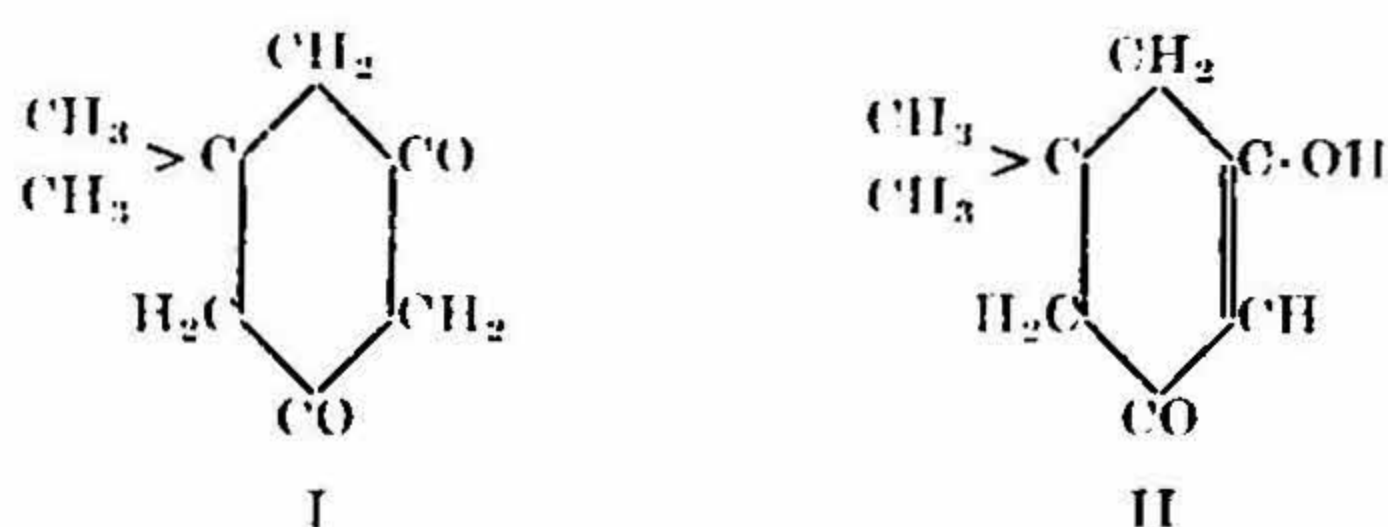


# REACTIVITY OF DIMETHYLDIHYDRORESORCIN, PART III.

## AZO-DYES AND DIAZO-OXY COMPOUNDS.

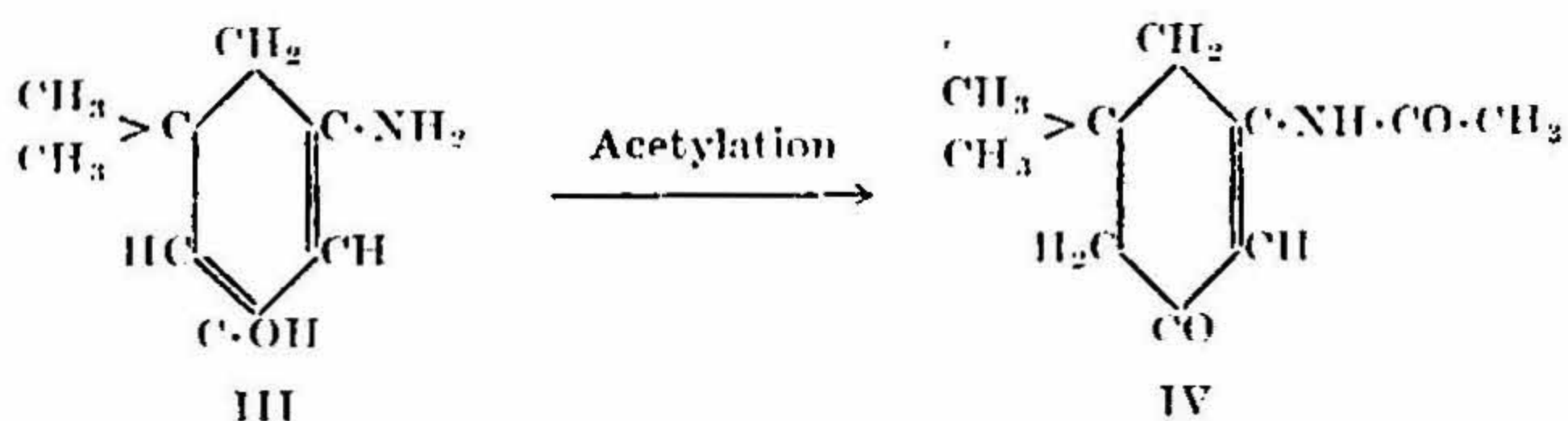
By B. H. Iyer and G. C. Chakravarti.

