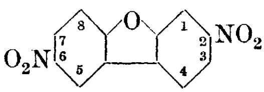
341. *Investigations in the Diphenylene Oxide Series. Part III.*

By N. M. Cullinane.

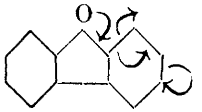
The 2-nitro-derivative obtained by the nitration of diphenylene oxide in acetic acid or carbon tetrachloride (Cullinane, J., 1930, 2267; compare Ryan and Cullinane, *Sci. Proc. Roy. Dublin Soc.*, 1924, **17**, 321) yields on further nitration in acetic acid (Ryan and Cullinane, *loc. cit.*) a dinitro-derivative, m. p. 245°, which is also formed by the direct nitration of diphenylene oxide with fuming nitric acid or nitrogen peroxide vapour. The orientation of the second nitro-group has now been determined.

Reduction yielded a different *diamine* from 2 : 7-diaminodiphenylene oxide (Bayer and Co., D.R.-P. 48,709). Partial reduction afforded a *nitroamino*-compound which, on replacement of the amino-group by hydrogen, yielded 6(= 3)-nitrodiphenylene oxide, m. p. 151°. As both nitro-groups are not substituted in the same benzene nucleus, the dinitro-compound, m. p. 245°, is 2 : 6-dinitrodiphenylene oxide (I). The 3-nitrodiphenylene oxide, m. p. 151°, was identical with an authentic specimen prepared by Brumberg (*Diss.*, Göttingen, 1925) and was converted by reduction and the Sandmeyer process into Mayer and Krieger's 3-bromodiphenylene oxide (*Ber.*, 1922, **55**, 1661).

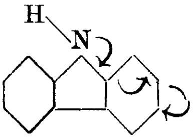
Modern electronic theory would lead one to expect the oxygen atom in diphenylene oxide to be *op*-directing (II), yet the main mononitration product is the 2-derivative. Professor R. Robinson has kindly suggested the following explanation. The nitration of carbazole proceeds normally (III), producing 3-nitrocarbazole, and thus there is a direct electromeric system involving the aromatic nucleus that is substituted and the imino-group. The same thing appears to hold also for tetrahydrocarbazole (IV), but if the imino-group is acetylated or benzoylated nitration occurs in the position indicated (V), and it was suggested by Robinson (see Perkin and Plant, J., 1923, **123**, 684) that this anomalous orientation is the result of the route selected for the electromeric changes. In any aromatic system comprised of fused homocyclic aromatic groups



(I.)

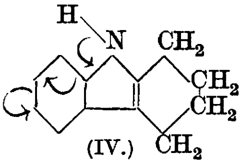


(II.)

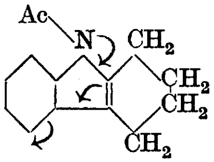


(III.)

such as naphthalene, anthracene, and phenanthrene, no alteration in the results to be expected can be made by altering the route taken by electromeric changes. But the case is different wherever one of the fused rings comprises an odd number of atoms, and the results obtained in the present work can be accounted for by the electromeric change in the course of nitration taking the route indicated (VI or VII).

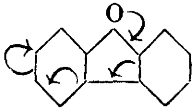


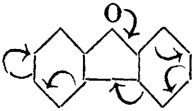
(IV.)



(V.)

(VI.)





(VII.)

In all probability bromination is a more facile process than nitration and can take advantage of a smaller degree of polarisation occurring more frequently than the activations of greater amplitude required to facilitate nitration: diphenylene oxide, therefore, is brominated normally, giving the 3-bromo-derivative.

The substitution of the second nitro-group in 2 : 6-dinitrodiphenylene oxide proceeds normally, for the positive field of the first nitro-group will inhibit any electromeric changes from passing out of the nucleus containing it.

EXPERIMENTAL.

2 : 6-*Dinitrodiphenylene Oxide*.—To a nearly boiling solution of 2-nitrodiphenylene oxide (10 g.) in AcOH (100 c.c.), HNO_3 (50 c.c.; *d* 1·5) was added in several portions. Pptn. was complete in 1—1½ hrs. The dinitro-compound, washed with H_2O, formed pale yellow needles (10 g.), m. p. 245°, from Me_2CO; yield, 83% (compare Ryan and Cullinane, *loc. cit.*, p. 325).

2 : 6-*Diaminodiphenylene Oxide*.—The dinitro-compound was reduced with Sn or Fe and HCl aq. The *diamine* (yield, 80%) crystallised from EtOH in colourless plates, m. p. 152°, slightly sol. in hot H_2O and sol. in the usual org. solvents (Found: C, 73·0; H, 5·1; N, 14·1. $C_{12}H_{10}ON_2$ requires C, 72·7; H, 5·05; N, 14·1%). It gave a deep blue colour with $FeCl_3$ aq. No quinoxaline was produced with benzil, showing that the base was not the 2 : 3-diamine (compare Borsche and Schacke, *Ber.*, 1923, **56**, 2505).

