528. *The Indirect Synthesis of* 2 : 2′-*Dihydroxy*-3 : 3′-*di*-(2-*hydroxybenzyl*)*diphenylmethane.*

By P. A. Jenkins.

2 : 2′-Dihydroxy-3 : 3′-di-(2-hydroxybenzyl)diphenylmethane has been synthesised by condensation of 3 : 5 : 5′-trichloro-2 : 2′-dihydroxydiphenylmethane with formaldehyde, followed by dehalogenation. Modification of the initial condensation caused cyclic acetal formation, subsequent reduction of the intermediate giving 8-2′-hydroxybenzylbenzo-1 : 3-dioxan.

A study [1] of the phenol–formaldehyde condensation in the preparation of " high ortho " Novolak resins required the synthesis of a number of possible intermediates as standards for comparison by paper chromatography and infrared spectroscopy. One of these was the previously unreported 2 : 2′-dihydroxy-3 : 3′-di-(2-hydroxybenzyl)diphenylmethane (I). A number of workers [2,3,4] have employed halogen-blocking of some of the reactive positions of the phenolic nucleus, in order to obtain compounds with the required substitution, the halogen being later removed. The starting material, in this case, 3 : 5 : 5′-trichloro-2 : 2′-dihydroxydiphenylmethane (II), was prepared by condensing 2 : 4-dichloro-6-hydroxymethylphenol [5] with an excess of *p*-chlorophenol under acid conditions.[6]

This compound with aqueous formaldehyde in the presence of acetic and sulphuric acid appeared to require the presence of hydrochloric acid to give good yields of 5 : 5′-dichloro-3 : 3′-di-(3 : 5-dichloro-2-hydroxybenzyl)-2 : 2′-dihydroxydiphenylmethane (III), consistently with the chloromethylation of the dihydroxydiphenylmethane described by Finn, James, and Standen.[4] In the absence of hydrochloric acid, an appreciable quantity of the cyclic acetal (IV) was also formed and if the half-molar proportion of formaldehyde was replaced by a molar quantity of trioxymethylene it formed the bulk of the product.

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[1] Fraser, Hall, Jenkins, and Raum, unpublished works.

[2] Bender, Farnham, Guyer, Apel, and Gibb, *Ind. Eng. Chem.*, 1952, **44**, 1619.

[3] Carpenter and Hunter, *J. Appl. Chem.*, 1951, **1**, 217; Davis, Hayes, and Hunter, *ibid.*, 1953, **3**, 312; Carpenter and Hunter, *ibid.*, p. 486.

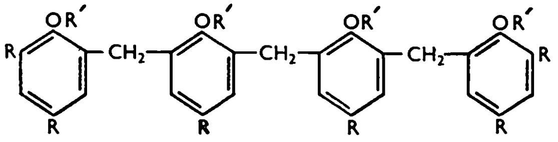
[4] Finn, James, and Standen, *ibid.*, 1954, **4**, 296, 497.

[5] G.P. 510,447.

[6] F. Addn. P. 39,585/1930; *Chem. Abs.*, 1932, **26**, 4827.

Indeed, the cyclic acetal group was formed so readily that use of the acetyl or ethoxycarbonyl derivatives (V and VI) was considered : this, however, was abandoned when the diacetyl derivative had been recovered substantially unchanged after several hours' refluxing with formaldehyde in the presence of acetic and sulphuric acid.

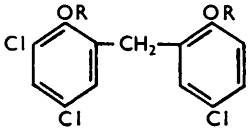
The final stage in the synthesis, the removal of chlorine from the hexachloro-derivative to give the required tetranuclear " Novolak," was easily accomplished by using Raney alloy in the presence of sodium hydroxide, the method also being successful in the reduction of the chlorinated benzylbenzodioxan.



(I) $R = R' = H$

(III) $R = Cl, R' = H$

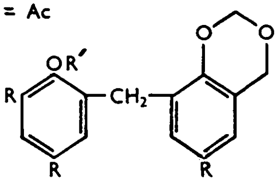
(VII) $R = H, R = Ac$



(II) $R = H$

(V) $R = Ac$

(VI) $R = CO_2Et$



(IV) $R = Cl, R' = H$

(VIII) $R = R' = H$

(IX) $R = H, R' = Ac$

The structures of the two compounds are supported by the infrared spectra, that of the four-ring compound being similar to that of 2 : 6-di-(2-hydroxybenzyl)phenol prepared by condensing 4-bromo-2 . 6-di(hydroxymethyl)phenol with an excess of *p*-bromophenol under acid conditions, followed by dehalogenation.[3] That the central methylene bridge joining the nuclei did not involve the phenolic hydroxyl groups was shown by the absence of absorption due to an ether linkage. The spectrum of 8-2′-hydroxybenzyl-1 : 3-benzodioxan did however show the presence of a cyclic ether linkage.

EXPERIMENTAL

2 : 4-Dichloro-6-hydroxymethylphenol was prepared in variable yield (26—38%) by the hydroxymethylation of 2 : 4-dichlorophenol in alkaline solution at 45° for 20 hr.