The structure of dimethyldihydroresorcin has been represented in two tautomeric forms, (I) and (II).



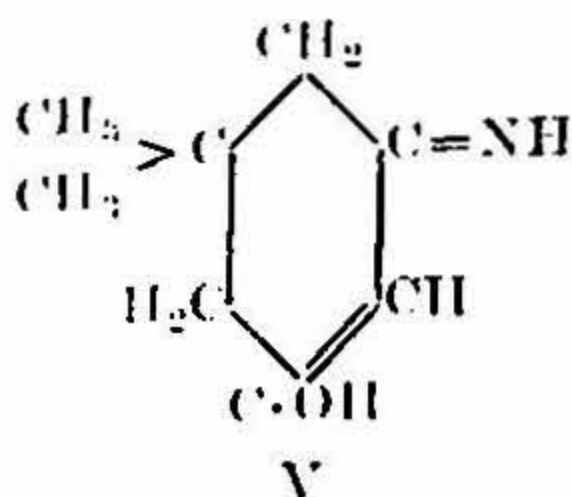
A series of investigations on the reactivity of aldehydes towards dimethyldihydroresorcin has been conducted by Vörländer (*Z. anal. Chem.*, 1929, **77**, 241), Chakravarti, Chathopadyaya and Ghosh (*J. Indian Inst. Sci.*, 1931, **XIV A**, 141) and Iyer and Chakravarti (*ibid.*, p. 157) and the mechanism of the reactions explained on the assumption of structure (II).

Haas (*J. C. S.*, 1906, **89**, 187) condensed dimethyldihydroresorcin with ammonia and various aromatic mono- and di-amines. From his data he maintains that as soon as the hydroxyl group is attacked by a molecule of the base, the other keto group becomes enolised. For instance when the resorcin is condensed with ammonia, 1:1-dimethyl-3-amino-5-hydroxydihydrobenzene (III) is obtained. The acetylamino-compound obtained from (III) on acetylation, however, behaves as a ketone (IV).



From his experiments it would appear that the enolisation was caused by the wandering of a hydrogen atom from the  $\text{NH}_2$ -group and this wandering was arrested by acetylation, so that the constitution of the

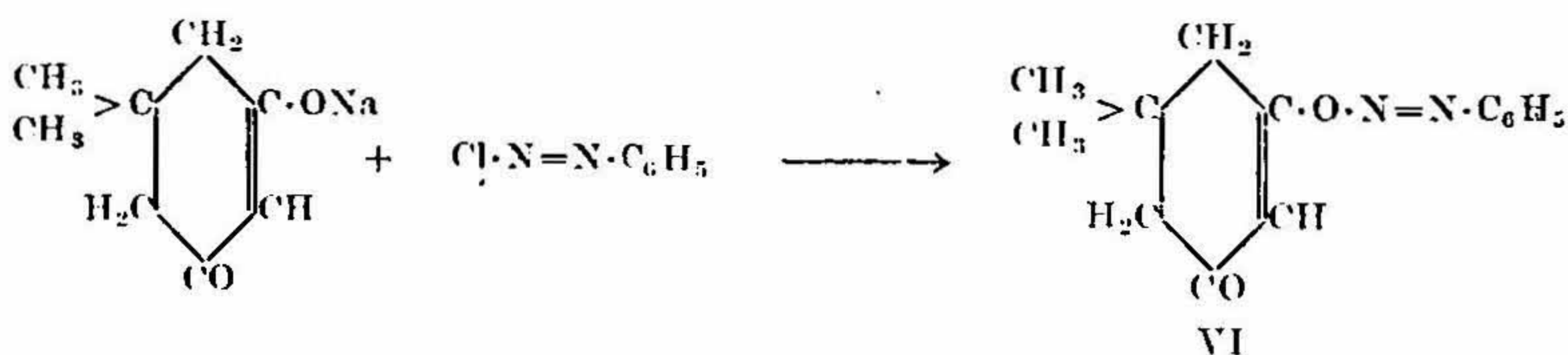
amino-compound should more properly be represented by formula (V) and not by (III).



