

### 130. The Reactivity of Resorcinol Monoalkyl Ethers towards Diazonium Compounds.

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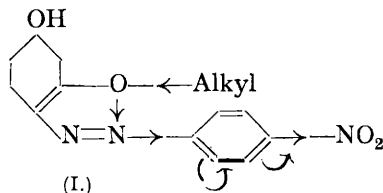
ALTHOUGH resorcinol monomethyl ether is nitrosated almost entirely in position 6 (Hodgson and Clay, *J.*, 1929, 2775), it couples with diazotised aniline in sodium acetate-acetic acid-water, at first solely in position 4; any excess (over 1 mol.) of the diazo-compound subsequently couples in position 6. The product obtained by Orndorff and Thebaud (*Amer. Chem. J.*, 1901, **26**, 159) by pouring a solution of equimolecular quantities of resorcinol monomethyl ether and benzenediazonium chloride in aqueous alcohol into alcoholic sodium acetate, and regarded by them as 2:4-bisbenzeneazoresorcinol 3-methyl ether, is now shown to be 4:6-bisbenzeneazoresorcinol 3-methyl ether. Although coupling in a sodium acetate medium takes place in the two definite stages, if caustic alkali is present a mixture of 4-benzeneazo- and 4:6-bisbenzeneazo-resorcinol 3-methyl ethers is always produced. A like reactivity has been found for resorcinol monoethyl ether. Coupling in the position 6 independent of position 4 has not been detected.

With the mono-*n*-propyl and the monoisopropyl ether, coupling takes place under the above conditions only in 4-position. No coupling whatever occurs with resorcinol *n*-butyl ether. In all three cases, the excess of benzenediazonium chloride couples readily with resorcinol or  $\beta$ -naphthol, added subsequently. Repression of ionisation by the alkoxy-group has consequently progressively deactivated the 4-carbon atom as the series is ascended.

The energetically coupling diazonium salts prepared from sulphanilic acid, *o*-, *m*-, and *p*-nitroaniline all couple smoothly with the above resorcinol monoalkyl ethers in position 4 (compare also Heidelberger and Jacobs, *J. Amer. Chem. Soc.*, 1919, **41**, 1450). It is noteworthy that the 4-*o*-, -*m*-, and -*p*-nitrobenzeneazoresorcinol 3-alkyl ethers fuse more readily as the series is ascended:

	M. p. of 3-alkyl ethers.				
	Me.	Et.	Pr <sup>a</sup> .	Pr <sup>b</sup> .	<i>n</i> -Bu.
4- <i>o</i> -Nitrobenzeneazoresorcinol .....	189°	167°	133°	115°	88°
4- <i>m</i> - " .....	153	125	114	95	86
4- <i>p</i> - " .....	198—199	185—187	156—157	145—146	149—150

We attribute the regularity in the three series to a form of co-ordination (I) which increases in intensity with the size of the alkyl group.



The diazonium salt prepared from *p*-chloroaniline also gives rise, with resorcinol methyl and ethyl ether, to 4-azo-compounds, m. p. 142° and 133° respectively, but it reacts differently with the other ethers.

The constitutions of 4:6-bisbenzeneazoresorcinol 3-methyl and 3-ethyl ethers were established by nitration, the 2-nitro-4:6-bisbenzeneazoresorcinol 3-methyl and 3-ethyl ethers obtained being different from the 6-nitro-2:4-bisbenzeneazo-compounds pre-

pared by coupling benzenediazonium chloride (2 mols.) with 6-nitroresorcinol 3-methyl and 3-ethyl ether respectively.

4-Benzeneazoresorcinol 3-methyl and 3-ethyl ethers gave 4-benzeneazoresorcinol on dealkylation, and their constitutions were established by reduction to 4-aminoresorcinol 3-methyl and 3-ethyl ethers respectively, which were also obtained by reduction of the 4-nitrosoresorcinol 3-methyl and 3-ethyl ethers. These amino-compounds were readily oxidised by potassium dichromate and dilute sulphuric acid to the corresponding methoxy- and ethoxy-*p*-benzoquinones, m. p. 140° and 120° respectively. 4-Benzeneazoresorcinol 3-*n*-propyl and 3-isopropyl ethers were dealkylated to 4-benzeneazoresorcinol, and were readily methylated both with diazomethane and with methyl sulphate and alkali, which is an indication of coupling in the para-position to the hydroxyl (compare Orndorff and Thebaud, *loc. cit.*), since the isomeric 6-benzeneazoresorcinol 3-methyl ether is not methylated by these reagents.

