CCCCXXXIII.—*The Interaction of Piperidine with Nitro- and Halogenonitro-derivatives of Xanthone and Diphenylene Oxide.*

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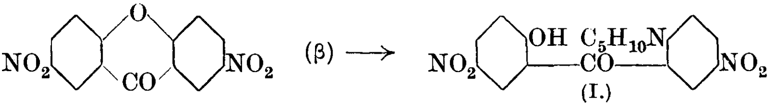
The interaction of various ethers with piperidine (Le Fèvre, Saunders, and Turner, J., 1927, 1168) suggested a method of comparing the strengths of attachment of radicals to the ethereal oxygen atom. In a similar way attempts have now been made to compare the activities of the ethereal oxygen atoms in diphenyl ether, xanthone, and diphenylene oxide. Owing to the stability of the parent substances the interactions of analogously constituted dinitro-derivatives (the nitro-groups being in each case in the *p*-positions to the ethereal oxygen atom) with piperidine were examined, and the following observations were made.

3 : 6-Dinitrodiphenylene oxide was recovered unchanged after several hours' boiling with piperidine or aniline. α- and β-Dinitroxanthones readily combined with piperidine in the cold, giving unstable yellow substances which, after a few hours' heating at 100°, became yellowish-orange piperidino-compounds (I). The piperidino-derivative from α-dinitroxanthone was not obtained in the pure state—a fact explained by the observation that 5 : 5'-*dinitro-2'-piperidino-2-hydroxybenzophenone* (I) lost piperidine at its melting point, the original dinitro-compound being regenerated. The



(I.)

observations that β-dinitroxanthone could be recovered unchanged from boiling aniline, and tetranitroxanthone from boiling piperidine (in both cases coloured addition compounds were formed in the cold), may similarly be explained by decomposition of the respective expected products at temperatures lower than the boiling points of the reagents.

The interaction of piperidine with 4 : 4′-dinitrodiphenyl ether was fairly rapid and led to normal scission products (Le Fèvre, Saunders, and Turner, *loc. cit.*).

Tetrabromodinitroxanthone (Dhar, J., 1916, **109**, 747) reacted only slowly with piperidine.

In the hope of revealing the orienting influence of oxonium oxygen the dinitration of 2 : 7-dibromoxanthone was examined. The crude dinitration products obtained by the action of nitric acid in acetic acid and in excess of sulphuric acid were boiled with piperidine. Neither product yielded a perceptible quantity of piperidine hydrobromide, but instead 3 : 3′-dibromo-5 : 5′-dinitro-6-piperidino-6′-hydroxybenzophenone was formed. Therefore either oxonium salt formation does not affect nitration in this instance or sulphuric acid solutions of xanthones contain little quadrivalent oxygen. Since the xanthone structure does not hinder the normal activation of ethereal oxygen by *o*-nitro-groups, the possibility that in the above example nitro-groups in the 3 : 3′-positions could not render bromine atoms in the 2 : 2′-positions labile is small.

EXPERIMENTAL.

Action of Piperidine on α- and β-Dinitroxanthones.—The dinitroxanthones (Dhar, *loc. cit.*) were crystallised from phenol–alcohol.

(1) When α-dinitroxanthone (2 g.) was covered with piperidine (10 c.c.), a bright yellow substance was formed. (If isolated, this lost piperidine and became almost colourless.) The mixture, after 5 hours' heating on the water-bath, gave a deep red solution, from which, on dilution with water, an amorphous, yellow powder was obtained which could not be crystallised (Found: N, 10·8—11·1% in different samples).

(2) β-*Dinitroxanthone.* The preliminary development of colour was not so strong as in the preceding case and the yellow compound dissolved much more slowly. After 10 hours' heating at 100° the mixture was worked up as described above; the 5 : 5′-*dinitro-2′-piperidino-2-hydroxybenzophenone* (I) obtained crystallised from acetic acid in yellow prisms, m. p. (rapid heating) 155° (Found: N, 11·4. $C_{15}H_{17}O_6N_3$ requires N, 11·3%).

When heated slowly, the substance melted at about 150° and changed to a red solid, which became yellower and finally melted at about 250° to a brown liquid. 4 G. of (I) were therefore heated at 200°. Piperidine was evolved. The brown product was repeatedly extracted with boiling acetic acid and obtained as a cream-coloured powder (Found : N, 9·9. Calc., N, 9·8%), m. p. 260—262° (alone or mixed with β-dinitroxanthone).

5 : 5′-*Dinitro-2′-piperidino-2-acetoxybenzophenone* was prepared by refluxing the piperidino-compound in acetic acid–acetic anhydride, containing anhydrous sodium acetate, until the solution was almost colourless; it was precipitated by water, and crystallised from acetic acid in small needles, m. p. 253—255° (Found: N, 10·8. $C_{20}H_{19}O_7N_3$ requires N, 10·2%).

Action of Aniline on β-*Dinitroxanthone.*—When 10 g. of β-dinitroxanthone and 35 g. of aniline were mixed in the cold, a red addition compound formed. After 4 hours' boiling, however, β-dinitroxanthone, m. p. 261—262°, was recovered (Found : N, 10·0%). Similar results were obtained with methyl aniline and *o*-toluidine.

Dinitration of 2 : 7-*Dibromoxanthone.*—(*a*) To 1 g. of dibromoxanthone, dissolved in 25 c.c. of concentrated sulphuric acid, 4 c.c. of nitric acid (*d* 1·5) were added; small needles soon began to appear. Cold water was then added and the product was collected, boiled with hot water, and dried on the water-bath; m. p. 208—214° (Found : N, 7·0. Calc. for $C_{13}H_4O_6N_2Br_2$: N, 6·3%). The product reacted readily with piperidine, giving an oily piperidino-compound. The aqueous extracts of the reaction mixture contained no bromine precipitable by silver nitrate. (*b*) A solution of 1 g. of dibromoxanthone in 20 c.c. of nitric acid (*d* 1·5) and 20 c.c. of glacial acetic acid was warmed at 90° for 6 hours. The product, on treatment with piperidine, gave the same result as before, the absence of nitro-groups in any of the 1 : 3 : 6 : 8-positions being thus indicated.

2 : 7-*Dibromo*-4 : 6-*dinitroxanthone* was prepared by allowing 3 g. of dibromoxanthone to dissolve in 60 c.c. of fuming nitric acid at about 60°. The product was isolated in the usual way; after being extracted with a little benzene and crystallised from much benzene, it had m. p. 265—266° (Found : N, 6·4. $C_{13}H_4O_6N_2Br_2$ requires N, 6·3%). The action of piperidine on it gave a gummy product which could not be separated.

Nitration of β-*Dinitroxanthone.*—A solution of 10 g. of the dinitro-compound in 100 c.c. of sulphuric acid and 100 c.c. of fuming nitric acid was heated on a water-bath for 3 hours. Dilution with water then gave 2 : 4 : 5 : 7-*tetranitroxanthone* as a white powder, not molten at 300° (Found : N, 14·8. $C_{13}H_4O_{10}N_4$ requires N, 14·9%).

Action of Piperidine on 2 : 4 : 5 : 7-*Tetranitroxanthone.*—When the reactants were mixed in the cold a bright red colour developed, but after the mixture had been heated for 8 hours at 100°, the tetranitro-compound was recovered (Found : N, 15·0%).

Piperidine reacted vigorously with 6-nitropiperonal, giving a tar from which no individual was isolated.

The author wishes to acknowledge the receipt of a grant from the Chemical Society which has helped to defray the cost of the materials used in this investigation.

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[*Received, October 30th,* 1928.]