Vörlander, and Iyer and Chakravarti (*loc. cit.*) have shown that dimethyldihydroresorcin could react only in the keto-enol form and never in a dihydroxy form as indicated by the work of Haas. Desai's observation (*J. C. S.*, 1932, p. 1081) that the resorcin can give either a C- or an O-alkylated product or a mixture of the two, but never a di-O-alkylated compound lends further support to this view. These considerations proved of sufficient interest to study further the nature of dimethyldihydroresorcin, especially as regards its structure.

Dimethyldihydroresorcin behaves like an acid and so it appeared probable that like phenols it might couple with diazonium compounds to form azo-dyes. As will be evident from the following results, this expectation has been found correct.

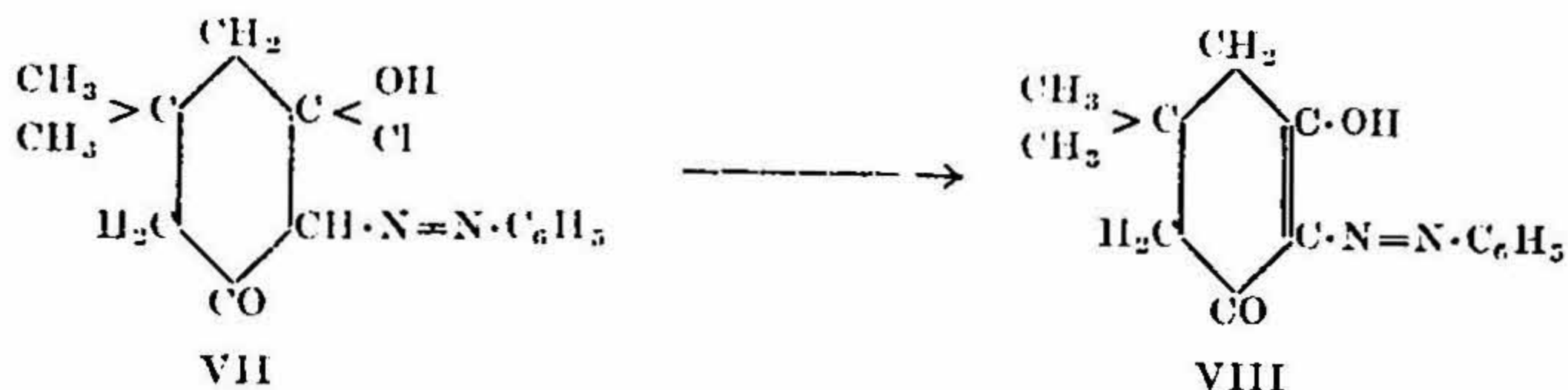
When dimethyldihydroresorcin is coupled with phenyldiazonium chloride in an alkaline medium, phenyldiazo-oxydimethyldihydroresorcin (VI) is formed, which is not readily soluble in alkali, the reaction taking the following course:



Similar abnormalities have been observed in compounds obtained from phenols possessing strongly acid character (*cf.* Cain and Thorpe, "Synthetic Dyestuffs", p. 54).

