# THE REACTIVITY OF DIMETHYLDIHYDRORESORCIN. Part I. CONDENSATION WITH AROMATIC ALDEHYDES.

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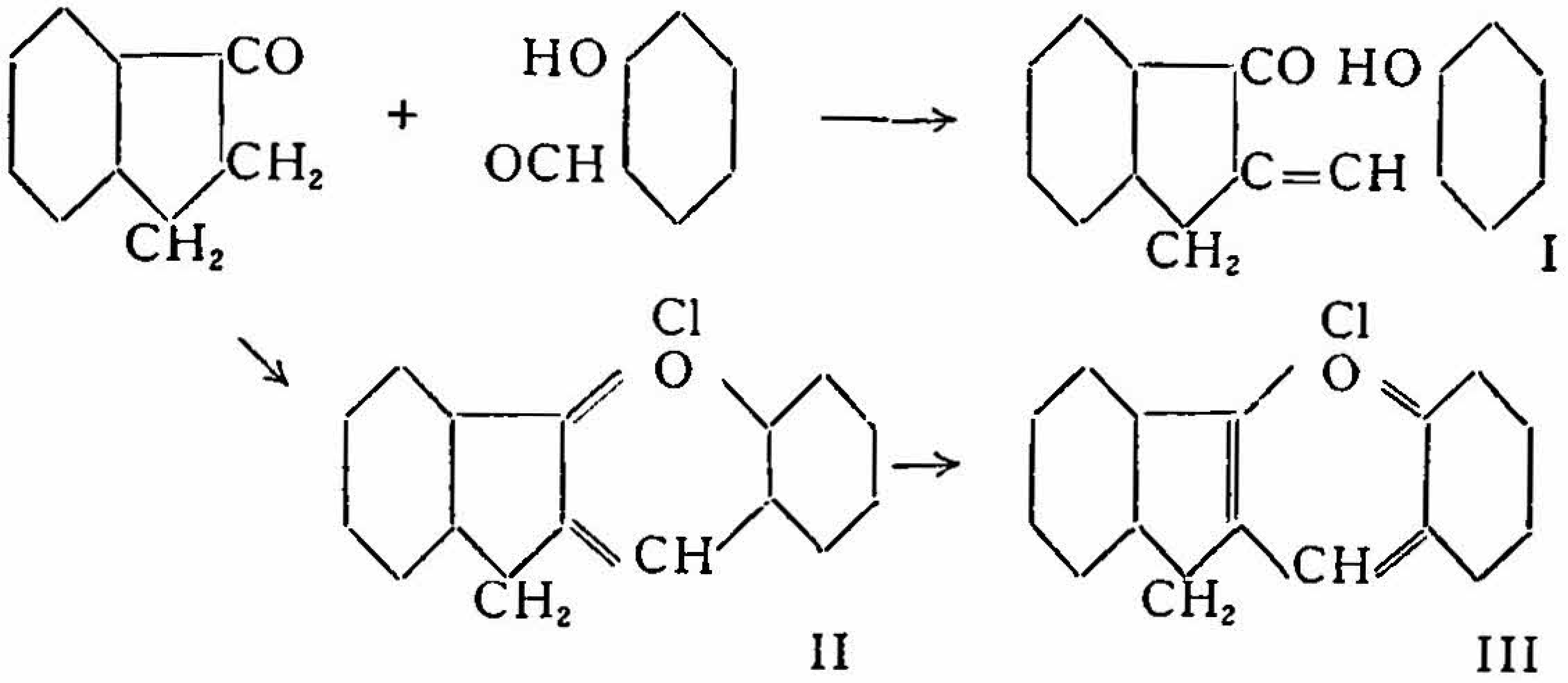
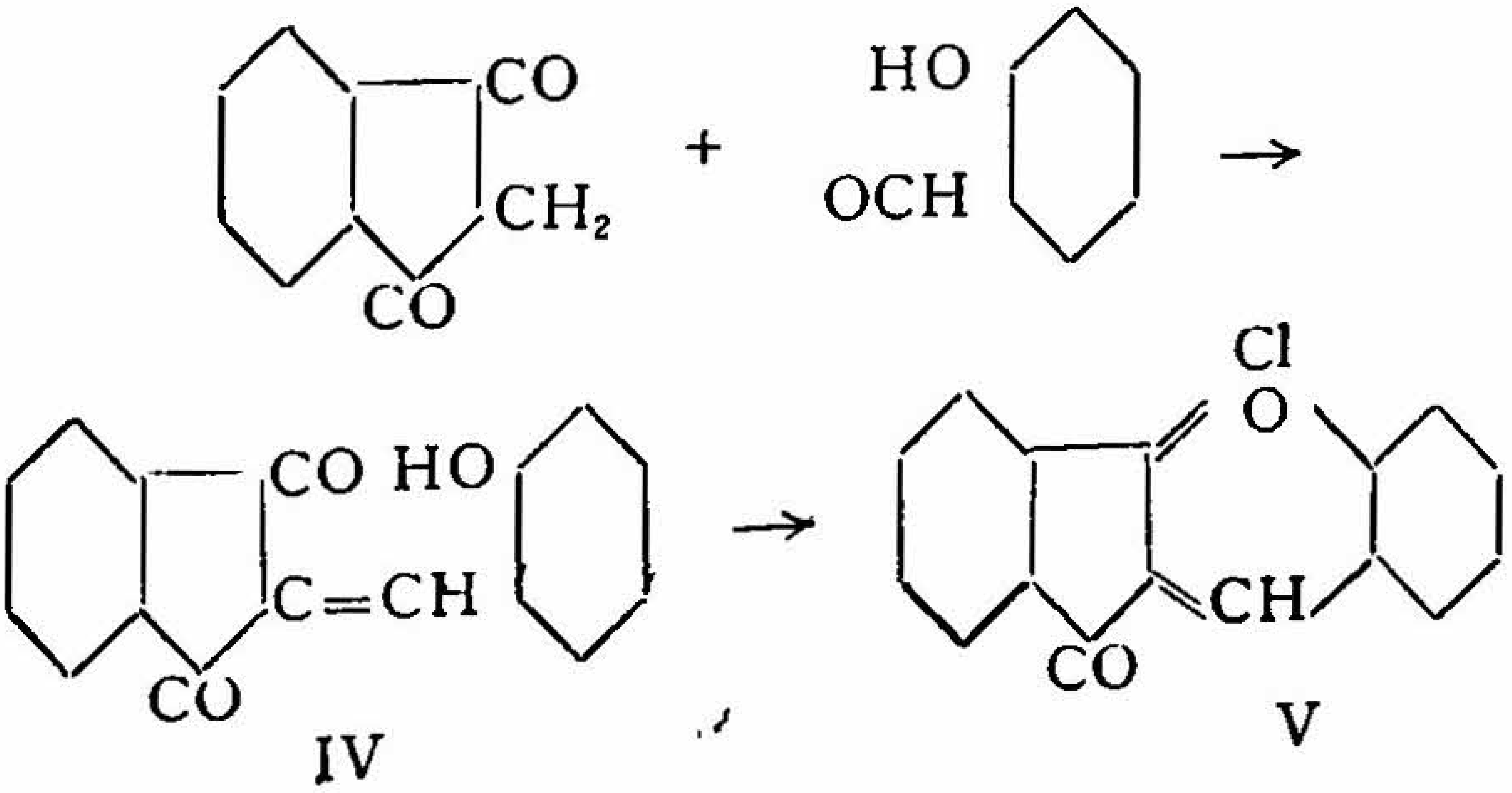
Monoketohydrindene reacts with salicylaldehyde in presence of hydrogen chloride yielding indenobenzopyranol anhydrochloride (Perkin, Robinson and Turner, *J.C.S.*, 1908, **93**, 1085) :—



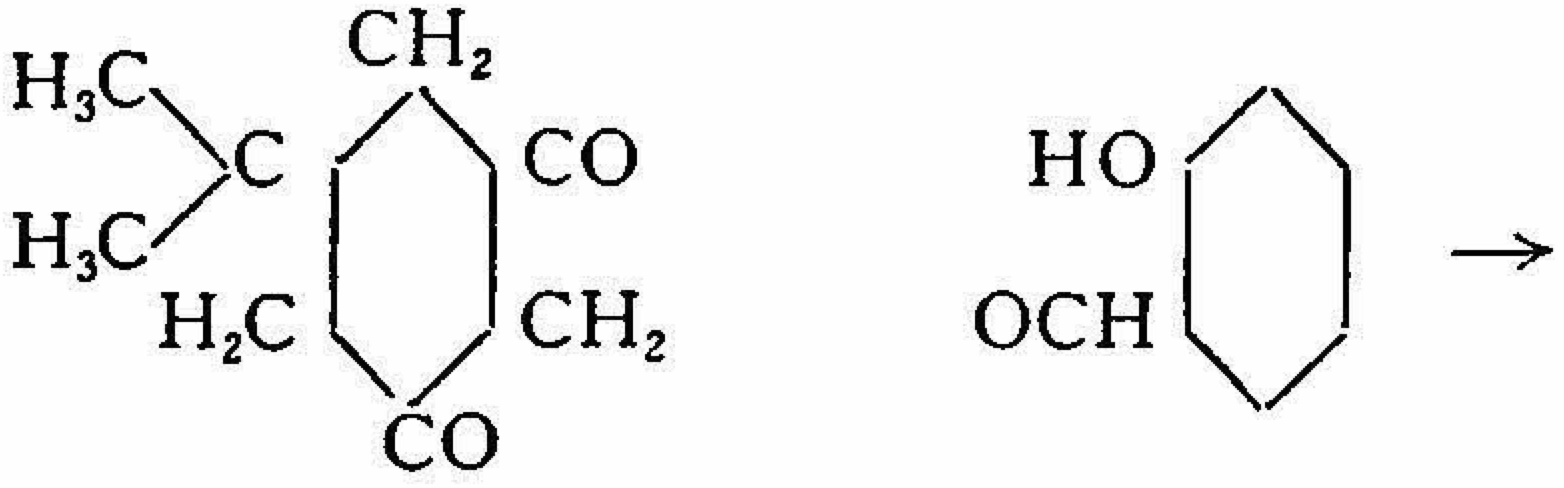
The strong colour of the compound, and various other considerations led the authors to assume that its constitution is best represented by the orthoquinonoid formula (III), involving a rearrangement of the double bonds in formula (II). Sastry and Ghosh later (*J.C.S.*, 1915, **107**, 1442) obtained keto-indenobenzopyranol anhydrochloride (V) from diketohydrindene and salicylaldehyde,



