

## A NOTE ON SOME 4-METHOXYBENZENEAZO DERIVATIVES OF RESORCINOL

By P. H. GORE, M.Sc.,  
and G. K. HUGHES, B.Sc.

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On coupling molar equivalents of diazotised p-anisidine with resorcinol monacetate in alkaline solution, both a mono- (I, 33%) and a bis-azo compound (II, 29%) were obtained, but no appreciable amounts of acetyl derivatives could be isolated. The same two products were also isolated (I, 47%; II, 17%) by coupling molar proportions of diazotised p-anisidine with resorcinol in the presence of alkali. (I) must be 2:4-dihydroxy-4'-methoxyazobenzene.

The formation of bis-azo compounds by coupling diazotised aniline with resorcinol was first reported by Wallach and Fischer (1882) (cf. Typke, 1877; Will and Pukall, 1887). It was later found that the pH of the solution determines which of two bis-azo isomers is formed. In the presence of sodium carbonate or acetate, 2 moles of diazotised aniline couple with one of resorcinol to give 2:4-bis(benzeneazo)-1:3-dihydroxybenzene (Kostanecki, 1888; cf. Liebermann and Kostanecki, 1884; Kostanecki, 1887; Orndorff and Ray, 1907), whilst in dilute excess sodium hydroxide 4:6-bis(benzeneazo)-1:3-dihydroxybenzene is formed (Kostanecki, 1888).

It is thus reasonable to assume that the structure of the bis-azo compound (II) formed above is 4:6-bis(4'-methoxybenzeneazo)-1:3-dihydroxybenzene.

On coupling molar proportions of diazotised p-anisidine with resorcinol monomethyl ether, two compounds  $C_{14}H_{14}O_3N_2$  are formed (cf. Hodgson *et al.*, 1934). One isomer, m.p. 116°, occurs to about 90%, the other, m.p. 134°, to about 10% in the mixture. Separation was achieved by exhaustive steam distillation, the higher melting isomer being slightly volatile. This isomer probably identical with the hydroxyazo compound, m.p. 121° (crude), isolated by Cumming and Ferrier (1925) from 4:4'-dimethoxyazoxybenzene by the action of light, is therefore 2-hydroxy-4:4'-dimethoxyazobenzene (III). The other isomer, m.p. 116°, would then be 4-hydroxy-2:4'-dimethoxyazobenzene (IV).

On methylation with diazomethane of (I) yields of (III) (68%) and (IV) (26%) were obtained. This result is to be expected from a hydrogen bonded o-hydroxyazo compound.

### EXPERIMENTAL.

*4'-methoxy-2:4-dihydroxyazobenzene* (I), and *4:6-bis(4'-methoxybenzeneazo)-1:3-dihydroxybenzene* (II)

(A) p-Anisidine (1 mol.) was diazotised in hydrochloric acid (3 mol.) in the usual way, and added to a freshly prepared dilute solution of resorcinol monacetate (1 mol.) in sodium hydroxide (5 mol.) at 0° C. After stirring for 30 min., the solution was made faintly acid, and the red-brown precipitate filtered off. Extraction with hot 20% acetic acid removed (I), which crystallised out on cooling, and after recrystallisation from dilute acetic acid, formed glistening carmine needles (33%), m.p. 150°, which became dull orange needles, m.p. 150–151°, on drying in the desiccator, or at 110°.



Found : N, 11.8 ; -OMe, 12.9%.

Calculated for  $C_{13}H_{12}O_3N_2$  : N, 11.5 ; -OMe, 12.7%.

The residue (II) crystallised from glacial acetic acid in minute brown-violet flakes, m.p. 225°, yield 29%.

Found : N, 14.8 ; -OMe, 16.1%.

Calculated for  $C_{20}H_{18}O_4N_4$  : N, 14.8 ; -OMe, 16.4%.

(B) Preparation as above, using resorcinol instead of its monacetate. Yields : (I), 47% ; (II), 17%.

*4 : 6-Bis(4'-methoxybenzeneazo)-1 : 3-dimethoxybenzene (V).*

(V) was formed by methylation of (II) in boiling acetone solution with excess methyl iodide in the presence of potassium carbonate. It formed red needles from dilute acetic acid.

Found : N, 13.8%.

Calculated for  $C_{22}H_{22}O_4N_4$  : N, 13.8%.

*2-Hydroxy-4 : 4'-dimethoxyazobenzene (III) and 4-hydroxy-2 : 4'-dimethoxyazobenzene (IV).*

Preparation as for (I) and (II), using resorcinol monomethyl ether instead of resorcinol monacetate. Before acidification, the solution was extracted with ether, which removed a small quantity of red crystals of (III) (m.p., after one crystallisation from aqueous acetic acid, 127–128°). Another crop of (III) (total 5%) was obtained by acidification of the liquor, followed by exhaustive steam distillation. (III) forms glistening red monoclinic crystals from aqueous alcohol or dilute acetic acid, m.p. 134°.

Found : N, 10.8%.

Calculated for  $C_{14}H_{14}O_3N_2$  : N, 10.9%.

It is only slightly soluble in cold 0.5% to 10% sodium hydroxide solution.

The steam distillation residue affords (IV) (60%) after three crystallisations from aqueous acetic acid, aqueous alcohol or aqueous pyridine. From the former it crystallises in red needles, m.p. 85°, which after drying lose their solvent of crystallisation and become dull salmon coloured, m.p. 116°.

Found : N, 11.0% ; -OMe, 23.9%.

Calculated for  $C_{14}H_{14}O_3N_2$  : N, 10.9% ; -OMe, 24.3%.

The *benzoyl derivative* crystallises from dilute acetic acid in shimmering orange-brown flakes, m.p. 144.5°.

Found : N, 7.8% ; -OMe, 16.7%.

Calculated for  $C_{21}H_{18}O_4N_2$  : N, 7.7% ; -OMe, 17.1%.

*Methylation of (I).*

(I) (0.25 g.) in dry ether (50 ml.) was treated with a solution of a large excess of diazomethane (from nitrosomethylurea, 2 g.) in ether (50 ml.), and allowed to stand overnight. The filtered solution was extracted three times with 10% sodium hydroxide solution (20 ml.). The alkali extract afforded (IV) (impure, 0.07 g., 26%), the ether extract (III) (pure, 0.18 g., 68%).

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School of Chemistry,  
University of Sydney.

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