When dimethyldihydroresorcin is coupled with phenyldiazonium chloride in an acid medium, phenylazodimethyldihydroresorcin (VIII) is formed. The presence of the hydroxyl group in compound (VIII) is proved by the readiness with which it dissolves in alkali. In another experiment the diazonium salt was coupled with an aqueous solution of dimethyldihydroresorcin. No precipitate separated as long as the reaction mixture was at a low temperature; but on attaining the room temperature and on long standing a small quantity of the compound,

(VIII) separated. It may be that the additive compound (VII) first formed loses a molecule of hydrochloric acid to give rise to the azo-compound (VIII).

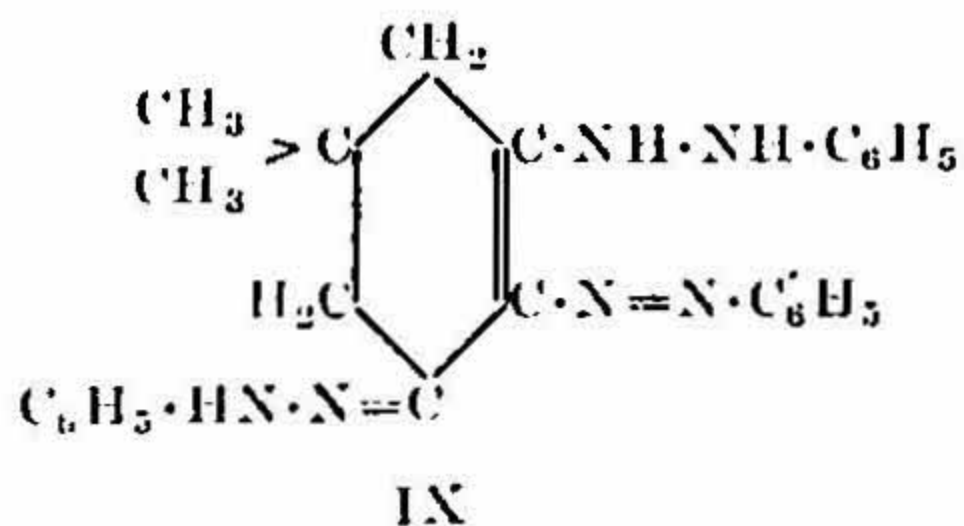


In the case of aniline, and *ortho*-, *meta*-, and *para*-toluidines, the two compounds obtained from acid and alkaline media have the same melting point, remaining undepressed even on admixture. They differ in the diazo-oxy-compound being much the deeper in colour. It appears that in these cases the transformation of the diazo-oxy-compound into the azo-compound is an extremely easy process and is facilitated by heat or treatment with alkali. Similar migration of groups from oxygen to carbon in dimethyldihydroresorcin has been observed by Dieckmann, and Stein (*Ber.*, 1904, 37, 3379) and by Mameli Efisio (*Gazzetta.*, 1926, 56, 759).

The diazo-oxy and azo-compound obtained from  $\alpha$ - and  $\beta$ -naphthyl amines from alkali and acid media respectively show marked difference in their melting points. The O-substituted derivatives are insoluble in alkali and alcohol, whereas the azo-compounds dissolve easily in alkali and can be crystallised from alcohol. In these cases the yields of both types of compounds are very satisfactory.

The easy conversion of phenyl- and tolyl-diazo-oxy-compounds into azo-derivatives and the comparative stability of the naphthyldiazo-oxy-compounds may be due to steric causes.

The azo-compound (VIII) reacts with two molecules of phenylhydrazine to give the phenylhydrazone (IX)



Having obtained these coloured azo-compounds it was thought worthwhile to test their dyeing properties. The process of dyeing was rendered difficult by the insolubility of the dyes in water, but the freshly precipitated substance in aqueous suspension was taken up by

woollen fibre with extreme ease. The products resulting from sulphanilic and naphthionic acid were easily soluble in water due to the presence of the sulphonic acid group in the molecules.

On dyeing wool direct from an acid bath bright yellow and red shades could be obtained which improved further on mordanting with dichromate. The dye can also be introduced into silk fibres. In the following table are given the results of a few of the dyeing experiments.

TABLE.