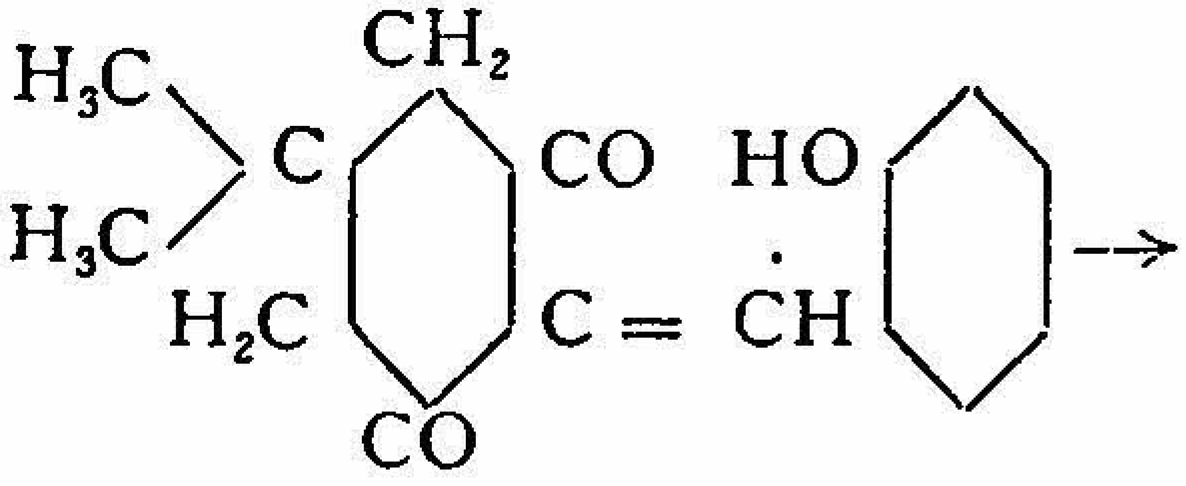
They think that the assumed shifting of double bonds to the benzene nucleus is unnecessary in view of the fact that compound IV and its acetyl derivative are coloured. The present work was undertaken with the object of arriving at a decision between the two views.

Many compounds containing the CO-$CH_2$-group have in recent years been shown to yield pyranol derivatives (*J.C.S.*, 1918, **113**, 444; *ibid.*, 1919, **115**, 817; 812 *et seq.*): but as none of these contains a hydroaromatic ring the orthoquinonoid arrangement is possible on both sides. If a hydroaromatic compound containing the CO-$CH_2$-group be condensed with *o*-hydroxyaldehydes, the resulting pyranol derivatives can have orthoquinonoid arrangement on one side only, namely, that containing the benzene nucleus.

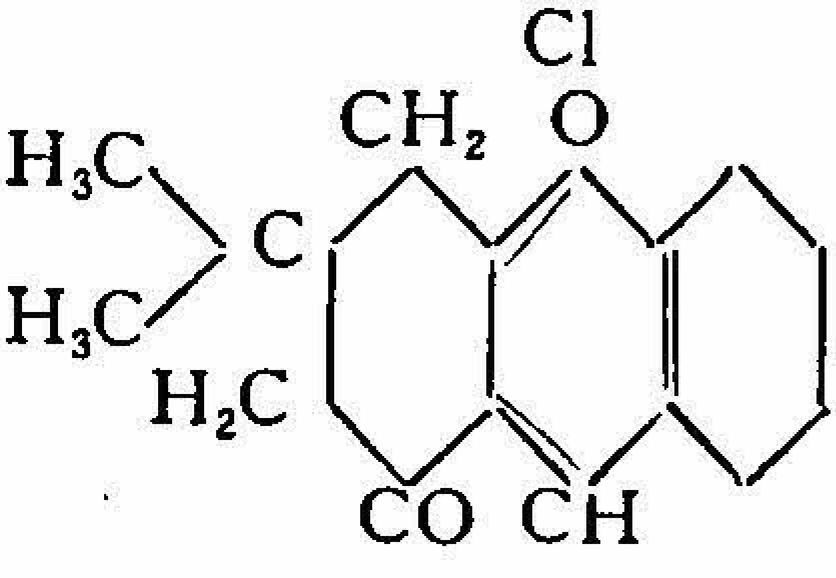
Dimethyldihydroresorcin is a well-crystallised, reactive cyclic compound containing two CO-$CH_2$-groups; it was therefore expected to yield pyranol derivatives by condensation with *o*-hydroxyaldehydes.



VI

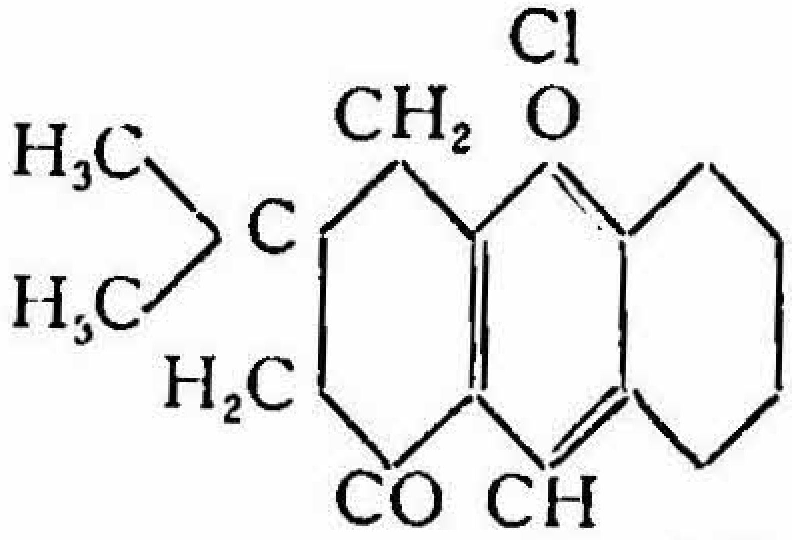


VII



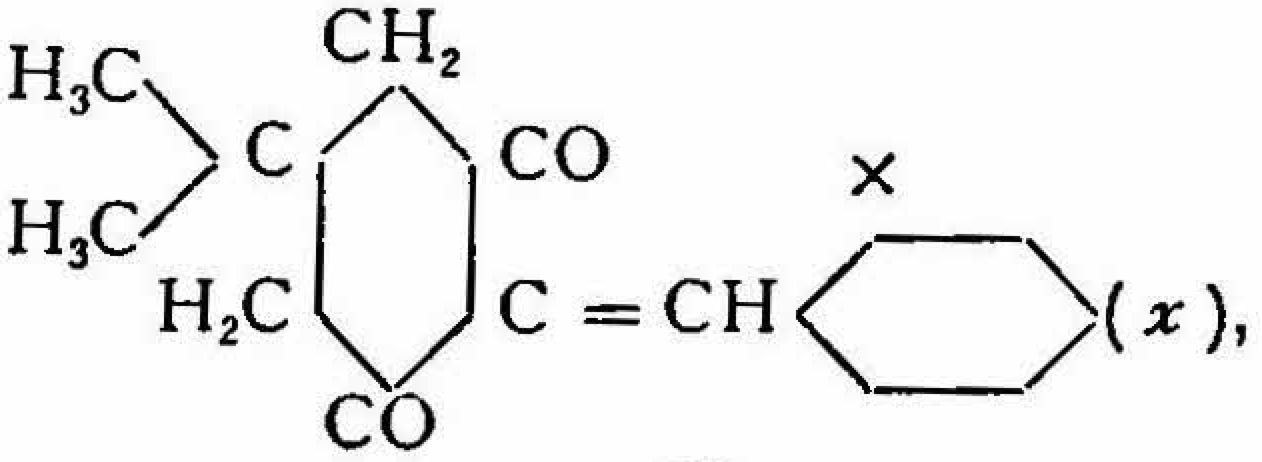
VIII

In the above formula double bonds are attached to the carbon atoms of a hexahydrobenzene nucleus and therefore do not form what is called orthoquinonoid arrangement. Now if the pyranol derivatives so produced be strongly coloured the double bonds must have been shifted to the benzene nucleus to produce the orthoquinonoid arrangement. The pyranol derivative obtained from salicylaldehyde is scarlet, so the double bonds must have been shifted during the course of the reaction and the compound has the formula :—



