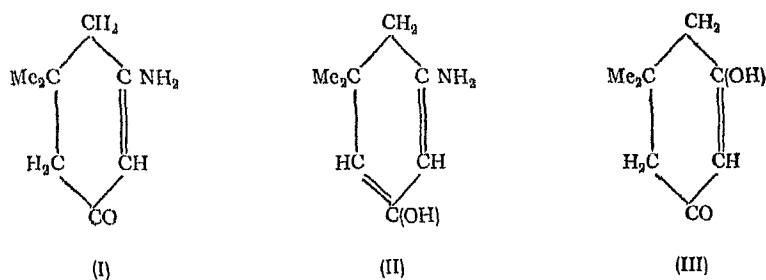


AZO-DYES COUPLING OF 5-HYDROXY-3-AMINO-1,1-DIMETHYL- $\Delta^3,5$ -DIHYDROBENZENE WITH DIAZONIUM AND TETRAZONIUM COMPOUNDS *

By Balkrishna H Iyer

Iyer and Chakravarti (*J Indian Inst Sci*, 1934, **17A**, 41) and Iyer (*ibid.*, 1938, **21A**, 65) prepared a number of azo-dyes from methone. Although they are good for dyeing wool, silk and leather, "their insolubility is one of the drawbacks for their technical application" (*Cf. Iyer, ibid*, p 69) It was thought that coupling of 5-hydroxy-3-amino-1,1-dimethyl- $\Delta^3,5$ -dihydrobenzene with diazonium and tetrazonium compounds would obviate this difficulty. The presence of the amino group in the resulting products is expected to make them soluble in dilute acids in which medium the dyeings are generally carried out.

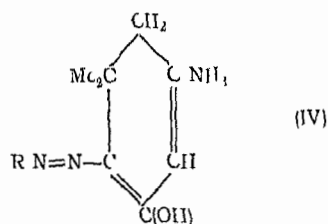


Haas (*JCS*, 1906, **89**, 191) prepared 5-hydroxy-3-amino-1,1-dimethyl- $\Delta^3,5$ -dihydrobenzene by condensing methone with ammonia. He assigned the tautomeric structure (II) for this substance in preference to (I), thus indicating that once the mono-enolic form of methone (III) was reacted, the remaining keto group also became enolic.

One molecule of (II) coupled with one molecule each of the diazotised aromatic amines (aniline, *o*-*m*-*p*-toluidines, α -naphthylamine and *p*-nitraniline) in acid medium to give the corresponding azo-com-

* Extracted from the author's thesis for the Ph.D Degree of the University of Bombay.

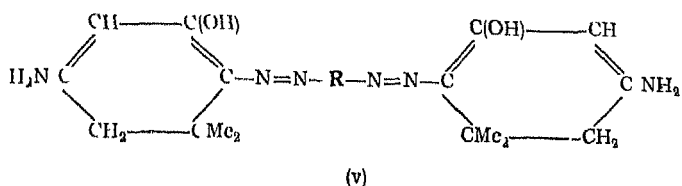
compounds According to the laws regulating the formation of azo compounds, the coupling should take place in the *para* position (*i.e.*, in position 6) to the amino group in (II) as the latter behaves essentially like a basic substance With reference to the tautomeric hydroxyl group in position (5) also, the coupling will take place with the carbon atom in position (6) only Because, it is known that in coupling diazonium salts with substances exhibiting keto-enol tautomerism, the azo-addendum attaches itself to the carbon atom (6 in this case) which is in the *ortho* position to the carbon atom (5) bearing the enolic hydroxyl (Mills and Nixon, *JCS*, 1930, 2512, Fieser and Lothrop, *J Amer Chem Soc*, 1936, 58, 2050) From these considerations and from analytical data, the resulting compounds have been assigned the structure (IV) where R stands for the nucleus of the respective aromatic amines



The following new compounds were thus prepared.—(1) 6-phenylazo-5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{1,6}$ -dihydrobenzene (IV, $R=C_6H_5$), (2) 6-*o*-tolylazo-5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{1,6}$ -dihydrobenzene (IV, $R=C_6H_4CH_3$), (3) 6-*m*-tolylazo-5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{1,6}$ -dihydrobenzene, (4) 6-*p*-tolylazo-5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{1,6}$ -dihydrobenzene, (5) 6-*p*-nitrophenyl-5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{1,6}$ -dihydrobenzene (IV, $R=C_6H_4NO_2$) and (6) 6-*a*-naphthylazo-5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{1,6}$ -dihydrobenzene (IV, $R=C_{10}H_7$)

When two molecules of (II) were coupled with one molecule each of tetrazotised benzidine and *o*-tolidine, dark brown, non-melting amorphous powders which could not be purified further, were obtained. They could not be combusted or analysed in any manner. When heated on spatula, both the products charred leaving an m-

fusible residue. From the mode of formation the structure (V)—where R stands for benzidine or *o*-tolidine nucleus—is suggested for these two products



All these compounds are useful dyes for silk and woollen fabrics. They impart fast shades varying from yellow to dark brown. They are fugitive on cotton. As anticipated in the beginning, their solubility in dilute acids is advantageous for dyeing purposes. If dyes of non-coal-tar origin become technically successful sometime in the future, it is hoped that "methone-dyes" will find some application. All these dyes are soluble in olive oil. With the increasing use of dyes in medicaments and with the fact that some methone derivatives do possess physiological properties, it may not be wrong to hope that the oil soluble methone dyes may exhibit some therapeutic properties. But this is entirely a conjecture and needs experimental verification.

