

112. *The Nitrosation of Phenols. Part XIV.*
Resorcinol isoPropyl Ether.

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Resorcinol isopropyl ether is nitrosated in position 4 to the extent of no less than 27%, and the *isopropyl* group therefore occupies its anticipated place in the series denoting the order of ionisation

repression of the *op*-directing phenolic group, *viz.*, $\text{Me} < \text{Et} < \text{Pr}^{\alpha} < \text{Pr}^{\beta}$.

Alternatively, should the *isopropoxy*-group exert an inductive electron-attraction, the 4-carbon atom (J., 1929, p. 2776, formula III, with Pr^{β} in place of Me), being much less deactivated in the *isopropoxy*- than in the *n*-*propoxy*-, *ethoxy*-, and *methoxy*-homologues, should be relatively more reactive.

The solubility (15.53%) of 6-*nitroso*-3-*isopropoxyphenol* in benzene is abnormally large compared with the solubilities of the homologues (Me, Et, $\text{Pr}^{\alpha} = 2.26, 1.32, 5.78\%$ respectively) and indicates that co-ordination (*loc. cit.*, formula V) between the *o*-*nitroso*- and the hydroxyl group is much more intensified than in the homologues, the increased activation of the chelating electrons of the *nitroso*-group greatly exceeding the concurrent increased repression of ionisation. This is to be anticipated, since the *isopropoxy*-group, being para to the *nitroso*-group, will produce a positive alternating effect far exceeding its general effect on the *m*-hydroxyl group.

The constitution of 6-*nitroso*-3-*isopropoxyphenol* has been established by its oxidation to 6-*nitro*-3-*isopropoxyphenol*, obtained also by nitration of *resorcinol isopropyl ether* and from 6-*nitro*-3-*isopropoxyaniline*, prepared from 3-chloro-4-*nitrophenol*.

The constitution of 4-*nitroso*-3-*isopropoxyphenol* was proved by its oxidation to 4-*nitro*-3-*isopropoxyphenol* and by its formation from 4-*nitroso*-3-*isopropoxydimethylaniline* by means of caustic alkali.

An attempted nitration of *resorcinol diisopropyl ether* showed that this was much more stable towards nitric acid than its *n*-*propyl isomeride*; a small quantity of 6-*nitro*-3-*isopropoxyphenol* was obtained. *Resorcinol diisopropyl ether* resembles *resorcinol dimethyl ether* in resisting completely the attack of nitrous acid, whereas the di-*n*-*propyl ether* behaves more like the diethyl ether, as would be expected.

EXPERIMENTAL.

Resorcinol isoPropyl Ether.—A mixture of *resorcinol* (30 g.), *isopropyl alcohol* (150 c.c.), sodium *isopropoxide* (6.5 g. of sodium in 150 c.c. of *isopropyl alcohol*), and *isopropyl iodide* (57 g.) was heated under reflux for 8 hours, the excess of alcohol distilled, and the oily product precipitated by water, separated, and steam-distilled. The distillate (4 litres) was saturated with sodium chloride and extracted with ether. From the ethereal solution, 10% aqueous sodium hydroxide extracted *resorcinol isopropyl ether* (10 g.), b. p. 249—250° [Found (Zeisel): OPr, 38.5. $\text{C}_9\text{H}_{12}\text{O}_2$ requires OPr, 38.8%].

The residual ethereal solution contained about 5 g. of a yellow oil, b. p. 235—250°.

Nitrosation of Resorcinol isoPropyl Ether.—A solution of the ether (10 g.) in alcohol (20 c.c.) and glacial acetic acid (20 c.c.) was treated gradually below 0° with sodium nitrite (10 g.) in water (10 c.c.), and after 1 hour's stirring, with frequent scratching, the reddish-brown crystalline precipitate was removed, and dried in a vacuum over quick-lime (yield, 8 g.). A portion (5 g.) was shaken for 30 minutes with cold sodium-dried benzene (50 c.c.) and after 12 hours the insoluble material (1.5 g.) was removed and dried; it crystallised from boiling alcohol in bright yellow prisms, m. p. 170—172° (decomp.) (Found: N, 7.9. $C_9H_{11}O_3N$ requires N, 7.7%), of 4-nitroso-3-isopropoxyphenol.