No.	Dye	Material	Direct Dyeing	Mordant Dyeing
1	Phenyl-azo-dimethyldihydroresorcin	Wool	Citron yellow	Canary green
2	<i>o</i> -Tolyl-azo-dimethyldihydroresorcin	"	Lemon yellow	Pea green
3	$\beta$ -Naphthyl-azo-dimethyldihydroresorcin	"	Chrome yellow	Canary yellow
4	$\alpha$ -Naphthyl-azo-dimethyldihydroresorcin sulphonic acid	"	Maroon	..
5	Phenyl-azo-dimethyldihydroresorcin sulphonic acid	"	Orange vermilion	Terra cotta
6	do.	Silk	Cream	..

Experiments are in progress to synthesise substantive cotton dyes by coupling methone with diazotised benzidine and allied compounds.

### EXPERIMENTAL.

Dimethyldihydroresorcin was prepared according to the modified method of Vörländer (*Z. anal. Chem.*, 1929, 77, 245).

*Phenyl-azo-dimethyldihydroresorcin* (VIII).—The clear diazonium solution obtained from aniline (4.5 g.) in the usual manner was run rapidly into a solution of dimethyldihydroresorcin (7 g.) in 2*N*-sodium hydroxide (50 c.c.), under mechanical stirring and ice-cooling, and the separated yellow flocculent precipitate allowed to stand in ice for a couple of hours under stirring. In the end the supernatant liquid had an *acid* reaction. The precipitate, after successive treatment with boiling water, very dilute sodium carbonate solution and finally with water, was crystallised from dilute alcohol; m.p. 142°, yield almost quantitative. It was soluble in ether, benzene, chloroform, acetone

and methyl alcohol but insoluble in petrol (Found: N, 11.80.  $C_{14}H_{16}N_2O_2$  requires N, 11.48 per cent.). The filtrate from the reaction mixture yielded a very small quantity of a red precipitate on basification with caustic soda and this was perhaps the di-azo-oxy-compound.

*Phenyldiazo-oxydimethyldihydroresorcin* (VI).—The above experiment carried out with dihydroresorcin dissolved in sufficient caustic soda solution to render the reaction mixture definitely *alkaline* yielded a very small quantity of a red precipitate, another crop of which was also obtained from the filtered liquid on salting out. The precipitate after being purified in the manner indicated in the foregoing experiment was crystallised from alcohol; m.p. 140–142° undepressed on admixture with phenylazodimethyldihydroresorcin. Yield very poor. On repeated treatment with caustic alkali the substance gradually goes into solution from which the yellow azo-compound is thrown out by acids. It thus appears that the diazo-oxy-compound is easily transformed into the C-azo-derivative. The final alkaline filtrate yielded a large quantity of the azo-compound on acidification.

*o-, m-, and p-Tolyl-azodimethyldihydroresorcin*.—The diazonium solution obtained from each of *o-*, *m-* and *p-*toluidines (5 g.) was added to dimethyldihydroresorcin (7 g.) dissolved in 2*N* caustic soda solution (50 c.c.) and worked up in the manner described under phenylazodimethyldihydroresorcin. The yield was almost quantitative in every case; the products crystallised from dilute alcohol in orange yellow needles.

*o-Tolylazodimethyldihydroresorcin*, m.p. 125° (Found: N, 11.34);  
*m-Tolylazodimethyldihydroresorcin*, m.p. 122–23° (Found: N, 11.22);  
*p-Tolylazodimethyldihydroresorcin*, m.p. 156–157° (Found: N, 10.92).  
 $C_{15}H_{15}O_2N_2$  requires N, 10.85 per cent.

*p-Tolyldiazo-oxydimethyldihydroresorcin*.—Diazotised toluidine (5 g.) was coupled with dimethyldihydroresorcin (7 g.) dissolved in water (65 c.c.) containing caustic soda (13 g.), the supernatant liquid reacting strongly alkaline. The small quantity of a red precipitate that had come down was filtered. The filtrate on salting yielded a small additional amount of red precipitate. The final filtrate on acidification yielded a considerable quantity of the yellow azo-compound.

*α- and β-Naphthylazodimethyldihydroresorcin*.—Each of *α-* and *β-*naphthyl amines (6.7 g.) was diazotised and coupled with dimethyldihydroresorcin (7 g.) dissolved in caustic soda solution (50 c.c.). The products were worked up as in the previous cases.

