169. *The Nitrosation of Phenols. Part XV. Resorcinol Mono*-n-*butyl Ether.*

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The extent of nitrosation of resorcinol mono-*n*-butyl ether in position 4 is no less than 34%, *i.e.*, 7% more than occurs with the apparently anomalous *iso*propyl ether (Hodgson and Clay, J., 1932, 869), so that the *n*-butyl group not only occupies its anticipated place in the series denoting the order of ionisation-repression of the *op*-directing phenolic group, *viz.*, $Me < Et < Pr^{\alpha} < Pr^{\beta} < Bu$, but also continues the abnormal increase first noted in the case of the *iso*propyl ether.

Alternatively, should the *n*-butoxy-group exert an inductive electron-attraction, the 4-carbon atom (J., 1929, p. 2776, formula III, with *n*-Bu in place of Me), being again much less deactivated in this compound than in any of the four previous homologues studied (Hodgson and Clay, J., 1929, 2775; 1930, 965; 1931, 2097; 1932, 870), should be relatively much more reactive.

The solubility (17·2%) of 6-nitroso-3-*n*-butoxyphenol in benzene is abnormally large compared with the solubilities of the three lower homologues (Me, Et, Pr^{α}: 2·26, 1·32, 5·78% respectively), but of comparable and anticipated order of magnitude with that of 6-nitroso-3-*iso*propoxyphenol (15·53%), which indicates that co-ordination (*loc. cit.*, formula V) between the *o*-nitroso- and the hydroxyl group is even more intensified than in these homologues. This fact establishes that in and beyond the Pr^{β} compound the increased activation of the chelating electrons of the nitroso-group very greatly exceeds the concurrent increased repression of ionisation. This result is a normal consequence, since the *n*-butoxy-group will produce a positive electromeric effect on the nitroso-group, para to it, far exceeding its general polar effect on the *m*-hydroxyl group, if indeed the latter effect exists at all.

The constitutions of the 6- and 4-*nitroso*-3-n-*butoxyphenols* have been established by their oxidation to the corresponding nitrophenols, which, in turn, have been obtained by nitration of resorcinol *n*-butyl ether. The 6- and 4-*nitro*-3-n-*butoxyphenols* have been oriented by: (*a*) debutylation to the same 4-nitroresorcinol, showing that neither nitro-group is in position 2; and (*b*) the direct synthesis of 4-nitroso-3-*n*-butoxyphenol from 4-*nitroso*-3-*butoxydimethylaniline* and its oxidation to 4-nitro-3-butoxyphenol, the relative 6- and 4-positions for the nitro-group being thereby fixed for the steam-volatile and the non-steam-volatile isomeride respectively.

EXPERIMENTAL.

Resorcinol mono-*n*-butyl ether (b. p. 268—269°; Klarmann, Gatyas, and Shternov, *J. Amer. Chem. Soc.*, 1931, **53**, 3397), nitrosated (5·0 g.) in the same way as the mono-*n*-propyl ether, gave a mixture of 4- and *6-nitrosoresorcinol* 3-n-*butyl ethers* (5·5 g.). Separation (5 g.) was effected by cold Na-dried C_6H_6 (50 c.c.). The sol. 6-nitroso-compound (3·3 g.) crystallised from light petroleum in green micro-prisms, m. p. 79° (to a dark green liquid) after previous browning, and from EtOH in brownish-yellow needles, m. p. 79° (Found : N, 7·3. $C_{10}H_{13}O_3N$ requires N, 7·2%). The insol. 4-nitroso-compound (1·7 g.) crystallised from EtOH or boiling H_2O in bright yellow micro-needles, m. p. 155—156° (decomp.) (Found : N, 7·4%). Both isomerides gave the Liebermann nitrosoamine reaction (bright greenish-blue).

Oxidation of the 6-nitroso-compound (1 g.) with dil. HNO_3 (see *n*-propyl ether; *loc. cit.*, p. 2100) [and also with alkaline $K_3Fe(CN)_6$] gave the steam-volatile *6-nitro-*3-n-*butoxyphenol* (0·45 g.), which crystallised from light petroleum in greenish-yellow needles, m. p. 43—44° (Found : N, 6·8. $C_{10}H_{13}O_4N$ requires N, 6·6%). The 4-nitroso-compound was resinified by this treatment, but was converted by alkaline $K_3Fe(CN)_6$ (for method, see *loc. cit.*, p. 2100) into non-steam-volatile *4-nitro-*3-n-*butoxyphenol*, which crystallised from hot H_2O (charcoal) in almost colourless needles, m. p. 96° (Found : N, 6·7%). The crude nitrosation mixture (2·5 g.) gave by the second method of oxidation 1·1 g. of 6-nitro- and 0·3 g. of 4-nitro-3-*n*-butoxyphenol.