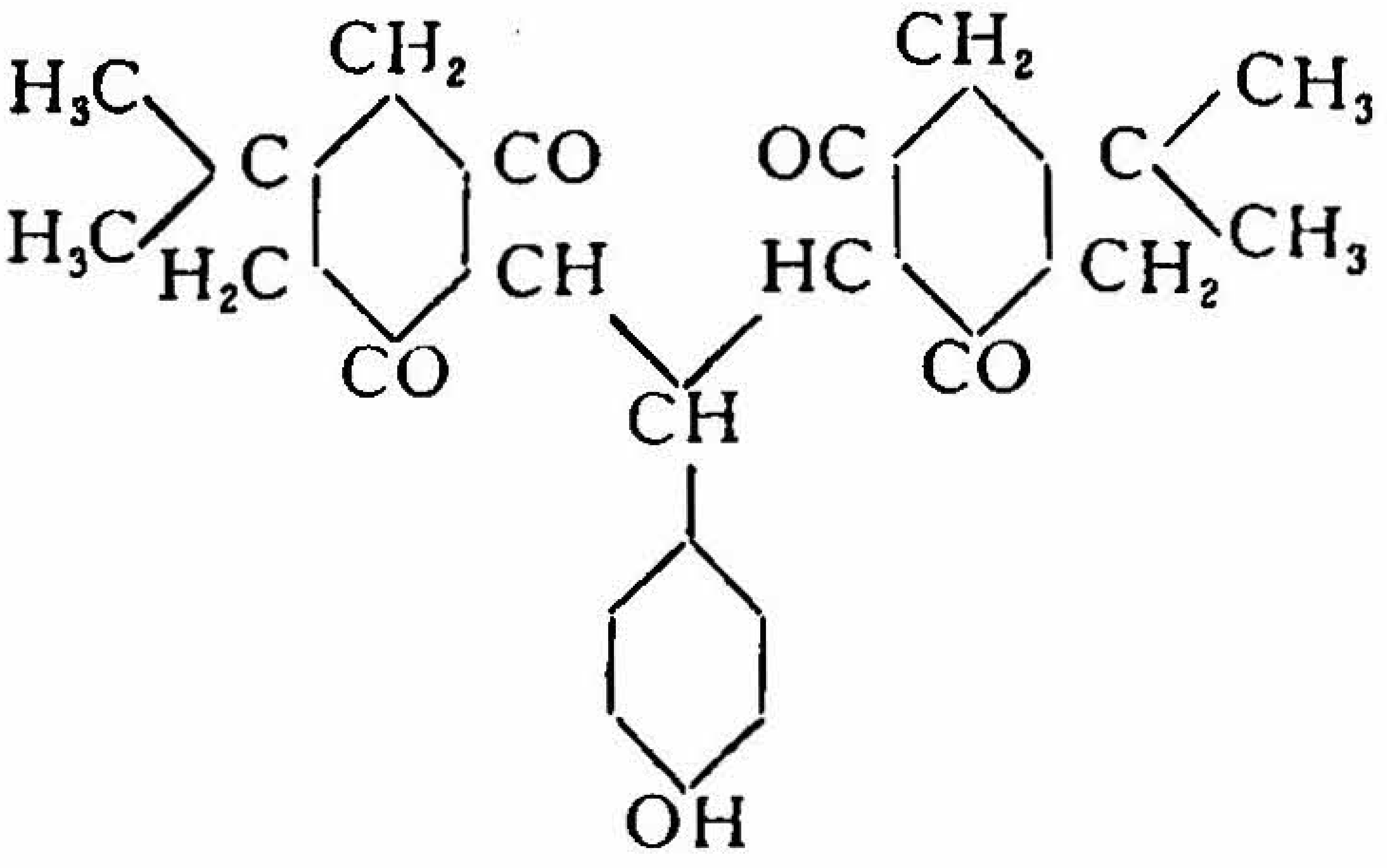
IX

If this is true, compounds of the type,



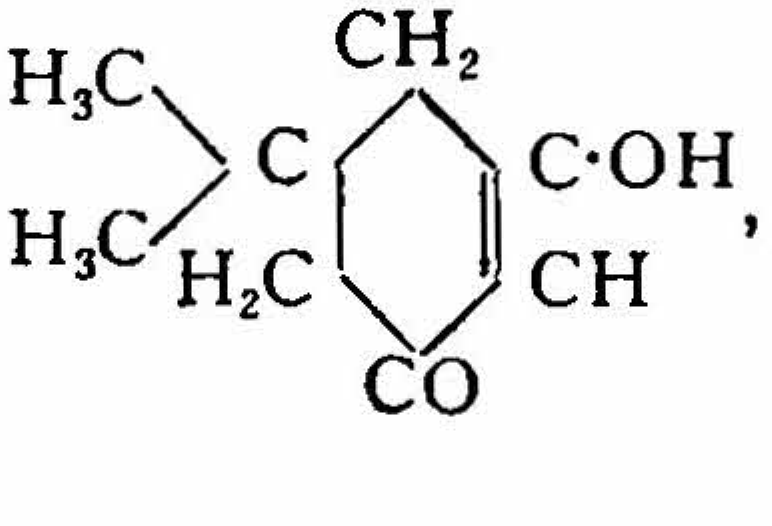
X

should either be colourless or be very lightly coloured. Attempts were therefore made to synthesise compounds of the type (X) by condensing dimethyldihydroresorcin with benzaldehyde and substituted benzaldehydes in presence of alkali, but in none of these cases was a benzylidene derivative obtained. On the other hand, mono- and diketo-hydrindenes and substances of allied nature are known to yield benzylidene derivatives (cf. Kipping, *J.C.S.*, 1894, 65, 498; Perkin and Robinson, *ibid.*, 1907, **91**, 1073 *et seq.*) of structures similar to (I) and (IV) almost exclusively by the same treatment. The experiments were conducted under various conditions, (1) by boiling the aldehyde and the resorcin dissolved in absolute alcohol, (2) by adding a few drops of alkali to the alcoholic solution, (3) by employing aqueous alcoholic potash and also (4) in presence of aqueous caustic soda and sodium carbonate solutions; but in every case two molecules of dimethyldihydroresorcin were found to condense with one molecule of aldehyde producing compounds of the benzamarone type. With *p*-hydroxybenzaldehyde the triphenylmethane derivative (XI), is

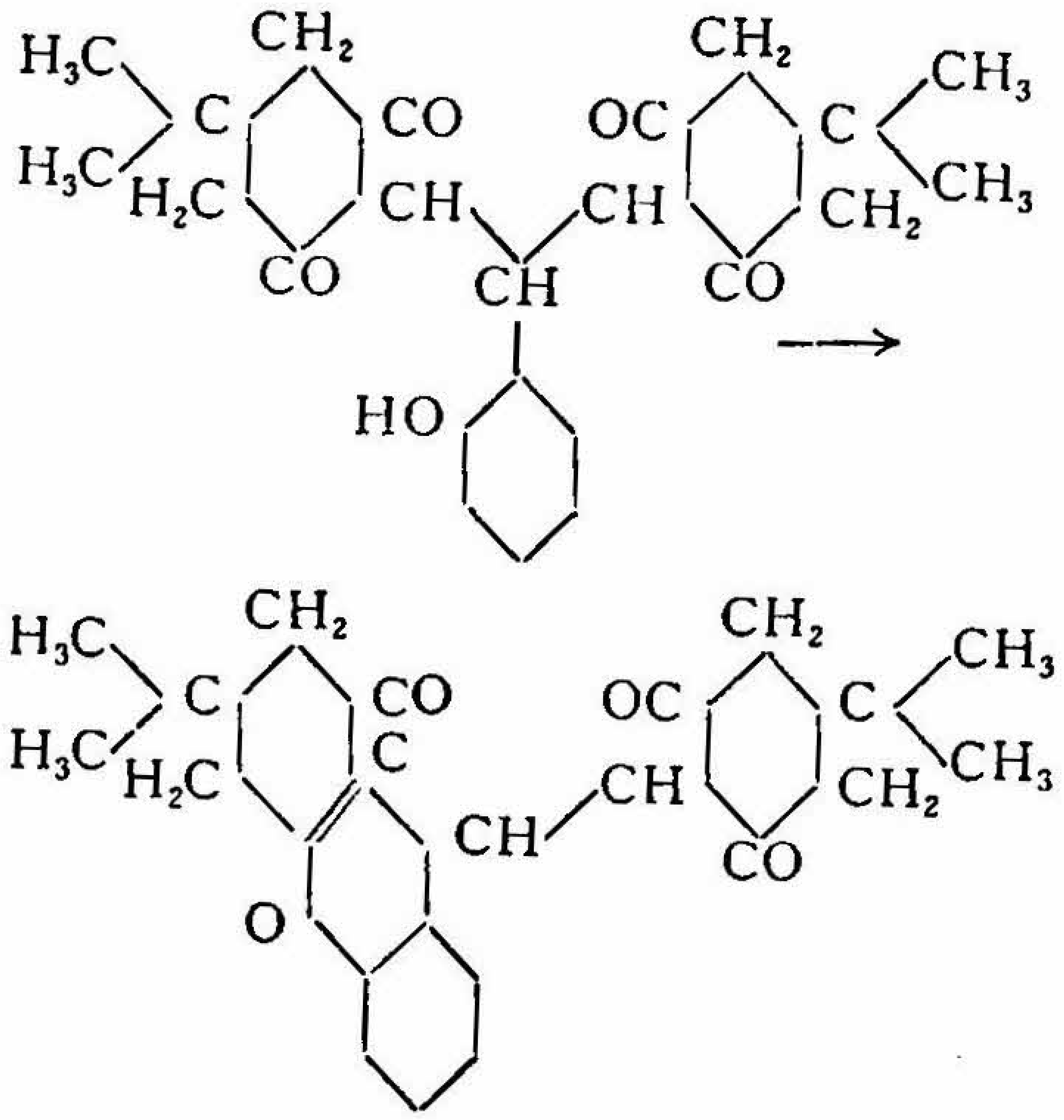


XI

formed; similar compounds have been obtained by the action of benzaldehyde, anisaldehyde, vanillin, piperonal, para- and meta-nitrobenzaldehydes, 3 : 4-dihydroxybenzaldehyde and cinnamaldehyde, on the ketone. The recent investigation of compounds (aldimethones) of dimethyldihydroresorcin with aldehydes occurring in plant products by Vorländer (*Z. anal. Chem.*, 1929, **77**, 321–327), Zeffmann and Pines (*Bull. Wagner Free Inst.*, 1929, **4**, 15–16) and Klein and Zinser (*Mikrochem.*, 1929, Pregl Fest, 204–234) also lends support to our observation that aromatic aldehydes react with dimethyldihydroresorcin in the manner suggested. The foregoing facts lead us to the conclusion that the reactions of dimethyldihydroresorcin itself are best explained if we assume that the latter has the constitution,

