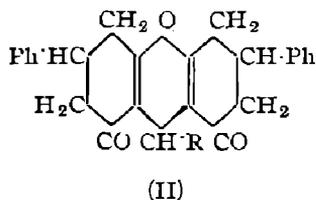
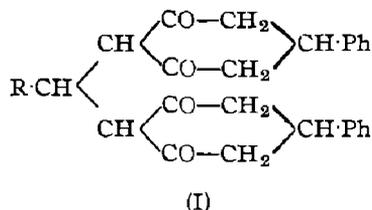


Dihydroresorcinols. Part IV. The Condensation of Phenyldihydroresorcinol with Aromatic Aldehydes.

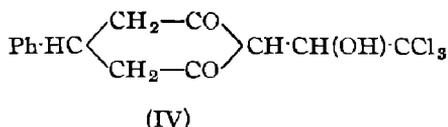
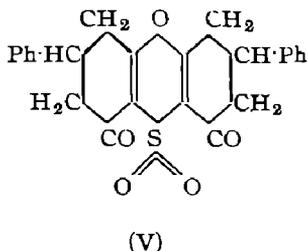
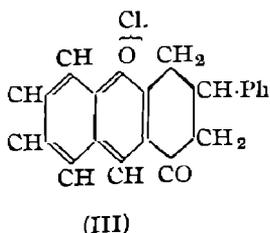
BY R. D. DESAI AND M. A. WALL.

In extending our work on the condensation of aldehydes with dihydroresorcinols, we have condensed phenyldihydroresorcinol with salicylaldehyde, benzaldehyde, cinnamic aldehyde, furfuraldehyde, piperonal, vanillin, *o*-nitrobenzaldehyde and *p*-dimethylaminobenzaldehyde. The bis-derivative (I) was formed in each case in presence of piperidine, at the ordinary temperature, and this could be dehydrated to the octahydroxanthene derivative by the methods reported in earlier papers (*J. Indian Chem. Soc.*, 1933, **10**, 663; *J. Univ. Bombay*, 1933, **2**, ii, 62).



In presence of gaseous hydrogen chloride, however, phenyldihydroresorcinol reacted with salicylaldehyde giving 2-phenyl-4-keto-1:2:3:4-tetrahydrobenzopyranol anhydrochloride (III). Chloral hydrate and thionyl chloride also underwent condensation readily, and the former gave 1-phenyl-4(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-cyclohexane-3:5-dione (IV). We have provisionally assumed the structure of the oxide of 2:7-diphenyl-4:5-diketo-1:2:3:4:5:6:7:8-octahydrophenothioxin (V) for the product obtained from thionyl chloride. Dimethyldihydroresorcinol condensed similarly with these reagents and we are

studying their degradation to the known phenothioxin derivatives (Shri Krishna, *J. Chem. Soc.*, 1923, 123, 2782; Mauthner *Ber.*, 1905, 38, 1411; Hildich and Smiles, *J. Chem. Soc.*, 1911, 99, 408).



Finally we have studied the condensation of furfural and *p*-dimethylaminobenzaldehyde with dimethyldihydroresorcinol, as these products were required for comparison with their analogues from phenyldihydroresorcinol. Our conclusion is that so far as the condensation of aldehydes is concerned, all the dihydroresorcinols behave similarly, the substituents in position-4 having no effect on the reactivity of the methylene group.

EXPERIMENTAL.

Phenyldihydroresorcinol was prepared by the method of Vorländer (*Annalen*, 1897, 294, 253). The hydrolysis of the dione ester was carried out by alcoholic potash, as this required only 3-4 hours, yield 80-85%.

Salicyl-bisphenyldihydroresorcinol.—A mixture of salicylaldehyde (1 g.), phenyldihydroresorcinol (3 g.), dry methyl alcohol (15 c.c.) and piperidine (4 drops) was kept at the ordinary temperature for 12 hours. The alcohol was removed by suction and the residue crystallised from dilute ethyl alcohol in short orange needles, m.p. 169-70°. The alcoholic solution gave brown colouration with ferric chloride. (Found: C, 77.3; H, 5.9. $C_{31}H_{28}O_5$ requires C, 77.5; H, 5.8 per cent).

