

AZO-DYES FROM FORMALDIMETHONE*

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SUMMARY

Formaldimethone has been coupled with the diazonium salts of aniline, *o*-toluidine, *o*- and *p*-xylydines, α - and β -naphthylamines, and *p*-bromaniline. The resulting azo compounds dye silk, wool and leather in fast colours varying from yellow to orange. They are fugitive on cotton. Coupling of formaldimethone with tetrazonium salt of benzidine has yielded a dye which also is fugitive on cotton.

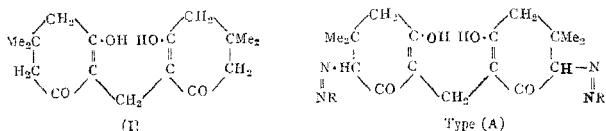
Iyer and Chakravarti¹ and Iyer² have found that the azo-compounds synthesised with methone (5:5-dimethyl-dihydroresorcinol) as the passive component possess good dyeing properties for silk and wool. Their observations regarding the dyeing capacity and the fastness of these dyes have been corroborated by the findings of foreign patentees³ who have also prepared dyes with substituted dihydroresorcinols. The first patent reads as follows: "Those products which do not contain water solubilising groups dye cellulose acetate rayon, cellulose ester and ether lacquers and vinyl, urea aldehyde and phenol aldehyde synthetic resins yellow shades of good fastness to light. Products containing sulphonic groups are used for dyeing wool, paper, silk, and viscose rayon and may be converted into barium and calcium lakes". In the second patent they say that: "The products which have not been converted into complex metal derivatives, dye in conjunction with a chromium mordant, wool and leather level yellowish to reddish brown shades of good fastness to light, washing and milling". These patents indicate the importance of the series of dyes prepared by Iyer and Chakravarti.¹ The novelty about these azo-dyes was the use of a hydroaromatic substance like methone as the passive component. Not many compounds of this type are known in diazo chemistry.

With a view to studying the azo-compounds derived from aldimethones which are the characteristic condensation products of aldehydes with methone,⁴ formaldimethone⁵ (I) has been coupled with the diazonium salts

* Cf. Note on "Azoformaldimethone dyes" by M. V. Kowjalgi and B. H. Iyer. *Current Sci.*, 1950, 19, 210.

of aniline, *o*-toluidine, *o*- and *p*-xylydines, α - and β -naphthylamines and *p*-bromaniline as well as with the tetrazonium salt of benzidine.

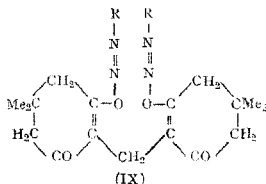
The molecule of formaldimethone (I) contains two methone nuclei linked through a methylene group. It has two hydroxyl groups and is soluble in alkali thus behaving like a phenolic body. Consequently, one molecule of formaldimethone coupled with two molecules of the diazonium salt of each of the seven aromatic mono-amines mentioned above to give the corresponding bis-(2-hydroxy-6-keto-4:4-dimethyl-5-aryl-azo-cyclo-hexyl) methanes (II) to (VIII), both inclusive, of type A, which for the sake of brevity may be named bis-aryl-azo-formaldimethones.



R stands for the following aromatic residues:

- | | |
|------------------------|-------------------------------|
| (II) phenyl- | (VI) α -naphthyl- |
| (III) <i>o</i> -tolyl- | (VII) β -naphthyl- |
| (IV) <i>o</i> -xylyl- | (VIII) <i>p</i> -bromophenyl- |
| (V) <i>p</i> -xylyl- | |

When the coupling was carried out in the usual manner in alkaline medium, a small quantity of an alkali-insoluble coloured product also was obtained which has probably the unstable diazo-oxy structure (IX).

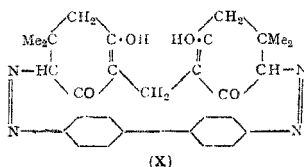


Formation of (IX) was not the normal course of coupling reaction and has been observed before in compounds obtained from phenols possessing strongly acidic nature.^{6, 1} Small quantities of these diazo-oxy-compounds formed during the course of the present investigation were not further investigated, as they were not the true azo dyes. They were insoluble in alkali and alcohol, whereas the azo-compounds dissolved easily in alkali and could be crystallised from dilute alcohol,

The structure (type A) given to these azo dyes has been based on the following arguments, viz.—

- (1) The hydroxyl group is *para* directing in this case.
- (2) The dye-stuffs are soluble in alkali.
- (3) Diazo compounds react with substances containing reactive methylene groups giving true azo-compounds (cf., Book: *The Aromatic Diazo Compounds*, by K. H. Saunders, p. 110).