Nitration of resorcinol mono-*n*-butyl ether (5 g.) in Et_2O (for procedure, see *loc. cit.*, p. 2100) gave 6-nitro-3-*n*-butoxyphenol (2·2 g.), m. p. and mixed m. p. 43—44° (Found : N, 6·7%), and 4-nitro-3-*n*-butoxyphenol (0·6 g.), m. p. and mixed m. p. 96° (Found : N, 6·8%).

*Constitutions of 4- and 6-Nitro-*3-n-*butoxyphenols*.—(a) *Debutylation by hydrobromic acid.* The respective nitrophenols (0·5 g.) were dissolved in AcOH (5 c.c.), fuming HBr aq. (1·5 c.c.) added, and the mixtures boiled under reflux for 6 hr.; H_2O (10 c.c.) was then added. After a second boiling (with a little charcoal), the solutions (filtered) each deposited 4-nitroresorcinol, m. p. (after crystn. from CCl_4) 122°, alone, together, or when mixed with an authentic specimen (Kauffmann and Kugel, *Ber.*, 1911, **44**, 753, 756) (Found : N, 9·1, 9·0, 9·2. Calc. : N, 9·0%).

(b) *Synthesis of 4-nitroso-*3-n-*butoxyphenol*. By the method adopted for the *n*-propyl ether (*loc. cit.*, p. 2101), m-*nitrophenyl* n-*butyl ether* was obtained as a pale yellow oil, b. p. 273—274° (Found : N, 7·3. $C_{10}H_{13}O_3N$ requires N, 7·2%); yield, 3·3 g. from 30 g. of *m*-nitrophenol and 50 g. of *n*-butyl iodide. The oil (30 g.) was boiled with a solution of Fe powder (5 g.) in HCl aq. (15 c.c. conc. HCl and 150 c.c. H_2O), to which Fe powder (29 g.) was gradually added during 90 min. After a further 60 mins.' boiling, the mixture was made slightly alkaline with NaOH, and the m-*aminophenyl* n-*butyl ether* (m-n-*butoxyaniline*) removed by steam-distillation and distilled; yield, 18 g. of a colourless oil, b. p. 264—265° (Found : N, 8·7. $C_{10}H_{15}ON$ requires N, 8·5%), which rapidly turned brown. The amino-compound (12 g.) was treated with Me_2SO_4 (25 c.c.), first in the cold and finally on the water-bath for 1 hr., the bases were liberated by 10% aq. NaOH and kept with Ac_2O (15 c.c.) for 2 hr., and the mixture was then poured into H_2O, made alkaline with Na_2CO_3, and steam-distilled, 3-n-*butoxydimethylaniline* being obtained as an almost colourless oil, b. p. 267—268° (Found : N, 7·5. $C_{12}H_{19}ON$ requires N, 7·3%). A solution of this compound (2 g.) in conc. HCl (8 c.c.) and H_2O (15 c.c.) was nitrosated at 0—5° by the gradual addition, with stirring, of $NaNO_2$ (1 g.) in H_2O (2 c.c.). The deep red solution rapidly deposited *4-nitroso-*3-n-*butoxydimethylaniline hydrochloride*, which crystallised from dil. HCl in bright yellow needles, m. p. 145—146° (Found: N, 11·0; Cl, 13·5. $C_{12}H_{18}O_2N_2$,HCl requires N, 10·8; Cl, 13·7%). The free *base* crystallised from benzene–light petroleum in small, bright green needles, m. p. 92—93° (Found : N, 12·7. $C_{12}H_{18}O_2N_2$ requires N, 12·6%). A solution of the hydrochloride (1 g.) in H_2O (20 c.c.) was slowly added to 5% aq. NaOH (40 c.c.) boiling under reflux, the free base, which separated as a green oil, being allowed to disappear before the next addition. The final clear red solution was filtered hot, cooled, and acidified with dil. HCl. The yellowish-brown ppt. of 4-nitroso-3-*n*-butoxyphenol crystallised from EtOH or boiling H_2O in bright yellow micro-needles, m. p. 156—157° (decomp.) (Found : N, 7·3%), identical with those described above. Oxidation with alkaline $K_3Fe(CN)_6$ gave 4-nitro-3-*n*-butoxyphenol, m. p. and mixed m. p. 96° (Found : N, 6·8%).

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