When its solution in absolute ethyl alcohol was saturated with hydrogen chloride and kept for 24 hours, *2:7-diphenyl-4:5-diketo-9-o-hydroxyphenyl-octahydroxanthene* was obtained, which crystallised from alcohol in short yellow needles, m.p. 230°. (Found: C, 80.2; H, 5.8. $C_{31}H_{26}O_4$ requires C, 80.5; H, 5.6 per cent).

The *acetyl* derivative, prepared by heating the bis-compound with acetic anhydride for 6 hours, crystallised from dilute alcohol in crimson-red short needles, m.p. 145°. (Found: C, 78.4; H, 5.6. $C_{33}H_{28}O_5$ requires C, 78.6; H, 5.5 per cent).

2-Phenyl-4-keto-1:2:3:4-tetrahydrobenzopyranol anhydrochloride.—A solution of salicylaldehyde (2 g.), phenyldihydroresorcinol (3 g.) in dry methyl alcohol (15 c.c.) was saturated with hydrogen chloride at 0°. The mixture became warm, changed to red and after some time began depositing red crystals, which were removed after 12 hours, washed with methyl alcohol and dried in vacuum over caustic potash. The substance contained chlorine and showed no tendency to melt up to 360°, but simply carbonised. (Found: C, 73.1; H, 4.9. $C_{19}H_{15}O_2Cl$ requires C, 73.4; H, 4.8 per cent).

The *anhydro-base*, prepared by adding sodium acetate solution to the warm solution of the anhydrochloride in a large excess of ethyl alcohol, was a pinkish powder, insoluble in most of the organic solvents, and did not melt below 360°. It was stable to concentrated alcoholic potash solution, and regenerated the anhydrochloride on treating with methyl alcoholic hydrogen chloride. (Found: C, 77.8; H, 5.6. $C_{19}H_{16}O_3$ requires C, 78.1; H, 5.5 per cent).

Benzal-bis-phenyldihydroresorcinol, prepared from benzaldehyde, crystallised from dilute alcohol in white needles, m.p. 110°. (Found: C, 80.1; H, 6.1. Calc. for $C_{31}H_{28}O_4$: C, 80.1; H, 6.0 per cent).

The *xanthene* derivative crystallised from alcohol in colourless needles, m.p. 228°. (Found: C, 83.0; H, 6.0. Calc. for $C_{31}H_{28}O_3$: C, 83.4; H, 5.8 per cent). (Vorländer, *Annalen*, 1899, 309, 379).

Cinnamal-bisphenyldihydroresorcinol crystallised from alcohol in short yellow needles, m.p. 155-56°. (Found: C, 80.4; H, 6.3. $C_{33}H_{30}O_4$ requires C, 80.8; H, 6.1 per cent).

The *xanthene* derivative crystallised from alcohol in yellow needles, not melting below 280°. (Found: C, 83.4; H, 6.1. $C_{33}H_{28}O_3$ requires C, 83.9; H, 5.9 per cent).

Furfuralbisphenyldihydroresorcinol crystallised from alcohol in

white needles, m.p. 122°. (Found : C, 76.6; H, 5.7. $C_{29}H_{26}O_5$ requires C, 76.4; H, 5.8 per cent).

The *xanthene* derivative crystallised from alcohol as a black micro-crystalline powder, m.p. above 280°. (Found : C, 80.1; H, 5.5. $C_{29}H_{24}O_4$ requires C, 79.8; H, 5.5 per cent).

p-Dimethylaminobenzal-bisphenyldihydroresorcinol, prepared from *p*-dimethylaminobenzaldehyde, crystallised from alcohol in orange needles, m.p. 107°-108°. (Found : C, 78.2; H, 6.4. $C_{33}H_{33}O_4N$ requires C, 78.1; H, 6.5 per cent).

The *xanthene* derivative crystallised from alcohol in small yellow needles, m.p. 200°. (Found : C, 80.9; H, 6.3. $C_{33}H_{31}O_3N$ requires C, 80.8; H, 6.2 per cent).

3 : 4-Methylenedioxybenzal-bisphenyldihydroresorcinol, prepared from piperonal, crystallised from alcohol in colourless, prismatic needles, m.p. 148°. (Found : C, 75.31; H, 5.8. $C_{32}H_{28}O_6$ requires C, 75.6; H, 5.5 per cent).

The *xanthene* crystallised from alcohol in colourless needles, m.p. above 280°. (Found : C, 78.0; H, 5.6. $C_{32}H_{26}O_5$ requires C, 78.3; H, 5.3 per cent).