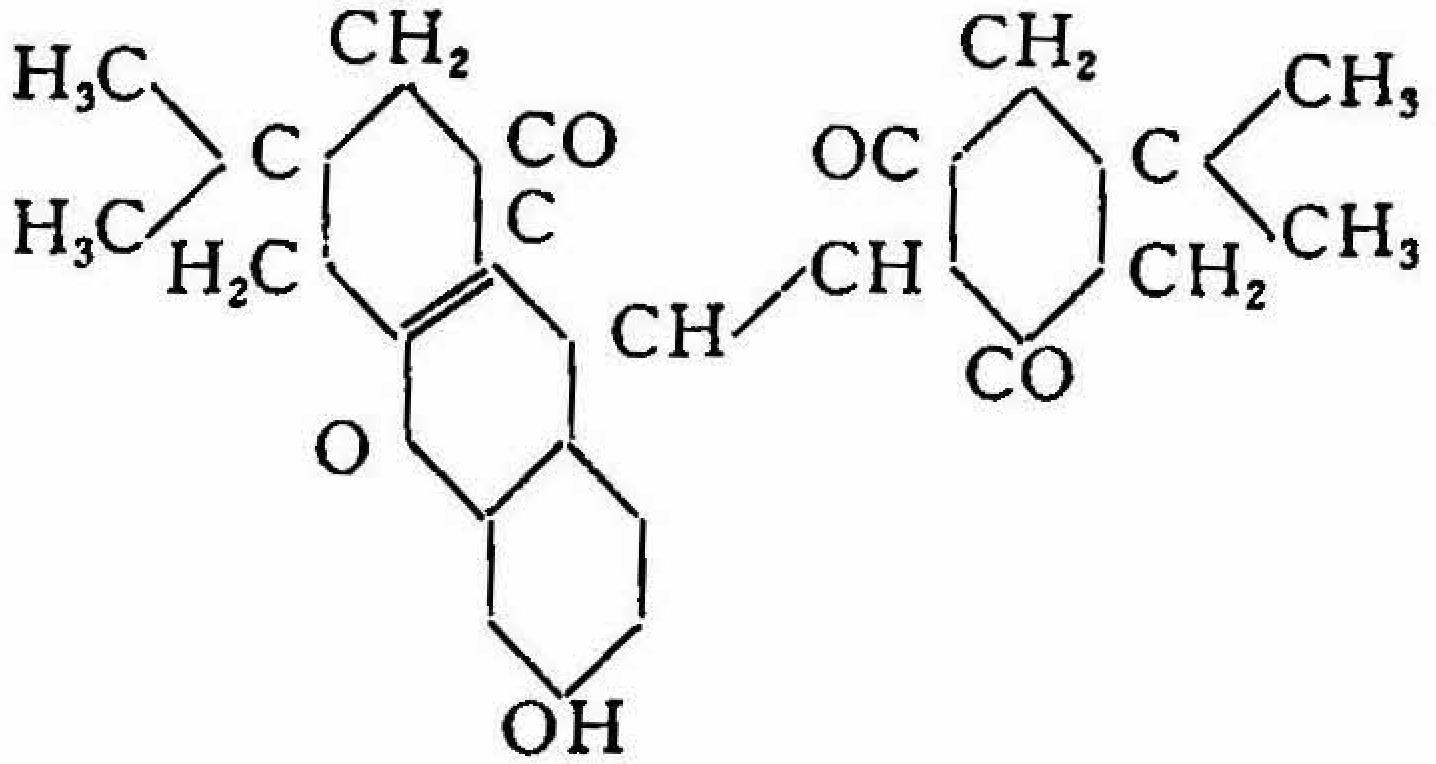


and not the customary formula (VI) by which it is usually represented; but we shall discuss this point in connection with further experiments which are about to be completed. The behaviour of salicylaldehyde is of special interest; as in the above cases, two molecules of the ketone condense with one molecule of the aldehyde, but the salical derivative which is undoubtedly first formed loses a further molecule of water yielding the pyran derivative (XII) :—



XII

In the same way 2 : 4-dihydroxybenzaldehyde reacts with dimethyldihydroresorcin forming the compound (XIII) :—

