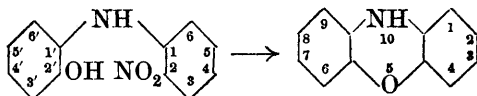


CLIV.—*The Formation of Phenoxazines.*

BY OSCAR L. BRADY and CECIL WALLER.

CERTAIN substituted 2-nitro-2'-hydroxydiphenylamines on treatment with alkali readily lose nitrous acid to give phenoxazines:



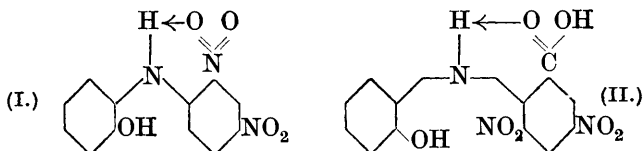
The reaction has been investigated by Turpin (J., 1891, **59**, 720), Ullmann (*Annalen*, 1908, **366**, 79), and Ullmann and Sané (*Ber.*, 1911, **44**, 3730), but no satisfactory explanation has been suggested for the influence of other groups present in the molecule upon the reaction.

It was found by these workers that the phenoxazines are formed when the following compounds are treated with alkali: 2:4:6-trinitro-, 2:6-dinitro-, 2:4-dinitro-6-carboxy-, 2:6-dinitro-4-carboxy-, 2:6-dinitro-4-benzoyl-, 2:4-dinitro-6-sulpho-, 2:6-dinitro-4-sulpho-, 2:4-dinitro-6-methyl-, and 2:6-dinitro-4-chloro-2'-hydroxydiphenylamines. No reaction occurred, however, with 2:4-dinitro-2'-hydroxydiphenylamine. Thus in all cases where the phenoxazine was formed the 6-position was occupied, and Ullmann concluded that this was a necessary condition for the reaction to occur. In order to test this view more fully, a number of similar compounds have been investigated. In all the cases previously studied, with the exception of 2:4-dinitro-2'-hydroxy-6-methyldiphenylamine, a "negative" group occupied the 6-position. It did not seem likely that groups of such different character as NO_2 and CH_3 would activate the 2-nitro-group, but in order to test this point a group at the other end of the scale, namely, methoxyl, was tried and it was found that 2:4-dinitro-2'-hydroxy-3:6-dimethoxydiphenylamine readily gave the phenoxazine.

The presence of a methyl group in another position in the nitrated ring had no influence; 2:6-dinitro-5-methyl- and 2:6-dinitro-4-methyl-2'-hydroxydiphenylamines readily gave phenoxazines, but 2:4-dinitro-5-methyl-2'-hydroxydiphenylamine did not do so. A methyl group in the 6'-position was also without effect, 2:6-dinitro-2'-hydroxy-3:6'-dimethyldiphenylamine giving the phenoxazine and 2:4-dinitro-2'-hydroxy-6'-methyl- and 2:4-dinitro-2'-hydroxy-5:6'-dimethyl-diphenylamines failing to do so.

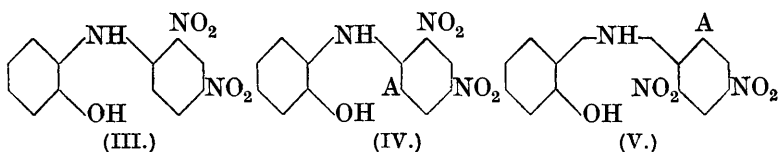
The lack of reactivity of, for example, 2:4-dinitro-2'-hydroxydiphenylamine might be due to chelation of the 2-nitro-group with

the imino-group (I) preventing its access to the hydroxyl group; the presence of another group in the 6-position which could itself



chelate (II) would negate this effect and most of the compounds investigated have such a group, but it is difficult to suppose that the methyl group would be effective in this respect. Attempts to prepare *N*-methyl derivatives in order to eliminate the possibility of chelation as in (I) were, however, unsuccessful.

The only explanation that can be suggested is a purely steric one: if the 6-position is free, for steric reasons the large nitro-group takes up a position remote from the hydroxyl group, thus bringing the



6-position near it (III). If there is a group in the 6-position, there is less reason for the compound to be oriented as (IV) than as (V). Experiments are in hand with the object of obtaining evidence of such orientation in compounds of this type.

EXPERIMENTAL.

