liquid and proved to be the foregoing addition compound (crude yield, 18 g., m. p. 163·5°). When decomposed with acetic acid containing a little hydrochloric acid, it gave 10 g. of a yellow substance, m. p. 126°, which, recrystallised from acetone and then from glacial acetic acid, gave tufts of pale yellow needles, m. p. 132°, identical with the *mm'*-dinitrobenzil isolated by Chattaway and Coulson's method (*loc. cit.*).

Molecular Compound of mm'*-Dinitrobenzil and* o*-Tolidine.*—Equimolecular quantities of the two constituents in hot alcohol yield a molecular *compound* which, recrystallised from alcohol containing a little *o*-tolidine, forms chocolate-coloured plates, m. p. 164° (Found: N, 11·2. $C_{28}H_{24}O_6N_4$ requires N, 10·94%).

*Dehydroacetophenone-*mm'*-dinitrobenzil* (II).—*mm'*-Dinitrobenzil (8 g.) and acetophenone (6·4 g.) were dissolved in warm alcohol, and 2 c.c. of *N*/10-alcoholic caustic soda added. The solid which separated on cooling and standing was washed with dilute hydrochloric acid, and separated from benzene in fine yellow needles, m. p. 158° (Found: C, 65·86; H, 3·48; N, 6·64. $C_{22}H_{14}O_6N_4$ requires C, 65·69; H, 3·47; N, 6·94%).

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