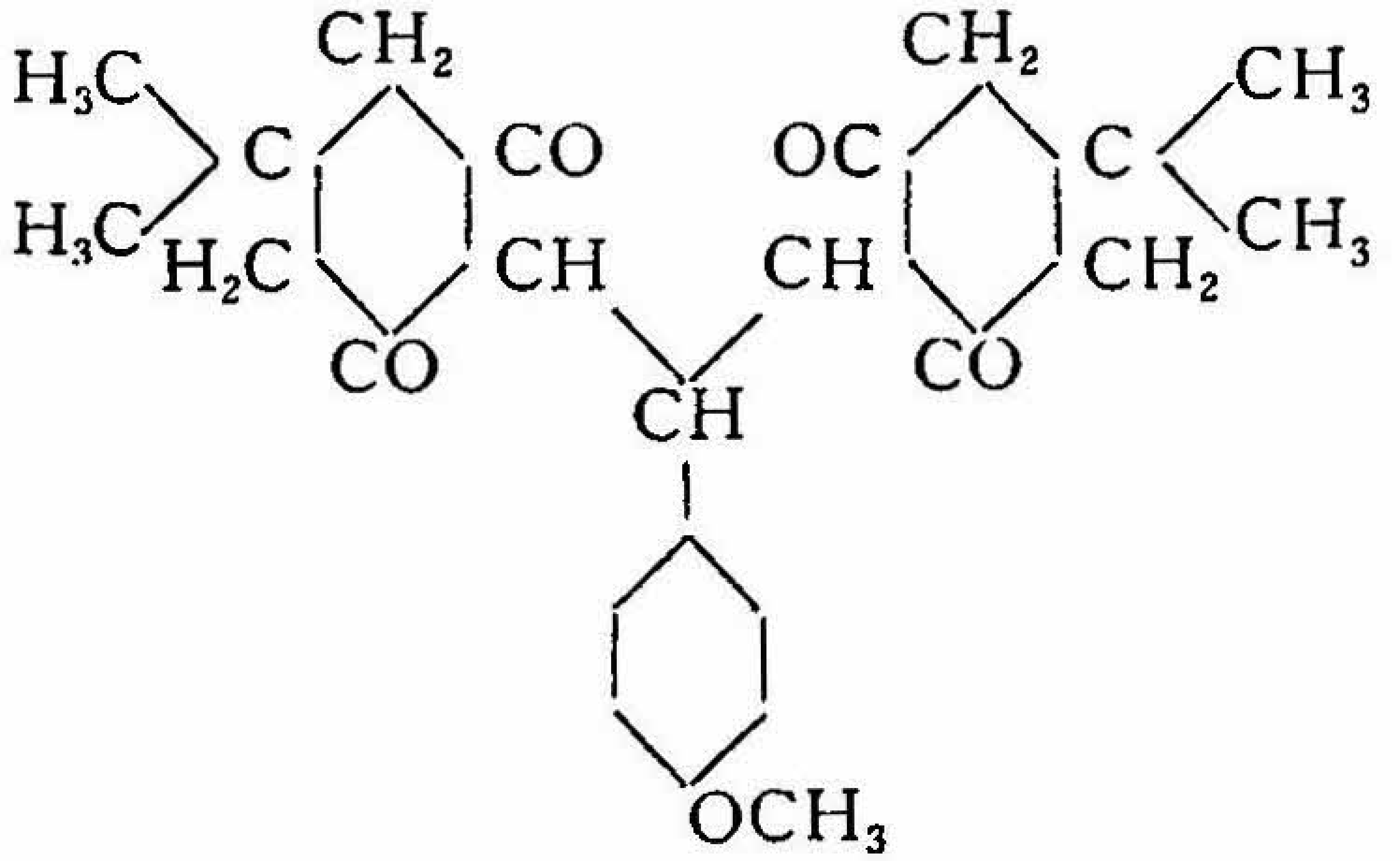


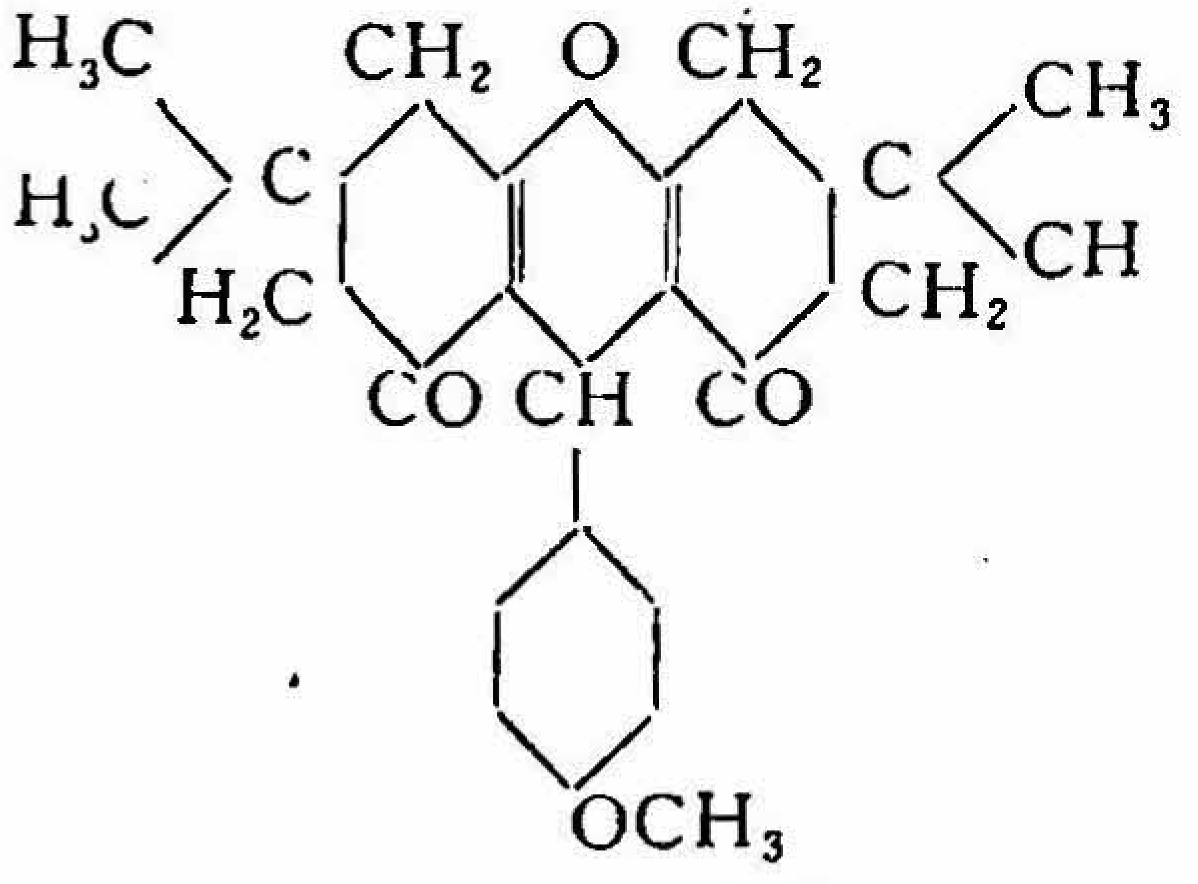
XIII

Evidence for such a supposition is (1) the results of analysis, which do not agree with any other possible formula, and (2) although the substance is colourless in the solid state and also in chloroform or alcohol solution, it is orange-yellow in the molten state and in glacial acetic acid solution, owing probably to the formation of a weak oxonium salt. The formation of 3 : 3′-diphenylacetylenedibenzo*spiro*pyran and of diphenylacetylenedi-β-naphtha*spiro*pyran from diphenyl*cyclo*pentanone and salicylaldehyde and 2-naphthol-1-aldehyde (Ruhemann and Levy, *J.C.S.*, 1913, **103**, 553–54), although not exactly analogous, may be cited as examples of the ready anhydride formation in which the hydroxyl group of salicylaldehyde and of naphtholaldehyde takes part.

Having failed to obtain the benzylidene derivatives by direct synthesis, the hydrolysis of the anhydrochloride (VIII) was attempted. It was expected that ortho-hydroxybenzylidenedimethyldihydroresorcin (VII) would be formed by such a treatment. The anhydrochloride was found to be remarkably stable towards alkali however; and no appreciable hydrolysis took place even by boiling it with concentrated alcoholic potash for six hours.

The benzamarone type of compounds mentioned above, on boiling with acetic anhydride or on heating their solution in strong sulphuric acid to about 100° undergo a xanthene-ring condensation. Anisaldehyde compound gives 2 : 7-tetramethyl-4 : 5-diketo-*p*-methoxyphenyloctahydroxanthene (XIV) :—

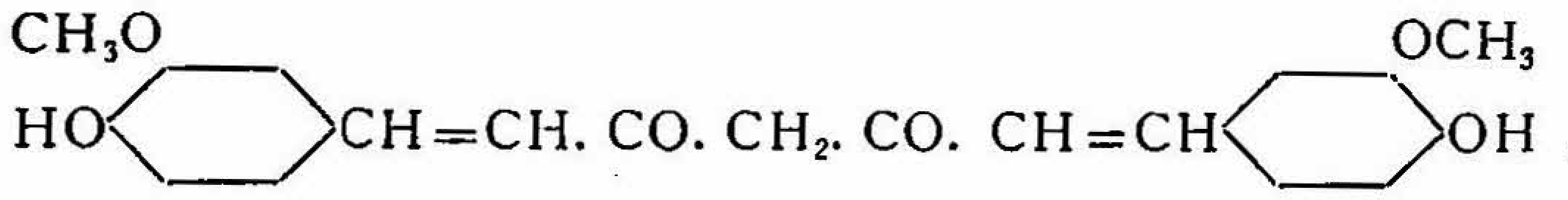




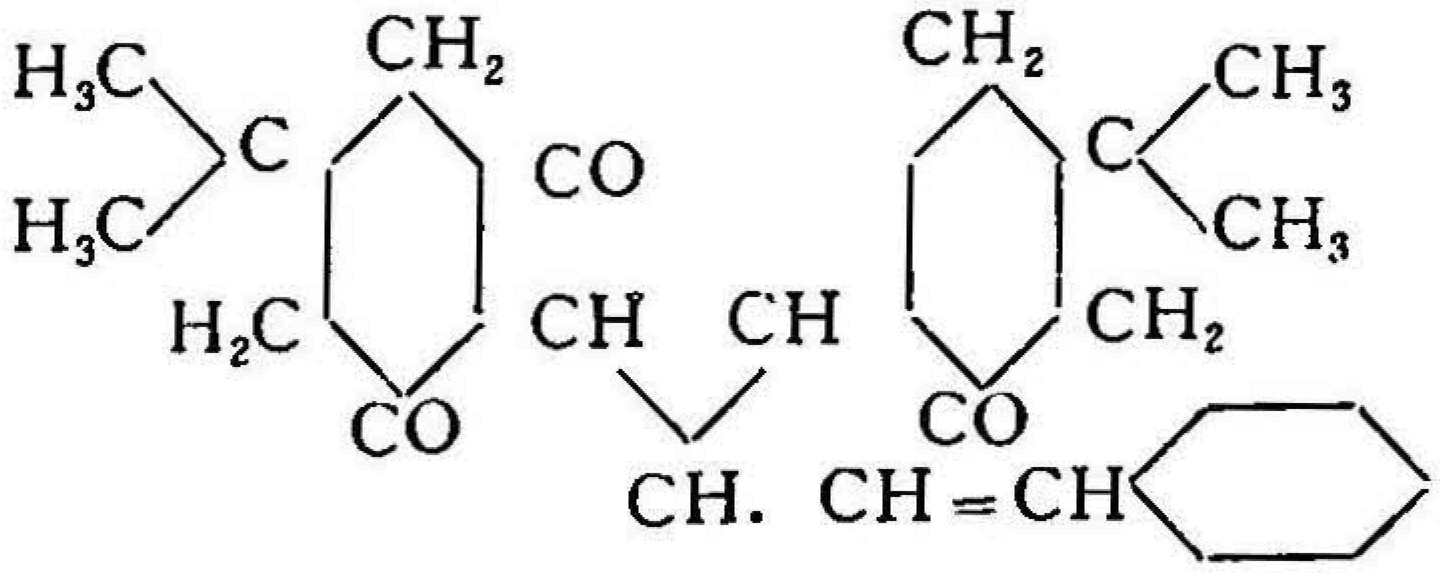
XIV

Compounds obtained from *p*-hydroxybenzaldehyde, vanillin and para- and meta-nitrobenzaldehyde with dimethyldihydroresorcin have also yielded similar hydrogenised phenylxanthene derivatives. The latter compounds are also formed along with the benzamarone derivatives by boiling the alcoholic solutions of the aldehyde and resorcin, the quantities of the products varying according to the duration of heating; and they are formed exclusively if such solutions in absolute alcohol are saturated with hydrogen chloride gas and allowed to stand. Hydrogenised phenylxanthene rings of this type are unknown; the nomenclature to be adopted for the compounds will be the same as for ordinary phenylxanthene derivatives.

It has been found by Ghosh (*J.C.S.*, 1919, **115**, 292) that curcumin, a diolefinic-β-diketone having the formula,



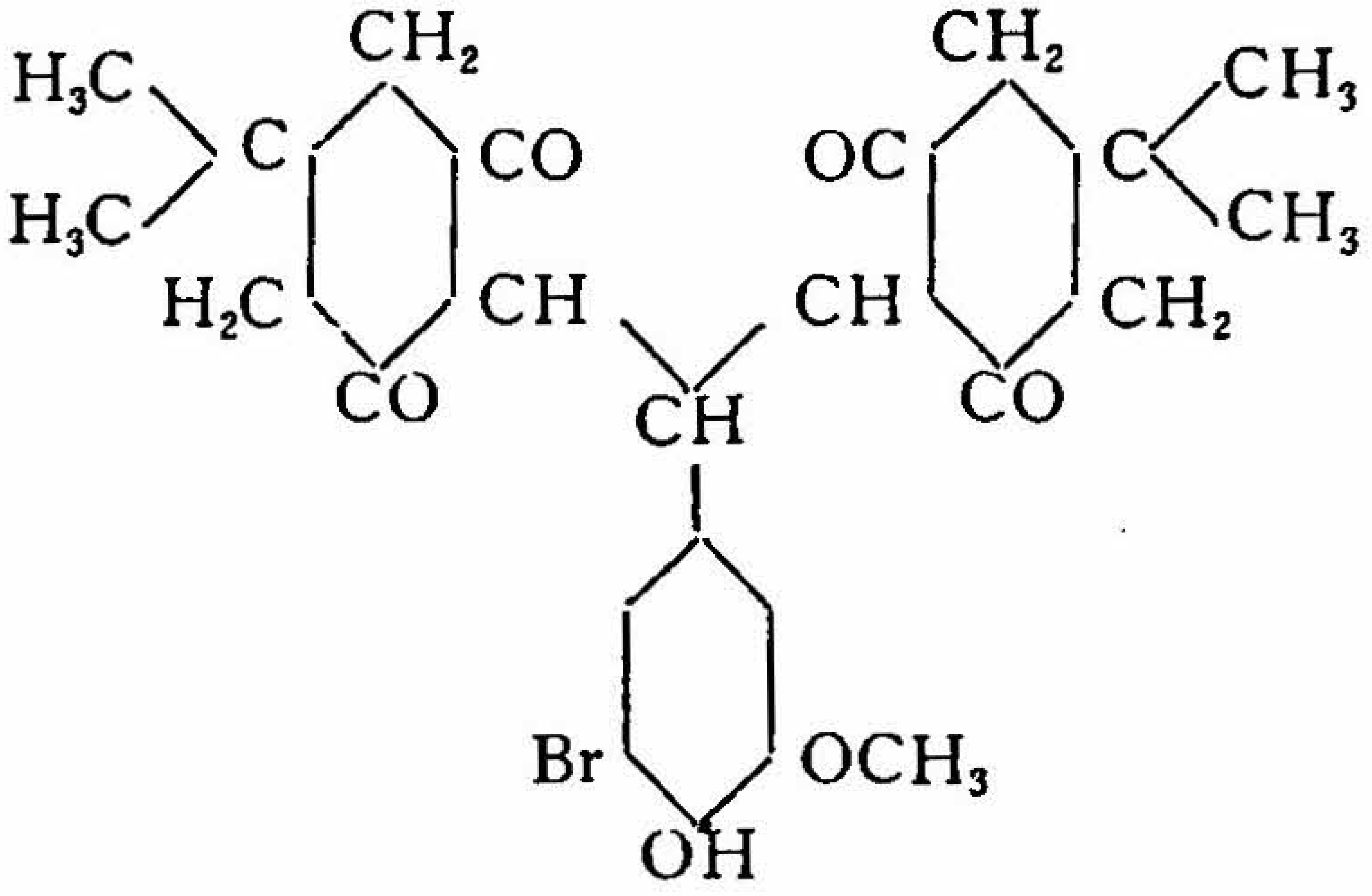
on bromination gives first a monobromo-derivative. He thinks that bromination attacks the labile hydrogen atom in preference to the double bonds. Cinnamaldimethyldihydroresorcin contains double bonds and labile hydrogen atoms. Bromination of this compound was therefore regarded as interesting; the cinnamal derivative (XV),



