79. *Studies in Chelation. Part IV. Some Properties of 2 : 3-Dihydroxyphenyl Ketones.*

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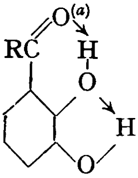
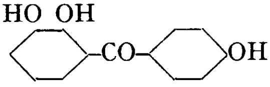
The properties of 2 : 3-dihydroxyphenyl ketones are of interest from the standpoint of chelation and because this type of grouping occurs in the dyes of the 2 : 3 : 4-trihydroxyphenyl ketone (Alizarin Yellow) class.

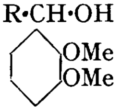
It was suggested in Part I (Baker, J., 1934, 1684) that the volatility and solubility of 2 : 3-dihydroxybenzaldehyde indicated a greater degree of chelation than the normal for a dihydroxybenzaldehyde, and, partly by analogy with 3-nitrocatechol, the structure (I; R = H) was proposed for the compound, in which the co-ordinate link (*a*) enhanced the usual feeble chelation between the two hydroxyl groups. The melting points of the dry and the wet substance are 106° and 84°, a difference of 22°.



(I.)



(II.)



(III.)

The same somewhat abnormal chelation for a catechol derivative appears to exist also in 2 : 3-dihydroxyacetophenone (I; R = CH_3), which has the same boiling point (245°) as catechol in spite of the increase in molecular weight. The low boiling point is significant when it is recalled that the introduction of the CO·CH_3 group into the *o*-position of phenol *raises* the boiling point from 182° to 203°. Again, the difference between the melting points of wet and dry 2 : 3-dihydroxyacetophenone is much less than that for other dihydroxyacetophenones, as shown below, in spite of the fact that it has the lowest melting point.

	M. p. (dry).	M. p. (wet).	Difference.
2 : 3-Dihydroxyacetophenone	98°	71°	27°
2 : 4- „	142	78	64
2 : 5- „	202	160	42
2 : 6- „	157	108	49

Alone among the dihydroxyacetophenones the 2 : 3-compound has a powerful odour, resembling that of *o*-hydroxyacetophenone, and is easily soluble in organic solvents.

The relatively high degree of chelation of 2 : 3-dihydroxyacetophenone appears to be connected with the fact that it is a mordant dye. On cotton mordanted with alumina it gives a light yellow dyeing, which, however, is appreciably weaker than that given by 2 : 3 : 4-trihydroxyacetophenone (Alizarin Yellow C). This behaviour appears to be unique among the dihydroxyacetophenones; none of the isomerides mentioned above give noticeable dyeings on an alumina-mordanted material. [The highly chelated 2 : 4-diacetylresorcinol possesses marked mordant-dyeing properties, but the feebly chelated, isomeric 4 : 6-diacetylresorcinol is without this power (Baker, *loc. cit.*).] Similarly, 2 : 3-*dihydroxybenzophenone* (I; R = Ph) and 2 : 3 : 4′-*trihydroxybenzophenone* (II) give strong yellow dyeings with an alumina mordant, which are but little weaker than that given by 2 : 3 : 4-trihydroxybenzophenone (Alizarin Yellow A). These facts indicate that the hydroxyl group in position 4 in the dyes of the Alizarin Yellow series plays no essential part in the dyeing.

The 2 : 3-dihydroxyphenyl ketones were prepared from *o*-veratraldehyde by treatment with a Grignard reagent to give a secondary alcohol (III), oxidation of this with chromic acid to the corresponding ketone, and demethylation with hydrobromic acid. An alternative method was the interaction of a Grignard reagent with *o*-veratronitrile, which gave directly the 2 : 3-dimethoxyphenyl ketones.

EXPERIMENTAL.

2 : 3-Dimethoxyacetophenone was prepared by oxidising 2 : 3-dimethoxyphenylmethylcarbinol (Pauly and von Buttlar, *Annalen*, 1911, **383**, 284) with chromic acid (Klages, *Ber.*, 1903, **36**, 3589; Krannichfeldt, *ibid.*, 1913, **46**, 4017), and also by the following method. 2 : 3-Dimethoxybenzonitrile (10·2 g.) (Baker and Eastwood, J., 1929, 2907), dissolved in anhydrous ether (50 c.c.), was added to a solution of methylmagnesium iodide prepared from magnesium (1·5 g.), methyl iodide (9 g.), and ether (50 c.c.). After 12 hours, the mixture was refluxed for 1 hour and decomposed with dilute acetic acid, and the ethereal layer separated, washed with sodium carbonate solution, dried, and distilled, leaving a residue (6·5 g.) of almost pure 2 : 3-dimethoxyacetophenone.

2 : 3-Dimethoxyacetophenone (6·5 g.) was refluxed for 5 hours with hydrobromic acid (*d* 1·5) and acetic acid (50 c.c. of each) (compare Krannichfeldt, *loc. cit.*), the mixture then being poured into water and extracted with ether; from the extracts, after the treatment described above, 2 : 3-dihydroxyacetophenone was obtained, which separated from dilute methyl alcohol in pale yellow plates (4 g.), m. p. 97°.