Reduction of the above dinitrodiphenylene oxide with Fe and AcOH gave the 2 : 6-diamine (contrast Mailhe, *Compt. rend.*, 1912, **154**, 1517).

The *diacetyl* derivative, prepared by means of Ac_2O, crystallised from EtOH in colourless plates, decomp. about 290°, readily sol. in AcOH or Me_2CO (Found: N, 10·2. $C_{16}H_{14}O_3N_2$ requires N, 9·9%).

The 2 : 7-diaminodiphenylene oxide prepared by Bayer and Co. (for a specimen of which we are indebted to Messrs. I. G. Farbenindustrie A.-G.) was similar in appearance to the 2 : 6-diamine, consisting of white needles, m. p. 150—152° (Found: N, 14·0%), and afforded a deep blue coloration with $FeCl_3$ aq. A mixture of the two bases, however, had m. p. 120—125°. The *diacetyl* derivative of 2 : 7-diaminodiphenylene oxide crystallised from EtOH in colourless plates, m. p. 322° (Found: N, 10·1%). Moreover, when the two diamines were bis-diazotised and coupled with salicylic acid, delta-acid, R-salt, and H-acid, dyes were formed which produced different colours on cotton, *viz.*, (2 : 6-diamine) brownish-yellow, rust-brown, reddish-violet, navy-blue, and (2 : 7-diamine) brownish-yellow, red with purple tint, blue-violet, navy-blue, respectively.

6-*Nitro*-2-*aminodiphenylene Oxide*.—A suspension of 2 : 6-dinitrodiphenylene oxide (10 g.) in EtOH (200 c.c.) and NH_3 aq. (10 c.c.; *d* 0·880) was twice saturated with H_2S with a 2-hr. interval. The EtOH was distilled off, and the residue extracted with boiling dil. HCl. NH_3 aq. pptd. the *nitroamino*-compound, which was washed with H_2O, dried, dissolved in Me_2CO, and recrystallised a few times from Me_2CO–EtOH; yellowish-orange needles (5·5 g.), m. p. 268° (Found: N, 12·4. $C_{12}H_8O_3N_2$ requires N, 12·3%), slightly sol. in EtOH, C_6H_6, or $CHCl_3$ and readily in hot AcOH or Me_2CO.

6(= 3)-*Nitrodiphenylene Oxide*.—The nitroamino-compound (which could not be diazotised with $NaNO_2$ and HCl aq.) (5 g.) was added to H_2O (25 c.c.), EtOH (125 c.c.), and oleum (25 c.c.; 40% SO_3), the temp. raised to 80°, $NaNO_2$ (12 g.) added in small portions, and the reaction completed by refluxing the mixture for 30 mins. Dilution with H_2O pptd. a solid, which was washed with boiling NaOH aq., dil. HCl, and H_2O and then extracted with Me_2CO. After crystn. from EtOH–Me_2CO, 3-nitrodiphenylene oxide was obtained as small, pale yellow needles (2–3 g.), m. p. 151° (Found: N, 6·7. Calc.: N, 6·6%), slowly volatile in steam, slightly sol. in EtOH, but readily in C_6H_6, AcOH, Me_2CO, or $CHCl_3$ (Ryan, Keane, and McGahon, *Proc. Roy. Irish Acad.*, 1927, **37**, [*B*], 372, give m. p. 141°). It did not depress the m. p. of a specimen of 3-nitrodiphenylene oxide prepared by Brumberg (*loc. cit.*), for which we are indebted to Professor W. Borsche.

3-*Aminodiphenylene oxide* was prepared by reduction of the nitro-compound with Sn and HCl aq. The hydrochloride was obtained as colourless leaflets. The base crystallised from dil. EtOH in colourless plates, m.p. 125°, sol. in the usual org. solvents (Found: N, 7·7. $C_{12}H_9ON$ requires N, 7·65%). It was diazotised at 0° with $NaNO_2$ and HCl aq. and then coupled with resorcinol (orange), H-acid (violet), R-salt (pink), delta acid (light brown), and gamma acid (purplish-brown): the colours in parentheses are those produced on cotton by the dyes.

3-*Bromodiphenylene Oxide*.—3-Aminodiphenylene oxide (2 g.) was diazotised, the clear solution (40 c.c.) poured gradually into 10 c.c. of a 10% solution of CuBr, and the mixture distilled in steam. The bromo-compound (0·5 g.) was deposited in the distillate, and on recrystn. from dil. EtOH furnished colourless leaflets, m. p. 109°, identical with the 3-bromodiphenylene oxide synthesised by Mayer and Krieger (*loc. cit.*).

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