XV

does in fact give first a monobromo-derivative.

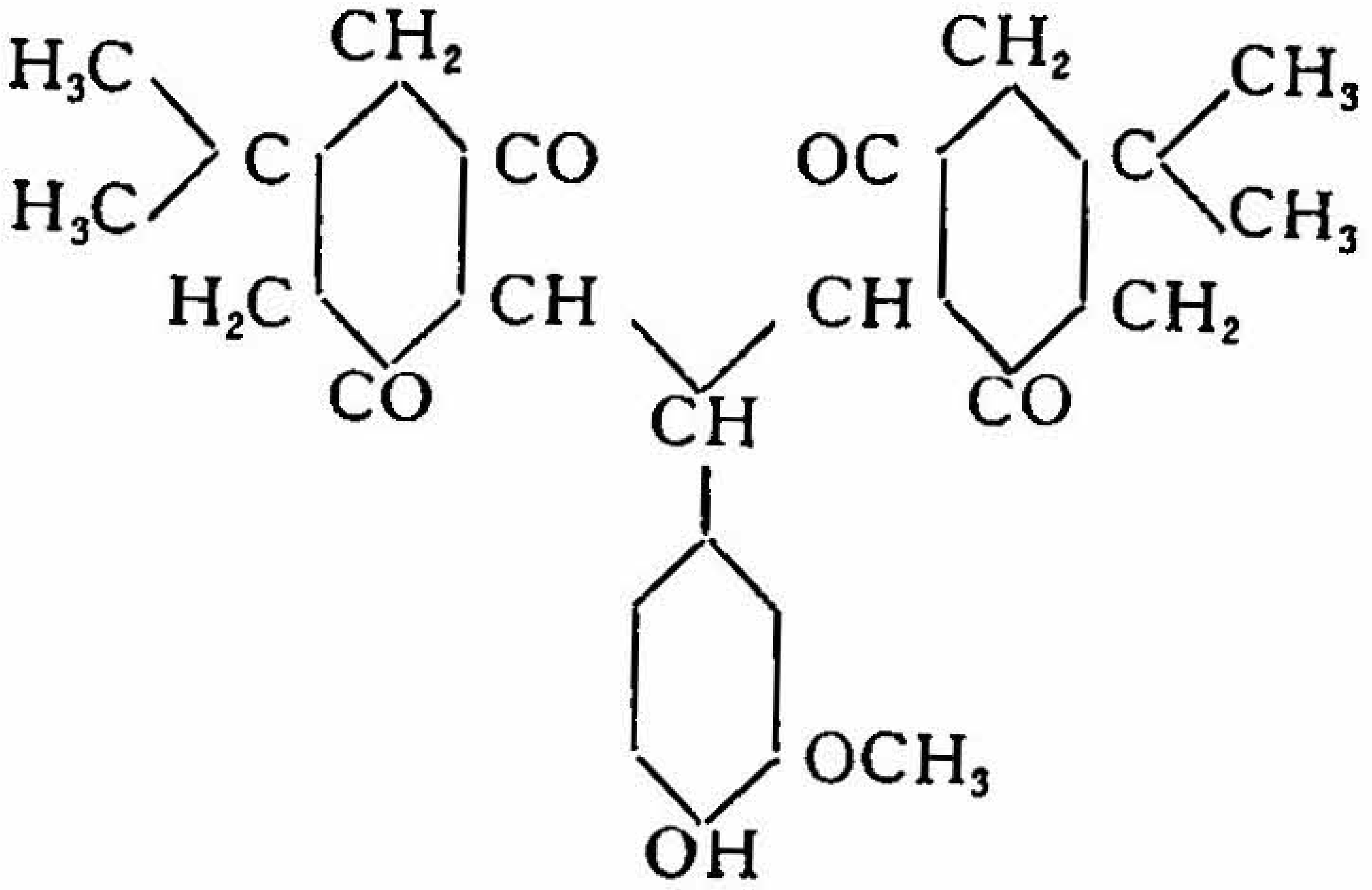
Crossley (*J.C.S.*, 1914, **105**, 165) has found that bromodimethyldihydroresorcins undergo a remarkable transformation to bromoxylenols. Some of the benzamarone type of compounds have been brominated to see whether these compounds undergo the same sort of transformation. The vanillin compound on bromination with 1½ molecules and 3 molecules of bromine gives only a monobromo-derivative whereas anisaldehyde compound with 3 molecules of bromine gives a mixture of tri- and tetrabromo-derivatives; with 1½ molecules of bromine also a mixture of two compounds both containing bromine is obtained, one of which has a very low halogen content (5·87 per cent.). Nothing can be said as to the nature of that compound. In these compounds the bromine atom can enter the benzene nucleus as well as the hydroaromatic. The monobromovanillin compound being the simplest for investigation has been studied in detail. If the bromine atom entered the benzene nucleus the monobromo-derivative must have the following constitution :—



XVI

The phenolic hydroxyl group directs the bromine atom into the ortho-position because the para-position is blocked, and this compound should be identical with the compound prepared from 5-bromovanillin and dimethyldihydroresorcin, which is the case. However it is difficult to understand why bromination with 3 molecules of bromine also produces the monobromo-derivative, the hydroaromatic ring being altogether unattacked. Tri- and tetrabromo-derivatives obtained from the anisaldehyde compound may improbably have all the bromine atoms in the benzene nucleus, or some of the bromine atoms might have attacked the hydroaromatic ring. In any case there is a progressive bromination which seems to militate against our experience with the vanillin compound. We are making experiments to elucidate this remarkable behaviour of very closely related compounds.

Further interest attached to the preparation of the above compounds is their expected physiological activity. The alkaline condensation product with vanillin possesses hydroaromatic rings containing the CO-CH$_2$-group as well as the hydroxy- and methoxy-groups in the ortho-position to one another in a benzene nucleus :—



XVII

It was therefore thought probable that it would be a good internal antiseptic, and in fact it inhibits the growth of the typhoid bacillus ; but its therapeutic value must be ascertained by clinical experiments.

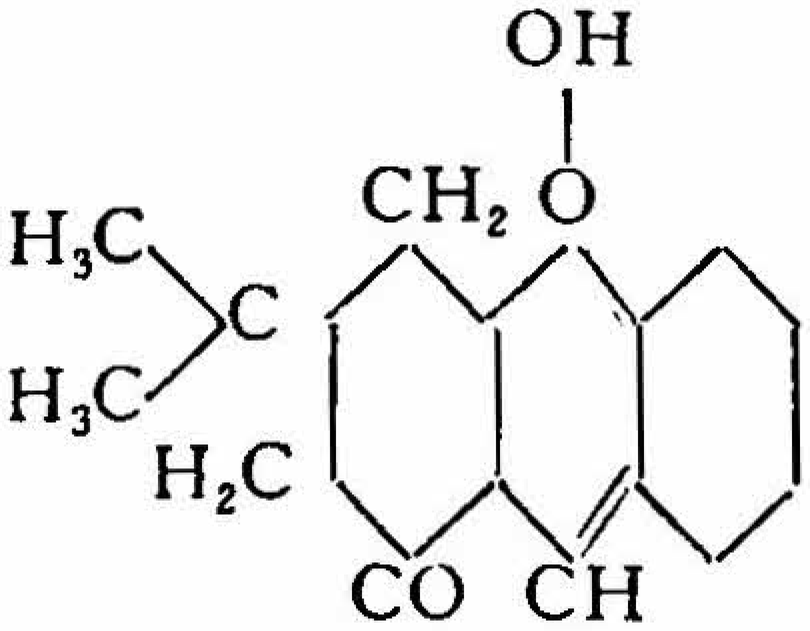
## EXPERIMENTAL.

Dimethyldihydroresorcin was prepared according to Komppa's method (*Ber.*, 1899, **32**, 1421) ; the 20 hours' heating recommended by him need not be continuous, but after pouring the condensation product of malonic ester and mesityl oxide into baryta solution, 7–8 hours' continuous heating is necessary to secure the yield obtained by Komppa.