#### EXPERIMENTAL.

*General Coupling Process.*—A solution (30 c.c.) of the diazotised aniline (2 g.) at 0°, in which free nitrous acid and free hydrochloric acid had been destroyed by urea and sodium acetate respectively, was added during 90 minutes to a vigorously stirred solution of the resorcinol monoalkyl ether (Me, 2.8 g.; Et, 3.1 g.; etc.) in ethyl alcohol to which had been added a saturated aqueous solution of sodium acetate (4 g.). After 2 hours' stirring, the azo-compound was filtered off, washed with water, and dried. In the individual descriptions below, the colour with concentrated sulphuric acid is given in parentheses after the m. p.

*Monoazo-compounds.*—4-Benzeneazoresorcinol 3-methyl ether crystallised from alcohol in yellow needles and from benzene in orange-red micro-plates, m. p. 137—138° (light red) (Found : N, 12.4.  $C_{13}H_{15}O_2N_2$  requires N, 12.3%). Methylation with ethereal diazomethane, and also with methyl sulphate in 10% aqueous sodium hydroxide, gave 4-benzeneazoresorcinol dimethyl ether, which crystallised from alcohol in long orange-yellow needles, m. p. 97° (Bechhold, *Ber.*, 1889, 22, 2377, gives m. p. 96—97°) (claret) (Found : N, 11.8. Calc. : N, 11.6%).

4-Benzeneazoresorcinol 3-ethyl ether formed orange-red needles, m. p. 145°, from alcohol (orange) (Found : N, 11.7.  $C_{14}H_{14}O_2N_2$  requires N, 11.6%).

4-Benzeneazoresorcinol 3-*n*-propyl ether was obtained in brick-red prisms by allowing an alcoholic solution of the crude product to evaporate slowly over-night; m. p. 117° (light red) (Found : N, 11.2.  $C_{15}H_{16}O_2N_2$  requires N, 10.9%).

4-Benzeneazoresorcinol 3-isopropyl ether, obtained in the same way as its isomeride, formed orange-red prisms, m. p. 92° (light red) (Found : N, 11.1.  $C_{15}H_{16}O_2N_2$  requires N, 10.9%).

*Bisazo-compounds.*—4 : 6-Bisbenzeneazoresorcinol 3-methyl ether, prepared by the general procedure (aniline, 4 g.) and also from 4-benzeneazoresorcinol 3-methyl ether, crystallised from alcohol or chloroform in light red needles, m. p. 190° (Orndorff and Thebaud, *loc. cit.*, give m. p. 189—190°) (crimson) (Found : N, 17.1.  $C_{19}H_{16}O_2N_4$  requires N, 16.9%). The corresponding 3-ethyl ether, similarly prepared, crystallised in light red needles, m. p. 147° (dark red) (Found : N, 16.4.  $C_{20}H_{18}O_2N_4$  requires N, 16.2%). Both ethers are slightly volatile in superheated steam.

*Proof of the Sole Formation of Monoazo-compounds from Resorcinol *n*- and iso-Propyl Ethers, and of the Non-reactivity of the *n*-Butyl Ether.*—Aniline (1.6 g.) was diazotised and added to sodium acetate solutions containing the *n*- and iso-propyl ethers (1.5 g.). Each mixture was stirred for 45 minutes and after filtration added to an excess of alkaline β-naphthol. The weights of washed and dried benzeneazo-β-naphthol obtained were 1.83 g. and 1.9 g. respectively, the calculated quantity (for mono-coupling only) for the excess of aniline being 1.78 g.

The *n*-butyl ether (1.66 g.) was similarly treated with diazotised aniline (0.93 g.), and an almost theoretical weight of benzeneazo-β-naphthol (2.42 g.) was obtained.

*Proof of the Constitutions of 4 : 6-Bisbenzeneazoresorcinol 3-Methyl and 3-Ethyl Ethers.*—The bisazo-compound (0.5 g.) was slowly added to nitric acid (10 c.c.; *d* 1.42), and the mixture heated at 30—40° for 30 minutes and poured on ice. 2-Nitro-4 : 6-bisbenzeneazoresorcinol 3-methyl ether crystallised from alcohol in light brown needles, m. p. 228° (orange) (Found : N, 18.8.  $C_{19}H_{15}O_4N_5$  requires N, 18.6%), and 2-nitro-4 : 6-bisbenzeneazoresorcinol 3-ethyl ether in brilliant light red needles, m. p. 225° (yellow) (Found : N, 18.0.  $C_{20}H_{17}O_4N_5$  requires N, 17.9%).

