CCXC.—*Investigations in the Diphenylene Oxide Series. Part II.*

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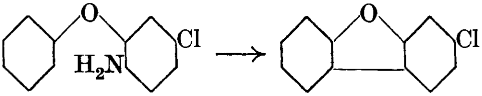
Borsche and Bothe (*Ber.*, 1908, **41**, 1940) regarded the main product of mononitration of diphenylene oxide as the 3-derivative, but as the work of Mayer and Krieger (*Ber.*, 1922, **55**, 1659; compare also Ryan, Keane, and McGahon, *Proc. Roy. Irish Acad.*, 1927, **37**, 368) showed this to be incorrect, Borsche and Schacke (*Ber.*, 1923, **56**, 2499) suggested that it was 2-nitrodiphenylene oxide. In continuation of previous work (Ryan and Cullinane, *Sci. Proc. Roy. Dublin Soc.*, 1924, **17**, 321) the mononitration of diphenylene oxide has been examined afresh, and it has been found that the main product (80%) is 2-nitrodiphenylene oxide, m. p. 182°.

Reduction of the nitrodiphenylene oxide, m. p. 182°, gives an amino-compound from which by the Sandmeyer process there results a *chlorodiphenylene oxide*, identical with the product obtained by diazotising 5-*chloro*-2-*aminodiphenyl ether* and heating the diazo-derivative in 50% sulphuric acid. It follows that the compound, m. p. 182°, is 2-nitrodiphenylene oxide.



In the mononitration of diphenylene oxide a very small quantity of another nitro-derivative, m. p. 110°, is produced (Borsche and Schacke, *loc. cit.*, p. 2500). The following is known concerning the constitution of this compound. 2-Diacetamidodiphenylene oxide, formed by reduction of the 2-nitro-derivative and acetylation of the amine produced, on nitration and subsequent hydrolysis yields a nitroamino-compound which gives a diamine on reduction (Borsche and Schacke, *loc. cit.*, p. 2504). This is an *o*-diamine, for it combines with benzil to give a quinoxaline. Hence it must be 1 : 2- or 2 : 3-diaminodiphenylene oxide. Borsche and Schacke considered it to be the latter. The nitroamino-derivative on replacement of the amino-group by hydrogen gives a nitrodiphenylene oxide which was considered by these authors to be identical with the substance of m. p. 110°. If this is so, the diamine cannot be 2 : 3- but must be 1 : 2-diaminodiphenylene oxide, for the 3-nitro-compound has m. p. 141° (Ryan, Keane, and McGahon, *loc. cit.*, p. 370), and the compound of m. p. 110° must be 1-nitrodiphenylene oxide.

EXPERIMENTAL.

Diphenylene oxide was prepared as follows (compare Galewsky, *Annalen*, 1891, **264**, 189) : a mixture of phenol (200 g.) and litharge (300 g.) was heated at about 150° for 7—8 hours, and the product distilled. The portion that distilled above 185° was shaken with warm dilute sodium hydroxide solution, cooled, washed with water, and crystallised from dilute alcohol, colourless plates (30 g.) being obtained, m. p. 87°, b. p. 288°.

2-*Aminodiphenylene Oxide.*—2-Nitrodiphenylene oxide was prepared in 80% yield by the nitration of the ether in glacial acetic acid solution by means of fuming nitric acid (Ryan and Cullinane, *loc. cit.*, p. 325). The nitro-compound was reduced with tin and hydrochloric acid (Borsche and Bothe, *loc. cit.*, p. 1941) to the amine, which crystallised from dilute alcohol in colourless needles, m. p. 94° (yield, 90%).

The hydrochloride was deposited from dilute hydrochloric acid in colourless plates.

2-*Chlorodiphenylene Oxide.*—The hydrochloride of 2-aminodiphenylene oxide (3 g.), suspended in dilute hydrochloric acid (50 c.c.), was diazotised at 0° with sodium nitrite (1·1 g.; 1·2 mols.) in water (3 c.c.), the diazo-compound separating as a brownish solid. After remaining at room temperature for 12 hours, the product was poured in small portions into boiling 10% cuprous chloride solution (60 g.) and the mixture was boiled under reflux for 15 minutes and steam-distilled. The distillate contained 2-*chlorodiphenylene oxide* (1·4 g.), which crystallised from alcohol in colourless leaflets, m. p. 101° (Found : Cl, 17·7. $C_{12}H_7OCl$ requires Cl, 17·5%), slightly soluble in water and readily soluble in light petroleum, ether, alcohol, benzene, chloroform, or acetone. The constitution of this chlorodiphenylene oxide was established by the synthesis described below.

5-*Chloro*-2-*aminodiphenyl Ether.*—The hydrochloride of this amine may be prepared by reduction of the corresponding nitro-compound by the iron filings–ferric chloride method of Roberts and Turner (J., 1925, **127**, 2011) or by means of tin and hydrochloric acid (90% yield). The amine was first obtained as an oil, but slow evaporation of a solution of this in alcohol yielded a solid which, recrystallised from the same solvent, gave greyish needles, m. p. 44° (Found : Cl, 16·15. $C_{12}H_{10}ONCl$ requires Cl, 16·15%). 5-*Chloro*-2-*aminodiphenyl ether* is slightly soluble in water, but dissolves readily in light petroleum or the usual organic solvents. The sulphate forms colourless needles.

The finely divided suspension obtained by cooling and shaking a solution of 5-chloro-2-aminodiphenyl ether (4 g.) in dilute sulphuric acid (60 c.c.) was treated at 0° with sodium nitrite (2·2 g. in 20 c.c. of water). After remaining at room temperature for 5 hours, the mixture was poured into sulphuric acid (40 c.c.) of such strength that the ultimate concentration of acid was 50% ; the whole was then boiled under reflux for 10 hours. Distillation with steam removed a small quantity of a solid, which was washed with dilute sodium hydroxide solution and with water and crystallised from alcohol. The colourless plates (0·1 g.) obtained had m. p. 101°, alone or mixed with the chlorodiphenylene oxide described above.

In conclusion, the author wishes to express his thanks to Mr. H. S. Dixon, who carried out the analyses.

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