### *Salicylaldehyde and Dimethyldihydroresorcin.*

2-*Dimethyl-4-ketotetrahydrobenzopyranolanhydrochloride* (VIII).—Dimethyldihydroresorcin (1 g.) and salicylaldehyde (0·8 g.) were dissolved in the minimum quantity of alcohol and saturated with a rapid current of dry hydrogen chloride during ice-cooling. The solution became dark red and overnight deposited scarlet needles ; these were filtered, washed with absolute alcohol and remained scarlet after drying in a vacuum desiccator. The substance does not melt below 290°, but becomes pale yellow ; it is sparingly soluble in almost all solvents and so cannot be recrystallised. In contact with air-moisture it becomes brown owing to conversion into the free base, and this rapid decomposition impairs the combustion results. The compound is stable in presence of hydrogen chloride, which is removed from it with water on heating (Found: C, 68·5; H, 6·2; Cl, 6·0-10·5. $C_{15}H_{15}O_2Cl$ requires C, 68·9; H, 5·7; Cl, 13·5 per cent.).

*Free Base,*



The anhydrochloride was warmed with a large excess of pyridine and after cooling was treated with dilute sodium acetate solution, filtered, washed with water and dried. The pale brown substance is transparent under the microscope, but has no definite geometrical form; being sparingly soluble in all the common solvents it cannot be recrystallised. It does not melt below 290°, and even when heated on the platinum foil it burns without fusion (Found: C, 72·8; H, 6·7. $C_{15}H_{16}O_3$ requires C, 73·7; H, 6·5 per cent.). This compound is also obtained by boiling the anhydrochloride for six hours with alcoholic potash; the ring is not broken.

o-*Hydroxybenzaldimethyldihydroresorcinanhydride* ( XII ).—Dimethyldihydroresorcin (7 g.) and salicylaldehyde (5·6 g.) were mixed with 30 c.c. of water, and heated on the water-bath for two hours with caustic potash (5·6 g.) dissolved in 11 c.c. of water. The orange-red solution was then cooled, poured into water, filtered and acidified with dilute hydrochloric acid. The product was oily at first, but crystallised from alcohol in milk white, rhombic prisms and melts at 206° after shrinking at 200°: the yield after one crystallisation was 6·2 grams (Found: C, 75·5; H, 6·5. $C_{23}H_{26}O_4$ requires C, 75·4; H, 7·1 per cent.). The compound dissolves in dilute caustic alkalis; the solution in chloroform and alcohol is colourless, and in glacial acetic acid orange-yellow.

*Acetyl derivative.*—One gram of the above compound, 8 c.c. of acetic anhydride and 3 drops of pyridine were heated on the sandbath for about an hour, the clear solution depositing colourless cubes on cooling; recrystallisation from alcohol gave colourless cubes melting at 188°, the yield being 0·7 gram (Found: C, 73·2; H, 6·8. $C_{25}H_{28}O_5$ requires C, 73·5; H, 6·8 per cent.).

*Benzoyl derivative.*—One gram of the substance was dissolved in pyridine with a few c.c. of 10 per cent. caustic soda; benzoyl chloride was then added producing an oil which solidified completely after a day. Crystallisation from alcohol gave colourless leaves melting at

152–53°, the yield being 0·7 gram (Found: C, 76·95; H, 7·0. $C_{30}H_{30}O_5$ requires C, 76·6; H, 6·4 per cent.).

*Bromo-derivative.*—The substance (1·2 g.) was almost completely dissolved in warm chloroform (50 c.c.), when 6 c.c. of a chloroform solution of bromine (0·5 c.c. bromine in 12 c.c. of chloroform) was added. On the first addition of 2 c.c. the whole of the substance went into solution, and fifteen minutes after all had been added the chloroform was evaporated by blowing air. The emulsion was dissolved in rectified spirit and poured into water, when the oil soon became semi-solid. Crystallisation from absolute alcohol gave colourless, clear-cut needles, melting and decomposing at 194° (Found: Br, 15·83. $C_{23}H_{25}O_4Br, C_2H_6O$ requires Br, 16·35 per cent.).

*Nitroso-derivative.*—The substance (0·4 g.) dissolved in boiling glacial acetic acid was gradually treated with potassium nitrite (0·4 g.); when all had dissolved the solution was cooled and on dilution with water yellow leafy crystals separated melting at 100–3°. It is soluble in acetic acid, alcohol, benzene and acetone, and dissolves in dilute caustic alkali with yellow colour, alcoholic ferric chloride producing an orange-red coloration (Found: N, 4·8. $C_{23}H_{24}O_6N_2$, $6H_2O$ requires N, 5·26 per cent.).

*Phenylhydrazone.*—The substance (1·2 g.) was dissolved in hot acetic acid and treated with phenylhydrazine (1·2 g.) dissolved in acetic acid. After warming for a few minutes water was added, the solid crystallising from absolute alcohol in colourless needles melting at 237–41°.

### *Resorcylaldehyde and Dimethyldihydroresorcin.*

2:4-*Dihydroxybenzaldimethyldihydroresorcinanhydride* (XIII).—Resorcylaldehyde (1 g.) and dimethyldihydroresorcin (1 g.) were dissolved in alcohol and treated with potash (1·5 g. dissolved in 3 c.c. of water), when the colour became deep yellow, and after boiling under reflux for about 45 minutes, brownish-red. On dilution with water the filtrate was very slightly acidified with hydrochloric acid, avoiding excess, and the solid crystallised from dilute alcohol; on recrystallisation it melted at 225–6° with gas evolution, the yield being 0·3 gram of colourless prismatic needles. It dissolves in alkali with slight yellow green fluorescence (Found: C, 72·3; H, 6·4. $C_{23}H_{26}O_5$ requires C, 72·2; H, 6·8 per cent.).

### p-*Hydroxybenzaldehyde and Dimethyldihydroresorcin.*

4-*Hydroxybenzaldimethyldihydroresorcin* ( XI ).—*p*-Hydroxybenzaldehyde (1 g.) and dimethyldihydroresorcin (1 g.) were dissolved in alcohol and heated on the water bath under reflux for half-an-hour with potash (0·8 g.) dissolved in water (1·5 c.c.). After pouring into water and filtration, the filtrate was acidified with dilute hydrochloric acid, the emulsion so produced being again dissolved in alkali and precipitated with dilute hydrochloric acid. Crystallisation from dilute alcohol gave colourless octagons melting at 184° to a yellow liquid (yield, 1·2 g.). It dissolves readily in caustic alkalis with yellow-red fluorescence (Found: C, 71·7; H, 6·6. $C_{23}H_{28}O_5$ requires C, 71·8; H, 7·2 per cent.).

2 : 7-*Tetramethyl*-4 : 5-*diketo*-p-*acetoxyphenyloctahydroxanthene*.—The above compound (0·5 g.) with acetic anhydride (4 c.c.) and 3 drops of pyridine was gently boiled on the sand-bath for 45 minutes. The crystals formed on cooling separated from spirit in long colourless silky needles melting at 208–9°; the yield was 0·25 g. (Found: C, 73·4; H, 6·3. $C_{25}H_{28}O_5$ requires C, 73·5; H, 6·8 per cent.).

### *Protocatechuic aldehyde and Dimethyldihydroresorcin.*

3 : 4-*Dihydroxybenzaldimethyldihydroresorcin*.—Equimolecular quantities of protocatechuic aldehyde and dimethyldihydroresorcin were dissolved in alcohol, poured into excess of concentrated aqueous potash, and gently boiled on the water-bath under reflux for an hour. The red colour darkened, and the solution was then diluted with water and filtered. Alternate acidification, dissolution in alkali and reprecipitation with dilute hydrochloric acid gave a black tarry mass, from which spirit extracted colourless prisms melting at 145° with decomposition. It dissolves in dilute caustic soda solution with orange-pink fluorescence (Found: C, 66·1; H, 7·2. $C_{23}H_{28}O_6,H_2O$ requires C, 66·02; H, 7·17 per cent.).

### *Piperonal and Dimethyldihydroresorcin.*

3 : 4-*Methylenedioxybenzaldimethyldihydroresorcin*.—Dimethyldihydroresorcin (1·4 g.) and piperonal (1·5 g.) were dissolved in the minimum of alcohol, and with potash (1 g.) in water (2 c.c.) boiled on the water-bath under reflux for half-an-hour; poured into water and filtered, the filtrate was acidified with dilute hydrochloric acid, the resulting oil becoming partly solid after several days. The white solid on crystallisation from alcohol melted at 131–34°. The semi-solid portion was repeatedly dissolved in glacial acetic acid and precipitated with water, but even then did not solidify completely. It was left for several days, rubbed with water in a mortar, and the collected solid dried and freed from gummy matter by alcohol. Crystallisation from rectified spirit gave large, colourless needles melting at 136–37° (Found: C, 69·06; H, 7·0. $C_{24}H_{28}O_6$ requires C, 69·9; H, 6·7 per cent.).

*Benzaldehyde* and *Dimethyldihydroresorcin.*—Benzaldehyde (3 g.) and dimethyldihydroresorcin (4 g.) were heated with absolute alcohol on the water-bath for 3 hours when most of the alcohol was distilled and the residue diluted with water, the precipitated solid being fractionally crystallised from alcohol. The first fraction on recrystallisation from the same medium melted at 193° and was found to be 2 : 7-*tetramethyl*-4 : 5-*diketophenyloctahydroxanthene* (Found: C, 78·6; H, 7·19. $C_{23}H_{26}O_3$ requires C, 78·8; H, 7·4 per cent.). The last fraction on crystallisation from alcohol melted at 175–76° and proved to be *benzaldimethyldihydroresorcin* (Found: C, 75·13; H, 7·8. $C_{23}H_{28}O_4$ requires C, 75·0; H, 7·6 per cent.).