4-Hydroxy-3-methoxybenzal-bisphenyldihydroresorcinol, prepared from vanillin, crystallised from alcohol in pale yellow needles, m.p. 116°. (Found : C, 75.1; H, 5.8. $C_{32}H_{30}O_6$ requires C, 75.2; H, 5.8 per cent).

The *xanthene* derivative crystallised from alcohol in white needles, m.p. above 280°. (Found : C, 77.8; H, 5.9. $C_{32}H_{28}O_5$ requires C, 78.0; H, 5.6 per cent).

o-Nitrobenzalbisphenyldihydroresorcinol crystallised from alcohol, in pale yellow needles, m.p. 160°. (Found : C, 73.0; H, 5.4. $C_{31}H_{27}O_6N$ requires C, 73.1; H, 5.3 per cent).

The *xanthene* derivative crystallised from alcohol in pale yellow needles, m.p. 272°. (Found : C, 75.6; H, 5.0. $C_{31}H_{25}O_5N$ requires C, 75.7; H, 5.0 per cent).

1-Phenyl-4-(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-cyclohexane-3 : 5-dione.—A mixture of chloral hydrate (1 g.), phenyldihydroresorcinol (2 g.), methyl alcohol (15 c.c.) and piperidine (4 drops) was kept at 25° for 24 hours. The solid, that separated out on dilution with water, was repeatedly crystallised from dilute alcohol, when pale yellow needles, m.p. 145-46°, were obtained. (Found : C, 50.0; H, 4.0. $C_{14}H_{13}O_3Cl_3$ requires C, 50.0; H, 3.8 per cent).

Oxide of 2 : 7-Diphenyl-4 : 5-diketo-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenothioxin (?).—A mixture of thionyl chloride (2 c.c.) phenyl-dihydroresorcinol (2 g.) and dry benzene (15 c.c.) was refluxed on a water-bath for 6 hours till fumes of hydrochloric acid ceased to be evolved. Much of the benzene was removed and white prismatic needles, m.p. 216°, were obtained. The compound contained sulphur and gave blue colouration with concentrated sulphuric acid on slight warming. (Found : C, 71·2; H, 4·9. $C_{24}H_{20}O_4S$ requires C 71·2; H, 4·9 per cent).

Oxide of 2 : 2 : 7 : 7-tetramethyl-4 : 5-diketo-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrophenothioxin (?) was similarly obtained from dimethyldihydroresorcinol and thionyl chloride. It crystallised from benzene in pale yellow rhombohedra or from alcohol in pale yellow needles, m.p. 181-82°, and gave blue colour with concentrated sulphuric acid on slight warming. (Found : S, 10·1. $C_{16}H_{20}O_4S$ requires S, 10·4 per cent).

1 : 1-Dimethyl-4-(α -hydroxy- $\beta\beta\beta$ -trichloroethyl)-cyclohexane-3 : 5-dione was prepared from dimethyldihydroresorcinol and chloral hydrate. It crystallised from dilute alcohol in short, white needles, m.p. 120°. (Found : C, 41·3; H, 4·6. $C_{10}H_{13}O_3Cl_3$ requires C, 41·7; H, 4·5 per cent).

Furfuralbisdimethyldihydroresorcinol, obtained by the usual method from furfuraldehyde (2 g.), dimethyldihydroresorcinol (5·69 g.) and piperidine (4 drops), crystallised from dilute alcohol in white needles, m.p. 160°. (Found : C, 70·1; H, 7·1. $C_{21}H_{26}O_5$ requires C, 70·7; H, 7·2 per cent).

The *xanthene* derivative crystallised from alcohol as a black microcrystalline powder and did not melt up to 280°. (Found : C, 74·0; H, 7·0. $C_{21}H_{24}O_4$ requires C, 74·1; H, 7·0 per cent).

p-Dimethylaminobenzal-bisdimethyldihydroresorcinol crystallised from dilute alcohol, m.p. 114°. (Found : C, 72·7; H, 8·1. $C_{25}H_{33}O_4N$ requires C, 72·9; H, 8·0 per cent).

The *xanthene* derivative crystallised from alcohol in white short needles, m.p. 220°. (Found : C, 76·2; H, 7·8. $C_{25}H_{31}O_3N$ requires C, 76·3; H, 7·8 per cent).