2 : 6-Dinitro-3-methyl-, 2 : 4-Dinitro-5-methyl-, and 2 : 6-Dinitro-4-methyl-2'-hydroxydiphenylamines.—*2 : 3 : 4-, 3 : 4 : 6-, or 3 : 4 : 5-Trinitrotoluene* (4 g.), *o*-aminophenol (4 g.; 2 equivs.), and benzene (240 c.c.) were boiled for 4 hours under reflux, nitrous fumes being evolved; the mixture was then cooled and filtered. In the case of *2 : 3 : 4-trinitrotoluene* the filtrate was evaporated to dryness, and the residue crystallised four times from dilute alcohol; *2 : 6-dinitro-2'-hydroxy-3-methyldiphenylamine* was then obtained in reddish-purple needles (3 g.), m. p. 148° (Found: N, 14.7. $C_{13}H_{11}O_5N_3$ requires N, 14.5%).

In the second case the filtrate was evaporated to small bulk and, while it was still hot, boiling light petroleum was added until precipitation commenced. On cooling, a brown solid separated which, crystallised from benzene and light petroleum, gave *2 : 4-dinitro-2'-hydroxy-5-methyldiphenylamine* as a deep purple-brown, micro-crystalline powder (2.7 g.), m. p. 203° (Found: N, 14.8%).

Crystallised from methyl alcohol or from somewhat diluted acetic acid, this compound separated as an orange-red solid of the same m. p.

In the third case the tarry solid obtained on evaporation of the benzene was crystallised repeatedly from dilute alcohol; 2 : 6-dinitro-2'-hydroxy-4-methyldiphenylamine was then obtained in lustrous purple-brown needles, m. p. 152° (Found : N, 14.4%).

2-Chloro-6-nitro-2'-hydroxy-3-methyldiphenylamine.—A solution of 3 : 4-dinitro-*o*-chlorotoluene (2.3 g.) and *o*-aminophenol (5 g.) in alcohol (150 c.c.) was boiled under reflux for 20 hours, and cooled. Water and a little hydrochloric acid were then added and the precipitated tarry mass was extracted with boiling light petroleum; the precipitate obtained from the cooled extract was crystallised from the same solvent, 2-chloro-6-nitro-2'-hydroxy-3-methyldiphenylamine being obtained in purple-red needles (1 g.), m. p. 106° (Found : N, 10.2. $C_{13}H_{11}O_3N_2Cl$ requires N, 10.0%).

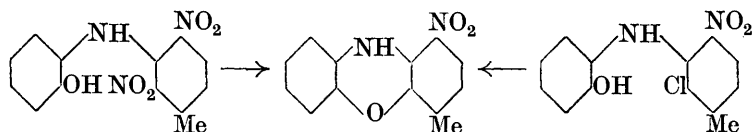
2 : 4-Dinitro-2'-hydroxy-3 : 6-dimethoxydiphenylamine.—This was prepared from trinitroquinol dimethyl ether (2.6 g.) and *o*-aminophenol (2.1 g.) in benzene (100 c.c.) as before. The reaction mixture was cooled, the liquid filtered and heated to boiling, and boiling light petroleum (200 c.c.) added. The precipitate produced on cooling was crystallised from benzene and light petroleum, 2 : 4-dinitro-2'-hydroxy-3 : 6-dimethoxydiphenylamine being obtained in brown prisms (1.5 g.), m. p. 186° (Found : N, 12.6. $C_{14}H_{13}O_7N_3$ requires N, 12.5%).

2 : 4-Dinitro-2'-hydroxy-5 : 6'-dimethyl-, 2 : 6-Dinitro-2'-hydroxy-4 : 6'-dimethyl-, and 2 : 4 : 6-Trinitro-2'-hydroxy-6'-methyldiphenylamines.—3 : 4 : 6- and 3 : 4 : 5-Trinitrotoluenes and picryl chloride were each heated with 2 equivalents of 2-amino-*m*-cresol in benzene under reflux for 4 hours, and the solutions cooled and filtered. In the first and second cases the filtrates were evaporated to dryness, and the residues crystallised repeatedly from dilute alcohol; there were then obtained 2 : 4-dinitro-2'-hydroxy-5 : 6'-dimethyldiphenylamine as brick-red prisms, m. p. 173° (Found : N, 14.1. $C_{14}H_{13}O_5N_3$ requires N, 13.9%), and 2 : 6-dinitro-2'-hydroxy-4 : 6'-dimethyldiphenylamine as purple plates, m. p. 198° (decomp.) (Found : N, 14.0%). In the third case light petroleum was added to the filtered solution, and the precipitate crystallised from benzene and light petroleum; 2 : 4 : 6-trinitro-2'-hydroxy-6'-methyldiphenylamine was then obtained as a bright crimson, microcrystalline powder, m. p. 176° (Found : N, 16.7. $C_{13}H_{10}O_7N_4$ requires N, 16.8%).