*α-Naphthylazodimethyldihydroresorcin* crystallised in fine light orange coloured needles from dilute alcohol; m.p. 141° (Found: N, 9.60.  $C_{18}H_{18}N_2O_2$  requires N, 9.52 per cent.).

*β-Naphthylazodimethyldihydroresorcin* was not so easily soluble in dilute alcohol as the previous compounds and was crystallised from 95 per cent. alcohol in light orange needles; m.p. 200° (Found: N, 9.65.  $C_{18}H_{18}N_2O_2$  requires N, 9.52 per cent.).

*α- and β-Naphthyldiazo-oxydimethyldihydroresorcin.*—The diazotised solution obtained from each of *α-* and *β-*naphthylamines (6.7 g.) was coupled with dimethyldihydroresorcin (7 g.) dissolved in water (65 c.c.) containing caustic soda (13 g.). The products, after freeing from any unchanged dimethyldihydroresorcin, were further purified by washing with hot absolute alcohol and by precipitating with petrol from benzene solution. They could not be crystallised.

*α-Naphthyldiazo-oxydimethyldihydroresorcin* was obtained as a chocolate-brown precipitate; m.p. above 200° (decomp.) (Found: N, 8.97.  $C_{18}H_{18}N_2O_2$  requires N, 9.52 per cent.).

*β-Naphthyldiazo-oxydimethyldihydroresorcin*; m.p. above 255° (decomp.) (Found: N, 9.70.  $C_{18}H_{18}N_2O_2$  requires N, 9.52 per cent.).

*Phenylazodimethyldihydroresorcin sulphonic acid.*—Sulphanilic acid (8.65 g.) was dissolved in 75 c.c. of water containing 3 g. anhydrous sodium carbonate. Sodium nitrate (3.6 g.) dissolved in water (40 c.c.) was added and concentrated hydrochloric acid (15 c.c.) was slowly run in. The diazonium solution thus obtained was coupled with dimethyldihydroresorcin (7 g.) dissolved in water (60 c.c.) containing caustic soda (2 g.). As soon as the two liquids were mixed, a yellow precipitate separated out, the light yellow supernatant liquor having an acid reaction. In an ice-bath at the end of four hours the colour changed from yellow to red. On leaving the mixture overnight, all the solid went into solution which became red in colour and yielded a very small quantity of a precipitate on salting out. The filtrate, after neutralisation with caustic soda, was made slightly acidic and the water was distilled under reduced pressure. The solid residue after drying was extracted with absolute alcohol in a soxhlet apparatus and the yellow product obtained therefrom was crystallised in plates from absolute alcohol; m.p. above 360° (decomp.) with shrinking at 300° (Found: N, 7.54, 7.53; S, 9.04;  $H_2O$ , 5.29.  $C_{14}H_{16}N_2O_5S, H_2O$  requires N, 8.19; S, 9.36;  $H_2O$ , 5.26 per cent.).

When the coupling of diazotised sulphanilic acid was carried out in an alkaline medium, a very tarry product resulted which being much contaminated with the azo-compound as in the previous cases, could not be worked up. Azonaphthyldimethyldihydroresorcin sulphonic acid could not be isolated in a crystalline form. A solution of the crude product was used for the dyeing experiments.

*Phenylhydrazones of phenyl- and p-tolylazodimethyldihydroresorcin.*—A gram each of the substances was dissolved in 50 per cent. acetic acid and heated during 10 minutes on the water bath with two molecular proportions of phenyl hydrazine and the separated solid crystallised from dilute alcohol in fine needles.

*Phenylhydrazone (IX) of phenylazodimethyldihydroresorcin* was obtained as orange yellow needles, m.p. 191–192° (Found: N, 20.01.  $C_{26}H_{28}N_6$  requires N, 19.81 per cent.).

*Phenylhydrazone of p-tolylazodimethyldihydroresorcin* had the same colour and melted at 185° (Found: N, 19.44.  $C_{27}H_{30}N_6$  requires N, 19.18 per cent.).

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[Accepted, 27-2-1934.]

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