After preparing these azo dyes (II-VIII both inclusive) it was thought worthwhile to study their dyeing properties. The process of dyeing was rendered difficult by the insoluble nature of these substances in the acid dye-bath. But when the dye was freshly precipitated in a finely divided state in the dye-bath itself, it was possible to dye woollen and silken fabrics fairly easily in shades ranging from yellow to orange. The colours have been found to be fast to the common tests of washing, handling and exposure. These dyes could be used for dyeing leather also but they were fugitive on cotton. It was felt that coupling of formaldimethone with tetrazonium compound of benzidine and its homologues might yield substantive cotton dyes. Accordingly benzidine was tetrazotised and coupled with formaldimethone to yield biphenyl-*pp'*-disazo-5:5'-*bis*-(2-hydroxy-6-keto-4:4-*di*-methyl-*cyclohexyl*)-methane (X).



EXPERIMENTAL

Bis-(2-hydroxy-6-keto-4:4-dimethyl-5-phenylazo-cyclohexyl) methane (II).—Aniline (1.86 g.) mixed with water (10 c.c.) containing concentrated hydrochloric acid (6 c.c.) was diazotised by adding slowly a solution of sodium nitrite (1.45 g.) in water (20 c.c.). The clear diazonium solution was run gradually into a well stirred solution of formaldimethone (2.92 g.) in 2 N-caustic soda (80 c.c.) cooled to 15°. When the whole of the diazo solution was added, the solution was distinctly alkaline. The mass was stirred for 2 hours longer when a small amount of precipitate separated out; this was probably the diazo-oxy compound of type (IX). This precipitate was filtered and rejected. On acidification of the filtrate with 2 N-hydrochloric acid (50 c.c.) the red dye separated. This was then filtered, washed

successively with hot water, dilute sodium carbonate solution and cold water, and finally crystallised from dilute alcohol. It gave fine red, crystals, m.p. 139°; yield almost quantitative. It was soluble in ether, benzene, chloroform, acetone and alkali. It was insoluble in acids and water (Found: N, 11.4. $C_{29}H_{32}O_4N_4$ requires N, 11.2 per cent.).

Bis-(2-hydroxy-6-keto-4 : 4-dimethyl-5-o-tolylazo-cyclohexyl)-methane (III).—*o*-Toluidine (2.12 g.) was mixed with 2 N-hydrochloric acid (50 c.c.) and crushed ice (100 g.) and diazotised with sodium nitrite (1.45 g.) in water (20 c.c.) maintaining the temperature below 5°. This was coupled with formaldimethone (2.92 g.) dissolved in 2 N-caustic soda (80 c.c.) and the product isolated and purified as before; red crystals from dilute alcohol, m.p. 125°. It was soluble in benzene, toluene, xylene, chloroform, ether and alkali (Found: N, 10.3. $C_{31}H_{38}O_4N_4$ requires N, 10.56 per cent.).

Bis-(2-hydroxy-6-keto-4 : 4-dimethyl-5-o-xylylazo-cyclohexyl)-methane (IV).—1, 2, 3-*o*-Xylidine (2.42 g.) dissolved in 2 N-hydrochloric acid (50 c.c.) was diazotised and coupled with formaldimethone (2.92 g.) dissolved in 2 N-caustic soda (80 c.c.). The product isolated and purified as before was crystallised from dilute alcohol, m.p. 125–27°. It was soluble in benzene, chloroform, ether, methyl alcohol and alkali; insoluble in water and acids (Found: N, 9.7. $C_{33}H_{44}O_4N_4$ requires N, 10.0 per cent.).

Bis-(2-hydroxy-6-keto-4 : 4-dimethyl-5- α -naphthylazo-cyclohexyl)-methane (VI).— α -Naphthylamine (2.86 g.) dissolved in 2 N-hydrochloric acid (100 c.c.) was diazotised and coupled with formaldimethone (2.92 g.) dissolved in 2 N-caustic soda (120 c.c.). The product was isolated as in the previous experiments and crystallised from alcohol; brownish red crystals, m.p. 135°. It was soluble in benzene, chloroform and ether, but was insoluble in acids (Found: N, 9.77. $C_{27}H_{36}O_4N_4$ requires N, 9.53 per cent.).