### *Anisaldehyde and Dimethyldihydroresorcin.*

4-*Methoxybenzaldimethyldihydroresorcin.*-Dimethyldihydroresorcin (5 g.) and anisaldehyde (5 g.) in alcohol were heated under reflux on the water-bath for half-an-hour with potash (2 g.) in water (4 c.c.). The orange solution was diluted with water, filtered and acidified with dilute hydrochloric acid; the oil crystallised overnight and was recrystallised from spirit, forming colourless, lustrous cubes melting at 139–40°, the yield being 5·6 grams (Found: C, 71·75; H, 7·3; $OCH_3$, 7·17. $C_{24}H_{30}O_5$ requires C, 72·3; H, 7·5; $OCH_3$, 7·7 per cent.).

2 : 7-*Tetramethyl*-4 : 5-*diketo*-p-*methoxyphenyloctahydroxanthene* (XIV).—The above compound (0·5 g.) with acetic anhydride (4 c.c.) and 3 drops of pyridine was heated on the sand-bath for 45 minutes, and the colourless crystals obtained on cooling recrystallised from a large volume of alcohol giving lustrous crystals melting at 243–46°, the yield being 0·3 gram (Found: C, 74·9; H, 7·2; $OCH_3$, 7·2. $C_{24}H_{28}O_4$ requires C, 75·7; H, 7·3; $OCH_3$, 8·1 per cent.).

### *Vanillin and Dimethyldihydroresorcin.*

4-*Hydroxy*-3-*methoxybenzaldimethyldihydroresorcin* (XVII).—Dimethyldihydroresorcin (3 g.) and vanillin (3·3 g.) dissolved in the minimum of alcohol, with potash (3 g.) in water (6 c.c.) were heated on the water-bath under reflux during half-an-hour. A solid appeared and redissolved, the solution being orange. Poured into water and filtered, the filtrate after acidification with dilute hydrochloric acid deposited colourless prisms which when recrystallised from dilute alcohol melted at 195° after softening slightly at 189°. It dissolves in alkali with deep orange-red fluorescence, and the yield was 3·2 grams (Found: C, 69·3; H, 6·7; $OCH_3$, 7·2. $C_{24}H_{30}O_6$ requires C, 69·5; H, 7·2; $OCH_3$, 7·4 per cent.).

2 : 3-*Tetramethyl*-4 : 5-*diketo*-p-*acetoxy*-m-*methoxyphenyloctahydroxanthene.*—The above compound (0·5 g.) with acetic anhydride (5 c.c.)

and 3 drops of pyridine was heated on the sand-bath during 45 minutes and poured into water, the oil soon solidifying. It crystallised from dilute alcohol in long, colourless needles melting at 148–49°, the yield being 0·4 gram (Found: C, 67·4; H, 6·2; $OCH_3$, 6·68. $C_{26}H_{30}O_6$, $H_2O$ requires C, 67·5; H, 5·87; $OCH_3$, 6·7 per cent.).

*Bromination of* p-*methoxybenzal* and p-*hydroxy*-m-*methoxybenzaldimethyldihydroresorcin.*—Bromine (1½ mol.) was dissolved in chloroform and gradually added to the chloroform solution of the *p*-methoxy-compound. There was copious evolution of hydrogen bromide, and when the bromine colour had almost disappeared the chloroform was vaporised. The residue dissolved in boiling alcohol deposited colourless prismatic needles melting at 193–198° (Found: Br, 6·8. The monobromo-derivative requires Br, 16·7 per cent.).

The product was therefore fractionally crystallised from spirit several times yielding two compounds melting at 200–3° and 232°, the latter being the less soluble. The former contains 5·5 per cent. of bromine and the compound melting at 232° also shows a low bromine content.

Using the double quantity of bromine and proceeding as before, a microcrystalline powder was obtained. It is soluble in alcohol, benzene, acetone and acetic acid, but as it is not crystallisable from any of these solvents, it was fractionally precipitated from alcoholic solution with water. The first fraction crystallised from spirit in prismatic needles melting at 207° (0·2 g.) and the second fraction, also from spirit, in needles which melted at 173°. This is the *tribromo-derivative* being more soluble in alcohol than the tetrabromo-compound (Found: Br, 34·95. $C_{24}H_{27}O_5Br_3$, $3H_2O$ requires Br, 34·83 per cent.); the compound melting at 207° being the *tetrabromo-derivative* (Found: Br, 44·94. $C_{24}H_{26}O_5Br_4$ requires Br, 44·81 per cent.).

From the *p*-hydroxy-*m*-methoxy-compound and bromine (1½ mol.) under similar conditions the solid product crystallised from dilute alcohol in colourless cubes melting at 211–13° (Found: C, 57·6; H, 5·5; Br, 15·94. $C_{24}H_{29}O_6Br$ requires C, 58·4; H, 5·8; Br, 16·22 per cent.). Using the double quantity of bromine (3 mols.) the same compound melting at 211–13° was obtained, and is identical with 5-bromo-4-hydroxy-3-methoxybenzaldimethyldihydroresorcin.

5-*Bromo*-4-*hydroxy*-3-*methoxybenzaldimethyldihydroresorcin* (XVI). 5-Bromovanillin (2 g.) and dimethyldihydroresorcin (1·5 g.) dissolved in alcohol with potash (1·5 g.) in water (3 c.c.) were heated on the water-bath under reflux during half-an-hour, poured into water and filtered. The rose-pink filtrate was acidified with dilute hydrochloric acid and the turbid liquid was decanted from a crystalline substance which on recrystallisation from alcohol was found to be 5-bromovanillin. The turbid liquid deposited a semi-solid mass after two days, and thrice crystallised from dilute alcohol melted at 210–13°. It is found by the mixed melting point to be identical with the foregoing compound from *p*-hydroxy-*m*-methoxybenzaldimethyldihydroresorcin.

### p-*Nitrobenzaldehyde and Dimethyldihydroresorcin.*

4-*Nitrobenzaldimethyldihydroresorcin.*—*p*-Nitrobenzaldehyde (1 g.) and dimethyldihydroresorcin (1 g.) in alcohol with potash (0·4 g.) in water (1 c.c.) were heated under reflux during half-an-hour on the water-bath. The preliminary orange-red colour changed to deep-red on heating. The solution was poured into water and filtered, acidified with dilute hydrochloric acid and the crystalline precipitate recrystallised from spirit, forming beautiful, colourless needles melting at 188–90°, the yield being 1·4 grams (Found: N, 3·31. $C_{23}H_{27}O_6N$ requires N, 3·36 per cent.).

2 : 7-*Tetramethyl*-4 : 5-*diketo*-p-*nitrophenyloctahydroxanthene.*—The above compound (2 g.) in concentrated sulphuric acid was heated on the water-bath during 45 minutes, then poured into a large volume of water and the precipitated solid crystallised from alcohol; recrystallisation gave needles melting at 222°, the yield being 1·2 grams (Found: N, 3·67. $C_{23}H_{25}O_5N$ requires N, 3·5 per cent.).

### m-*Nitrobenzaldehyde and Dimethyldihydroresorcin.*

3-*Nitrobenzaldimethyldihydroresorcin.*—*m*-Nitrobenzaldehyde (1 g.) and dimethyldihydroresorcin (1 g.) treated as above deposited a solid which was recrystallised from spirit in prismatic needles melting at 186–88°, the yield being 1·2 grams (Found: N, 3·8. $C_{23}H_{27}O_6N$ requires N, 3·36 per cent.).

### *Cinnamic aldehyde and Dimethyldihydroresorcin.*

*Cinnamaldimethyldihydroresorcin* (XV).—Cinnamic aldehyde (2 g.) and dimethyldihydroresorcin (2 g.) in alcohol with potash (0·8 g.) in water (1·6 c.c.) were heated on the water-bath during half-an-hour. After dilution with water the filtrate was acidified with dilute hydrochloric acid, and the viscous product, after solidification, was crystallised from dilute alcohol. It formed lustrous needles melting at 202°, unchanged on recrystallisation, the yield being 1·3 grams (Found: C, 76·4; H, 7·07. $C_{25}H_{30}O_4$ requires C, 76·1; H, 7·61 per cent.). The *bromo-derivative* was recrystallised from alcohol, forming colourless needles melting at 180–81° with decomposition (Found: Br, 19·1. $C_{25}H_{29}O_3Br$ requires Br, 17·89 per cent.).

*Action of acetic anhydride.*—The substance with acetic anhydride and a few drops of pyridine was heated on the sand-bath during 45 minutes, poured into water, and the solidified oil crystallised from dilute alcohol until the melting point reached 147–48°; the yield was very poor.

*Condensation with piperonal using hydrogen chloride.*—Dimethyldihydroresorcin (1·4 g.) and piperonal (1·5 g.) were dissolved in the minimum of alcohol, and submitted to a current of dry hydrogen chloride under ice-cooling to saturation. After two days the violet solution was poured into water when an oil separated which solidified after three days; powdered in a mortar under water, the dried substance was partially dissolved in boiling alcohol and filtered. Crystals remaining on the filter paper recrystallised from alcohol in prismatic needles, and finally melted at 214°, being 2: 7-*tetramethyl*-4: 5-*diketo*-3′; 4′-*methylenedioxyphenyloctahydroxanthene* (Found: C, 72·83; H, 6·9. $C_{24}H_{26}O_5$ requires C, 73·1; H, 6·6 per cent.).

*Condensation with* m-*nitrobenzaldehyde.*—*m*-Nitrobenzaldehyde and dimethyldihydroresorcin treated in the same way gave 2: 7-*tetramethyl*-4 : 5-*diketo*-m-*nitrophenyloctahydroxanthene*, which crystallised from spirit in colourless cubes melting at 169°, the yield being 40 per cent. (Found: N, 3·7. $C_{23}H_{25}O_5N$ requires N, 3·5 per cent.).[1]

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[1] A preliminary report of this paper appeared in the Indian Science Congress Abstracts, 1929, p. 22.

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