From the green benzene solution, only 6-nitroso-3-isopropoxyphenol could be isolated. This is easily soluble in cold chloroform and carbon disulphide, giving green solutions, but sparingly soluble in light petroleum, from which it crystallises in green prisms; these turn brown between 55° and 60° and melt at 91° to a dark green liquid. Contact with alcohol changes the green into a brownish-yellow modification, which crystallises from hot alcohol in leaflets, m. p. 91° (Found: N, 7.9. $C_9H_{11}O_3N$ requires N, 7.7%). Both forms give the Liebermann nitrosoamine reaction (greenish-blue). The brownish-yellow form is the more stable, the green modification passing into it during 2 days' keeping: reversion to the green form takes place on recrystallisation from benzene.

Oxidation of the nitrosation products. (a) 6-Nitroso-3-isopropoxyphenol (1 g. of either form) was dissolved in 10% aqueous potassium hydroxide (60 c.c.) and heated with a saturated aqueous solution of potassium ferricyanide (20 g.) on the water-bath until the colour of the solution was deep orange-yellow; the liquid was then filtered hot, cooled, and acidified with dilute sulphuric acid. The oil precipitated solidified after 2 hours and then crystallised from light petroleum in greenish-yellow prisms, m. p. 44°, of 6-nitro-3-isopropoxyphenol (0.8 g.) (Found: N, 7.3. $C_9H_{11}O_4N$ requires N, 7.1%).

(b) 4-Nitroso-3-isopropoxyphenol, similarly oxidised, gave 4-nitro-3-isopropoxyphenol, which crystallised from benzene in pale yellow prisms, m. p. 91° (Found: N, 7.3%), non-volatile in steam.

(c) The crude nitrosation product (2 g.) yielded on oxidation 1.3 g. of yellow crystals, of which 1.1 g., m. p. 44°, were volatile in steam and 0.2 g., m. p. 91°, was non-volatile.

Nitration of Resorcinol isoPropyl Ether.—An ethereal solution (200 c.c.) of the compound (5 g.) at -10° was treated gradually with nitric acid (2 c.c.; *d* 1.5) below -5°, boiled under reflux for

15 minutes, and kept over-night. Water (5 c.c.) was then added, the ether removed by distillation, and the residual yellow oil steam-distilled, yielding volatile 6-nitro-3-isopropoxyphenol (1.5 g.), m. p. 44° after recrystallisation (Found : N, 7.2%), and non-volatile 4-nitro-3-isopropoxyphenol (0.2 g.), m. p. 91° after recrystallisation (Found : N, 7.3%), identical (mixed m. p.'s) with the substances described above.

Nitration of Resorcinol Diisopropyl Ether.—The *diisopropyl* ether was prepared by the method of Wilson and Adams (*J. Amer. Chem. Soc.*, 1923, **45**, 534) for the di-*n*-propyl ether. A mixture of resorcinol (27.5 g.), isopropyl bromide (62 g.), acetone (250 c.c.), and potassium carbonate (90 g.) was heated under reflux for 5 hours, the acetone then removed by distillation, and water (500 c.c.) added to the residue. The brownish-yellow oil produced was extracted in ether and distilled, resorcinol diisopropyl ether being obtained as a colourless, highly refractive oil, b. p. 237—238° [Found (Zeisel) : OPr, 60.5. $C_{12}H_{18}O_2$ requires OPr, 60.8%].

The ether (5 g.), nitrated as described above, gave only 6-nitro-3-isopropoxyphenol (0.2—0.3 g.).