Bis-(2-hydroxy-6-keto-4 : 4-dimethyl-5- β -naphthylazo-cyclohexyl)-methane (VII).—Prepared as above from β -naphthylamine (2.86 g.) and formal-dimethone (2.92 g.); red-violet crystals from alcohol, m.p. 198° (Found: N, 9.83. $C_{27}H_{36}O_4N_4$ requires N, 9.53 per cent.).

Bis-(2-hydroxy-6-keto-4 : 4-dimethyl-5-p-bromophenylazo-cyclohexyl)-methane (VIII).—*p*-Bromoaniline (3.44 g.) was dissolved in 10 N-hydrochloric acid (10 c.c.) diluted with water (100 c.c.). The solution was cooled to 5–10° by addition of ice (100 g.). A solution of sodium nitrite (1.45 g.) in water (8 c.c.) was poured in all at once and the mixture was stirred till a clear solution was obtained. This clear diazo solution was added with stirring to formal-dimethone (2.92 g.), dissolved in 2 N-caustic soda (80 c.c.). Stirring was continued for about 2 hours. The small amount of precipitate that

separated out was rejected and the clear filtrate acidified with 2 N-hydrochloric acid (50 c.c.). The resulting yellow mass turned deep red after some time. This was filtered, washed, and crystallised from dilute alcohol; red needles, m.p. 202° (Found: N, 8.93; M.W. by Rast's method, 672; $C_{29}H_{30}O_4N_4Br_2$ requires N, 8.5 per cent., M.W., 658).

Biphenyl-pp'-disazo-5:5'-bis-(2-hydroxy-6-keto-4:4-dimethyl-cyclohexyl)-methane (X).—Benzidine (1.84 g.) was dissolved in hot water (30 c.c.) containing concentrated hydrochloric acid (4 c.c.). The solution was cooled in ice to 5°, a further quantity of concentrated hydrochloric acid (4 c.c.) added, and the solution tetrazotised with sodium nitrite (1.45 g.) in water (10 c.c.). The clear tetrazonium solution was poured under stirring to formaldimethone (2.92 g.) dissolved in 2 N-caustic soda (80 c.c.) and cooled to 15°. The solution was filtered and the clear filtrate acidified with 2 N-hydrochloric acid (30 c.c.), when a chocolate precipitate separated. This was filtered and washed as in previous cases. This precipitate was sparingly soluble in alcohol, benzene, methyl alcohol and acetic acid. It was purified by dissolution in alkali and precipitation with acid. m.p. 305° (Found: N, 10.93. $C_{29}H_{30}O_4N_4$ requires N, 11.48 per cent.).

DYEING EXPERIMENTS

Dyeing experiments were carried out with cotton, and woollen yarn, according to the instructions given in *The Synthetic Dyestuffs*, by Cain and Thorpe, pp. 402-07. Cotton yarn was boiled with soap solution and washed with water before using it for the dyeing experiments. Woollen yarn was boiled with water containing a little ammonia and then washed with water before use. Two typical experiments are described below:

Wool dyeing with bis-(phenyl-azo)-formaldimethone (II).—The dye (0.03 g.) was dissolved in acetic acid (2 c.c.) and poured into water (100 c.c.). To this was added 10% sodium sulphate solution (2 c.c.) and 10% sulphuric acid (1 c.c.). The woollen yarn (3 g.) treated as indicated above was introduced in the cold-bath and the temperature raised slowly to that of the boiling water. After steeping for 2 hours, the dyed yarn was removed and washed repeatedly with water and soap. The yarn had taken up a very light yellow shade.

Cotton dyeing with diphenyl-4:4'-disazo-formaldimethone (X).—The dye (0.06 g.) dissolved in 2 N-caustic soda (4 c.c.) diluted with water (60 c.c.) was mixed in a beaker with 10% sodium carbonate solution (1 c.c.) and 10% sodium chloride solution (10 c.c.). Cotton yarn (2 g.) was purified and introduced in the dye-bath in the cold. Then the temperature was gradually

raised to 60° C. and maintained there for 2 hours. After some time, the yarn was removed from the bath and washed with soap water. It was found that the yarn had not taken up the dye.

REFERENCES

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3. I.G.E.P., 461965 and 461884 .. *J. Soc. Dyers and Col.*, 1937, 53, 294, 295.
4. Wild .. *Book, Characterization of Organic Compounds*, 1947, p. 135.
5. Vorländer and Erig .. *Annalen*, 1897, 294, 316.
6. Cain and Thorpe .. *Synthetic Dyestuffs*, 1946, p. 96.