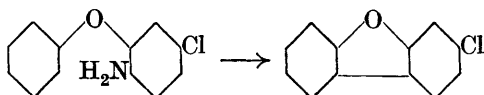


CCXC.—*Investigations in the Diphenylene Oxide Series. Part II.*

By NICHOLAS MICHAEL CULLINANE.

BORSCHÉ 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.

THE TATEM LABORATORIES, UNIVERSITY COLLEGE,
CARDIFF.

[Received, July 16th, 1930.]