3-Chloro-4-nitrophenyl isoPropyl Ether.—This was made by the action of isopropyl iodide on the silver salt of 3-chloro-4-nitrophenol and obtained as a colourless oil (Found : Cl, 16.2. $C_9H_{10}O_3NCl$ requires Cl, 16.5%). It was heated (1 g.) with concentrated aqueous ammonia (5 c.c.) and alcohol (5 c.c.) in a sealed tube at 160° for 6 hours, and the product (0.6 g.) isolated by dilution with water; crystallisation from water gave yellow needles, m. p. 102—103°, of 4-nitro-3-aminophenyl isopropyl ether (Found : N, 14.5. $C_9H_{12}O_3N_2$ requires N, 14.3%). This substance (0.5 g.) was converted through its diazo-compound (Hodgson, E.P. 200,714) into 6-nitro-3-isopropoxyphenol (0.3 g.), m. p. 44°, identical with the specimens mentioned above (Found : N, 7.3%).

m-Nitrophenyl isoPropyl Ether.—A mixture of sodium ethoxide (5 g. of sodium in 125 c.c. of absolute alcohol), *m*-nitrophenol (30 g.), absolute alcohol (125 c.c.), and isopropyl iodide (45 g.) was refluxed for 8 hours, the excess of alcohol and isopropyl iodide then removed by distillation, and the residual oil steam-distilled, *m-nitrophenyl isopropyl ether* being obtained as a pale yellow, highly refractive oil, b. p. 258—259°/744 mm. (Found : N, 7.9. $C_9H_{11}O_3N$ requires N, 7.7%).

The isopropyl ether (10 g.), in warm glacial acetic acid (30 c.c.) and water (30 c.c.), was reduced with iron powder (10 g.), and the mixture heated for 2 hours on the water-bath, made alkaline with sodium hydroxide, and steam-distilled, giving *m-aminophenyl isopropyl ether* (*m-isopropoxyaniline*) as a colourless liquid, b. p. 244—

245°/750 mm. (Found : N, 9.4. $C_9H_{13}ON$ requires N, 9.3%). The *hydrochloride* crystallised from dilute hydrochloric acid in leaflets, m. p. 175—180° (Found : N, 7.8; Cl, 18.6. $C_9H_{13}ON, HCl$ requires N, 7.5; Cl, 18.9%), and the *monoacetyl* derivative from dilute alcohol in silky needles, m. p. 100—101° (Found : N, 7.6. $C_{11}H_{15}O_2N$ requires N, 7.3%).

m-isoPropoxydimethylaniline.—*m*-isoPropoxyaniline (18 g.) and methyl sulphate (30 c.c.) were mixed, and heated on the water-bath for 2 hours; 10% aqueous sodium hydroxide was added to the cooled product and the bases liberated were isolated by means of ether, recovered, and kept in acetic anhydride (20 c.c.) for 2 hours. The mixture was then poured into water, heated for 1 hour on the water-bath, cooled, made alkaline with sodium carbonate, and steam-distilled, *m*-isopropoxydimethylaniline being obtained as a colourless, highly refractive oil (7.5 g.), b. p. 253—254°/750 mm. (Found : N, 8.0. $C_{11}H_{17}ON$ requires N, 7.8%).

Nitrosation of m-isoPropoxydimethylaniline.—The base (5 g.), dissolved in concentrated hydrochloric acid (10 c.c.) and water (15 c.c.), was nitrosated at 0° by the gradual addition, with stirring, of sodium nitrite (2.5 g.) in water (5 c.c.). The solution became deep red and then deposited the *hydrochloride* of 4-nitroso-3-isopropoxydimethylaniline; this, collected after 30 minutes and crystallised from water, formed bright golden-yellow needles (Found : N, 11.8; Cl, 14.3. $C_{11}H_{16}O_2N_2, HCl$ requires N, 11.5; Cl, 14.5%). The *base* crystallised from benzene in bluish-green prisms, m. p. 65° (Found : N, 13.8. $C_{11}H_{16}O_2N_2$ requires N, 13.5%).

4-Nitroso-3-isopropoxyphenol.—A solution of the above hydrochloride (4 g.) in water (50 c.c.) was added during 30 minutes to 5% aqueous sodium hydroxide (100 c.c.) boiling under reflux. The reddish-brown solution was filtered hot, cooled, acidified with cold dilute hydrochloric acid, and kept for 30 minutes in the ice-chest. The precipitate of 4-nitroso-3-isopropoxyphenol crystallised from benzene in bright-yellow prisms, which darkened above 160° and decomposed at 170—172° (Found : N, 7.9%). It gave Liebermann's nitrosoamine test (red, changing to bluish-green with alkalis) and was identical with the substance described on p. 871.

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