6-Nitro-2 : 4-bisbenzeneazoresorcinol 3-methyl ether, prepared by coupling benzenediazonium chloride (2 mols.) with 6-nitroresorcinol 3-methyl ether (1 mol.) by the general process, crystal-

lised from alcohol in long golden-yellow needles, m. p. 142° (yellow) (Found : N, 18.6%). 6-Nitro-2 : 4-bisbenzeneazoresorcinol 3-ethyl ether, similarly prepared from 6-nitroresorcinol 3-ethyl ether, crystallised from alcohol in light red needles, m. p. 126° (yellow) (Found : N, 18.0%).

*Monoazo-compounds from Resorcinol 3-Alkyl Ethers and Diazotised o-, m-, and p-Nitroanilines, p-Chloroaniline, and Sulphanilic Acid.*—The nitroaniline (5 g.) was diazotised at 0—5° in a mixture of concentrated sulphuric acid (6 c.c.) and water (20 c.c.), and the product coupled as described on p. 630. Unless otherwise stated, the azo-compounds were crystallised from alcohol.

4-o-Nitrobenzeneazoresorcinol 3-methyl ether formed orange needles, m. p. 189° (orange) (Found : N, 15.5.  $C_{13}H_{11}O_4N_3$  requires N, 15.4%); the 3-ethyl ether, orange needles, m. p. 167° (yellow) (Found : N, 14.7.  $C_{14}H_{13}O_4N_3$  requires N, 14.6%); the 3-n-propyl ether, orange needles, m. p. 133° (orange) (Found : N, 14.0.  $C_{15}H_{15}O_4N_3$  requires N, 13.9%); the 3-isopropyl ether, orange needles, m. p. 115° (light red) (Found : N, 14.1%); and the 3-n-butyl ether, orange micro-plates, m. p. 88° (orange-red) (Found : N, 13.4.  $C_{16}H_{17}O_4N_3$  requires N, 13.3%).

4-m-Nitrobenzeneazoresorcinol 3-methyl ether formed orange plates, m. p. 153° (yellow) (Found : N, 15.6%); the 3-ethyl ether, orange plates, m. p. 125° (yellow) (Found : N, 14.8%); the 3-n-propyl ether, light yellow plates, m. p. 114° (orange) (Found : N, 14.0%); the 3-isopropyl ether, orange micro-needles, m. p. 95° (orange) (Found : N, 14.1%); and the 3-n-butyl ether, orange needles, m. p. 86° (orange) (Found : N, 13.4%).

4-p-Nitrobenzeneazoresorcinol 3-methyl ether formed maroon-red micro-prisms, m. p. 198—199° (orange) (Found : N, 15.4%); the 3-ethyl ether, bright red, lustrous, microcrystalline aggregates, m. p. 185—187° (orange-red) (Found : N, 14.7%); the 3-n-propyl ether, bright red micro-prisms, m. p. 156—157° (orange-red) (Found : N, 14.1%); the 3-isopropyl ether, maroon-red microcrystalline aggregates, m. p. 145—146° (orange-red) (Found : N, 14.0%); and the 3-n-butyl ether, bright red micro-prisms, m. p. 149—150° (orange-red) (Found : N, 13.5%).

4-p-Chlorobenzeneazoresorcinol 3-methyl ether formed light brown micro-plates, m. p. 142° (red) (Found : Cl, 13.3.  $C_{13}H_{11}O_2N_2Cl$  requires Cl, 13.5%); and the 3-ethyl ether, light brown plates, m. p. 133° (orange-brown) (Found : Cl, 12.7.  $C_{14}H_{13}O_2N_2Cl$  requires Cl, 12.8%).

4-p-Sulphobenzeneazoresorcinol 3-n-propyl ether crystallised from hot water in maroon-red micro-needles which decomposed when heated (orange) (Found : N, 8.5; S, 9.7.  $C_{15}H_{16}O_5N_2S$  requires N, 8.3; S, 9.5%); and the 3-isopropyl ether in deep bluish-red micro-needles (Found : N, 9.6%).

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