Formation of Phenoxazines.—The general method adopted was to dissolve the diphenylamine compound (1 g.) in 1% aqueous sodium

hydroxide (25 c.c.) and heat the solution on the water-bath for a time varying from a few minutes to 2 hours according to the nature of the compound undergoing reaction. The phenoxazine, if formed, was precipitated and the time necessary for reaction was indicated by the amount of precipitate. Nitrite, or in one case chloride, was detected in the solution after reaction. The yields were excellent.

2 : 6-Dinitro-2'-hydroxy-3-methyldiphenylamine gave 1-nitro-4-methylphenoxazine, which separated from somewhat diluted acetic acid as a dark violet powder, m. p. 169° (Found : N, 11.9. $C_{13}H_{10}O_3N_2$ requires N, 11.6%). The same compound was obtained from 2-chloro-6-nitro-2'-hydroxy-3-methyldiphenylamine, this result showing which of the two nitro-groups in 2 : 6-dinitro-2'-hydroxy-3-methyldiphenylamine is the reactive one :



2 : 6-Dinitro-2'-hydroxy-4-methyldiphenylamine gave 1-nitro-3-methylphenoxazine, almost black needles, m. p. 165°, from light petroleum (Found : N, 11.8%). 2 : 4-Dinitro-2'-hydroxy-3 : 6-dimethoxydiphenylamine gave 3-nitro-1 : 4-dimethoxyphenoxazine, crimson needles, m. p. 173°, from benzene and light petroleum (Found : N, 9.5. $C_{14}H_{12}O_5N_2$ requires N, 9.7%). 2 : 4 : 6-Tri-nitro-2'-hydroxy-6'-methyldiphenylamine gave 1 : 3-dinitro-9-methylphenoxazine, deep purple prisms, m. p. 224°, from benzene (Found : N, 14.7. $C_{13}H_9O_5N_3$ requires N, 14.6%). 2 : 6-Dinitro-2'-hydroxy-4 : 6'-dimethyldiphenylamine gave 1-nitro-3 : 9-dimethylphenoxazine, a violet powder, m. p. 162°, from benzene (Found : N, 11.6. $C_{14}H_{12}O_3N_2$ requires N, 11.4%). 2 : 4-Dinitro-2'-hydroxy-5-methyl-, 2 : 4-dinitro-2'-hydroxy-6'-methyl-, and 2 : 4-dinitro-2'-hydroxy-5 : 6'-dimethyl-diphenylamines were not converted into phenoxazines under the above conditions, no precipitate formed, and no nitrite was produced.

3-Bromo-4 : 6-dinitrotoluene.—A hot alcoholic solution of 4 : 6-dinitro-*m*-tolylhydrazine (5 g.) (Brady and Bowman, J., 1921, **119**, 894) was treated with successive small quantities of cupric bromide (30 g.), the mixture was cooled, and the liquid filtered. The filtrate was heated with a little concentrated hydrochloric acid and hydrogen peroxide to oxidise any cuprous bromide and poured into water. The precipitate obtained, after crystallising from alcohol, gave 3-bromo-4 : 6-dinitrotoluene in pale yellow needles, m. p. 101° (Found : N, 10.5. $C_7H_5O_4N_2Br$ requires N, 10.7%).

2 : 4-Dinitro-2'-methoxy-N-methyldiphenylamine.—This was prepared by heating *N*-methyl-*o*-anisidine (3 g.) and 2 : 4-dinitrochlorobenzene (5 g.) together with a little anhydrous zinc chloride for 6 hours in an oil-bath at 130—140°. The product was distilled in steam to remove unchanged dinitrochlorobenzene, the solid residue extracted with boiling dilute hydrochloric acid, and the insoluble matter crystallised from alcohol; *2 : 4-dinitro-2'-methoxy-N-methyldiphenylamine* was then obtained in yellow needles, m. p. 169° (Found: N, 14.3. $C_{14}H_{13}O_5N_3$ requires N, 13.9%). The methoxyl group could not be demethylated by treatment with an aqueous or glacial acetic acid solution of hydrogen bromide.

N-Methyl-*o*-aminophenol decomposes when heated above 80°. No reaction occurred when it was boiled for many hours in benzene with 2 : 4-dinitrochlorobenzene or 3-bromo-4 : 6-dinitrotoluene.

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