2 : 3-*Dimethoxybenzhydrol*.—To a solution of phenylmagnesium bromide (prepared from magnesium 3·6 g., bromobenzene 15·7 g., and ether 150 c.c.) was added 2 : 3-dimethoxybenzaldehyde (24·9 g.) in ether (250 c.c.), and the whole heated on the steam-bath for 1 hour. The resulting magnesium compound was decomposed with ice and dilute acetic acid, and the ethereal layer treated as described above; the solid obtained, after contact with porous earthenware, crystallised from light petroleum in compact prisms, m. p. 79° (Found: C, 74·0; H, 6·5. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·6%).

2 : 3-*Dimethoxybenzophenone*.—(A) To the preceding compound (20 g.) was added a solution of potassium dichromate (40 g.) in dilute sulphuric acid (170 c.c. of water and 35 c.c. of concentrated sulphuric acid) at 50°, and the whole vigorously stirred; the mixture boiled and slight cooling was necessary. After the initial reaction had abated, the mixture was stirred for 20

minutes, cooled, and extracted with ether. The extract was treated in the usual way, and 2 : 3-dimethoxybenzophenone obtained as a thick yellow oil, b. p. 210°/14 mm. (yield, 13·3 g.; 66%). The 2 : 4-*dinitrophenylhydrazone*, prepared from equal weights (0·5 g.) of the reactants dissolved in alcohol (6 c.c.) and concentrated sulphuric acid (1 c.c.), separated from alcohol as an orange crystalline powder, m. p. 152° (Found: N, 13·5. $C_{21}H_{18}O_6N_4$ requires N, 13·3%). (B) The Grignard reagent made from bromobenzene (2·6 c.c.), magnesium (0·6 g.), and ether (25 c.c.) was added to a solution of 2 : 3-dimethoxybenzonitrile (4·1 g.) in ether (25 c.c.). After 12 hours the product was decomposed with dilute acetic acid and shaken with a further quantity of ether, and the ethereal layer treated in the usual way.

2 : 3-*Dihydroxybenzophenone*.—2 : 3-Dimethoxybenzophenone (5 g.) was demethylated by the process described above [acetic acid, 50 c.c.; hydrobromic acid (*d* 1·5), 50 c.c.; 8 hours' refluxing]. From the washed and dried ethereal extract a solid was finally obtained, which, pressed on porous earthenware and crystallised from 20% alcohol, formed lustrous yellow plates, m. p. 65° (m. p. under water, 54°) (Found: C, 72·7; H, 4·7. $C_{13}H_{10}O_3$ requires C, 72·9; H, 4·7%). 2 : 3-*Dihydroxybenzophenone* dyes iron-mordanted cotton chocolate-brown, and with a chromium mordant a very weak greenish-yellow is produced. It forms a reddish solution in aqueous sodium hydroxide and gives a dark green ferric chloride reaction in alcoholic solution.

2 : 3 : 4′-*Trimethoxybenzhydrol*.—2 : 3-Dimethoxybenzaldehyde (16·6 g.) in ether (200 c.c.) was added to anisylmagnesium bromide prepared from *p*-bromoanisole (12·5 c.c.), ether (300 c.c.), and magnesium (5 g.), and the mixture warmed for 1 hour on the water-bath. After decomposition with dilute acetic acid, the ethereal layer was separated, shaken with sodium carbonate solution, dried, and distilled. The remaining oil was subjected to steam-distillation to remove *p*-bromoanisole, taken up in ether, and finally distilled under diminished pressure. The first fraction (b. p. 150°/15 mm.) was 2 : 3-dimethoxybenzaldehyde; the 2 : 3 : 4′-*trimethoxybenzhydrol* then distilled at 250°/17 mm. as a yellow viscous oil (Found: C, 70·0; H, 6·8. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·6%).

2 : 3 : 4′-*Trimethoxybenzophenone*.—(A) The preceding compound (12 g.) was added gradually to a vigorously stirred solution of potassium dichromate (24 g.) in water (100 c.c.) containing concentrated sulphuric acid (20 c.c.) at 50°. After being heated for 1 hour on the steam-bath, the mixture was cooled and extracted with ether. The dried extract yielded a residue, which solidified and then separated from dilute methyl alcohol in compact colourless crystals (9 g.), m. p. 86° (Found: C, 70·6; H, 6·2. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%).

2 : 3 : 4′-*Trihydroxybenzophenone* (II).—2 : 3 : 4′-Trimethoxybenzophenone was demethylated with hydrobromic acid–acetic acid in the usual way, the mixture poured into water, and the solid collected and washed. Recrystallisation from dilute methyl alcohol (charcoal) gave minute, yellow, prismatic needles, m. p. 169° (Found: C, 63·0; H, 5·0. $C_{13}H_{10}O_4,H_2O$ requires C, 62·9; H, 4·9%). The substance gave an intense brownish-green colour with ferric chloride in alcoholic solution, and a deep olive-green in dilute alcohol. With iron and chromium mordants it gave a chocolate and a greenish-yellow dyeing respectively.

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