EXPERIMENTAL

Preparation of 5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{8,5}$ -dihydrobenzene (II) (Cf. Haas, *loc. cit.*)—Methone (20 g) was dissolved in liquor ammonia (15 c.c.) in a porcelain basin. The resulting solution at once solidified. This liquefied again on heating over a water bath. It was finally evaporated to dryness and the resulting yellow coloured solid was powdered and crystallised from dry chloroform, yield 17 to 18 g, m.p. 164–165°. Excess of ammonia reduced the yield.

6-phenylazo-5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{8,5}$ -dihydrobenzene (IV, R=C₆H₅)—Aniline (5 g) dissolved in hydrochloric acid (20 c.c. of 1:1 acid) was diazotised with sodium nitrite (3.4 g) in water (35 c.c.). The clear filtered diazonium solution was poured into

a well cooled solution of (II) (7 g) in a small quantity of very dilute hydrochloric acid. The light yellow coloured reaction solution soon turned red. After standing for an hour it was carefully alkalisied under ice cooling with ammonium hydroxide. The resulting product was collected on a Buchner funnel, washed with water and crystallised from dilute alcohol, yellow crystals, m.p. 216–217° decomp, yield 5 g. It was soluble in acetone, chloroform and dilute mineral acids, insoluble in petrol and ether. Gives yellow solution with concentrated sulphuric acid. (Found N 17.28 and 17.47, $C_{11}H_{17}ON_3$ requires N, 17.28 per cent.)

Hydrochloride of above—This was obtained by evaporating off a solution of the substance (2 g) in hydrochloric acid (10 c.c. of 1.1 acid) on a water bath.

0.2527 g of the hydrochloride required 17.9 c.c. of 0.0486 N. NaOH for neutralisation (phenolphthalein). (Found HCl, 12.48, $C_{13}H_{17}ON_3$, HCl requires HCl, 13.06 per cent.)

6-o-tolylazo-, 6-m-tolylazo- and 6-p-tolylazo-(5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{3,6}$ -dihydrobenzenes) (IV, R- C_6H_4Me).—Each of *o*-, *m*- and *p*-toluidines (2.7 g each) in hydrochloric acid (30 c.c. 1.2 acid) was diazotised with sodium nitrite (1.75 g) in water (20 c.c.) and coupled with (II) (3.5 g.) dissolved in very dilute HCl, as in the previous case. The products obtained on alkalisying the dark coloured reaction solution with ammonia were crystallised from alcohol. Yields were about 3 grams in all the three cases.

6-o-tolylazo-5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{3,6}$ -dihydrobenzene, m.p. 204–205° decomp. (Found N, 16.66 per cent.),

6-m-tolylazo-5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{3,6}$ -dihydrobenzene, m.p. 198° decomp. (Found N, 16.30 per cent.),

6-p-tolylazo-5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{3,6}$ -dihydrobenzene, m.p. 221° decomp. (Found N, 16.49, $C_{15}H_{19}ON_3$, requires N, 16.34 per cent.).

6-p-nitro-5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{3,6}$ -dihydrobenzene (IV, R=C₆H₄NO₂)—To a cooled solution of *p*-nitraniline (3.45 g) in hydrochloric acid (30 c.c. of 1:2 acid) a solution of NaNO₂ (1.75 g) in water (20 c.c.) was added all at once and diazotised. This solution was coupled with (II) (3.5 g.) and the product isolated as in the previous cases. Yellow crystals from alcohol, m.p. 230–231° decomp., yield 2 g. (Found N, 19.71, C₁₄H₁₆O₂N₂ requires N, 19.44 per cent.)

6- α -naphthylazo-5-hydroxy-3-amino-1,1-dimethyl- $\Delta^{3,6}$ -dihydrobenzene (IV, R=C₁₀H₇)—The diazonium solution from α -naphthylamine (3.6 g) was coupled with (II) (3.5 g) and the product isolated as before; crystallised from alcohol, m.p. 220–222° decomp., yield 3 g. (Found N, 14.29; C₁₈H₁₉ON₂ requires N, 14.33 per cent.)

Coupling of (II) with tetrazotised benzidine and o-tolidine—Tetrazonium compound from benzidine (2.3 g) was coupled with (II) (3.5 g) in the usual manner. The light orange coloured reaction mixture turned dark on standing. On alkalisng with ammonia, a dark brown, non-melting amorphous powder (4.9 g) was obtained. It could not be crystallised.

Tetrazonium compound from *o*-tolidine (2.65 g) was coupled with (II) (3.5 g) as above. Here also, only a dark brown non-melting product (5.6 g.) resulted.

Dyeing experiments.—These were carried out according to the instructions given in the book on "The Synthetic Dyestuffs" by Cain and Thorpe. The dye solutions were filtered prior to use so that very even dyeing of the fabrics resulted. While silk and woolen fabrics were dyed in fast shades varying from light yellow to reddish or dark brown, cotton fabrics were not at all dyed. The two products from benzidine and *o*-tolidine proved to be the best of the present series of azo-dyes.

SUMMARY

The diazonium salts of aniline, *o*-, *m*-, and *p*-toluidines, *p*-nitraniline and *α*-naphthylamine, and the tetrazonium salts of benzidine and *o*-tolidine have been coupled with 5-hydroxy 3-amino-1,1-dimethyl- $\Delta^{3,5}$ -dihydrobenzene. The resulting products exhibit good dyeing properties with silk and woollen fabrics. The presence of the amino group in the present series of azo-compounds makes them soluble in dilute mineral acids thus facilitating the process of dye absorption.

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