3 : 5 : 5′-*Trichloro*-2 : 2′-*dihydroxydiphenylmethane* (II).—2 : 4-Dichloro-6-hydroxymethylphenol (20 g.), *p*-chlorophenol (63 g.), and concentrated hydrochloric acid (1·5 ml.) were stirred at 60—70° for approx. 17 hr. After a further 1 hr. at 100° (bath) the mixture was cooled to room temperature and the solid removed on a sintered-glass filter. The residual solid (24 g.) had m. p. 184—185° after it had been washed with carbon tetrachloride, raised to 185—186° (lit.,[6] m. p. 187°) on recrystallisation from benzene (Found : C, 51·2; H, 3·0; Cl, 34·8. Calc. for $C_{13}H_9O_2Cl_3$: C, 51·4; H, 3·0; Cl, 35·1%).

The 2 : 2′-*diacetoxy-derivative* (V) was prepared by refluxing with acetic anhydride. After recrystallisation from methanol and then light petroleum (b. p. 60—80°), it had m. p. 107—108° (Found : C, 53·2; H, 3·6; Cl, 27·3. $C_{17}H_{13}O_4Cl_3$ requires C, 52·6; H, 3·35; Cl, 27·5%).

3 : 5 : 5′-*Trichloro*-2 : 2′-*di*(*ethoxycarbonyloxy*)*diphenylmethane* (VI).—Redistilled ethyl chloroformate (11·4 ml.) in chloroform (30 ml.) was cooled to *ca.* −20° and 3 : 5 : 5′-trichloro-2 : 2′-dihydroxydiphenylmethane (9·1 g.) in pyridine (10 ml.) and chloroform (30 ml.) was added fairly rapidly to give a yellow solution. The cooling bath was then removed, and after a further quantity of pyridine (5 ml.) had been added, the temperature of the solution was allowed to reach that of the room, a red colour gradually developing. Next morning the solution was refluxed for an hour, then cooled, and the chloroform washed several times with water to remove pyridine hydrochloride. The chloroform solution was dried (Na_2SO_4) and evaporated to an oil (12·8 g.) which with light petroleum (b. p. 40—60°) gave the *ester* (12·2 g.), m. p. 92·5°.

Recrystallisation from methanol raised the m. p. to 95—97°, unchanged on further recrystallisation from light petroleum (b. p. 100—120°) (Found : C, 51·3; H, 3·8; Cl, 23·5. $C_{19}H_{17}O_6Cl_3$ requires C, 50·9; H, 3·8; Cl, 23·8%).

5 : 5′-*Dichloro*-3 : 3′-*di*-(3 : 5-*dichloro*-2-*hydroxybenzyl*)-2 : 2′-*dihydroxydiphenylmethane* (III).—3 : 5 : 5′-Trichloro-2 : 2′-dihydroxydiphenylmethane (6·1 g.), acetic acid (15 ml.), concentrated hydrochloric acid (3 ml.) 40% aqueous formaldehyde (0·91 ml., 0·55 mol.), and concentrated sulphuric acid (0·3 ml.), were heated under reflux for 4 hr., an appreciable quantity of pink material separating. After cooling to room temperature, this solid (4·5 g.), m. p. 222° (decomp.), was filtered off, washed with a mixture of acetic acid (5 vol.) and water (1 vol.), and dried. The filtrate and washings were combined and refluxed for a further 5 hr., further solid (0·9 g.), m. p. 210° (decomp.), separating on cooling. Addition of water to the mother-liquor from this second crop produced some unchanged starting material. Recrystallisation from toluene (charcoal) gave the required 5 : 5′-*dichloro*-3 : 3′-*di*-(3 : 5-*dichloro*-2-*hydroxybenzyl*)-2 : 2′-*dihydroxydiphenylmethane*, m. p. 230° (decomp.) [Found : C, 51·9; H, 3·2; Cl, 34·0%; *M* (in acetone), 639, 620. $C_{27}H_{18}O_4Cl_6$ requires C, 52·3; H, 2·9; Cl, 34·4%; *M*, 619].

2 : 2′-*Dihydroxy*-3 : 3′-*di*-(2-*hydroxybenzyl*)*diphenylmethane* (I).—The above hexachloro-compound (4 g.) in 5% aqueous sodium hydroxide (82 ml.) was stirred on a steam-bath and 50/50 Raney alloy (13 g.) added portionwise. After a further 2 hours' heating, nickel was filtered off and the solution poured into concentrated hydrochloric acid. Solid which separated was filtered off, boiled with acidulated water, and dried. Crystallisation from carbon tetrachloride (charcoal) gave the *product* (2·2 g.), m. p. 152—154°, raised to 159—160° on further recrystallisation from benzene. After drying for 2 hr. at 100° over phosphoric oxide at 0·1 mm. the m. p. was 161—162° (Found : C, 79·0; H, 6·15; Cl, 0. $C_{27}H_{24}O_4$ requires C, 78·6; H, 5·8%).

2 : 2′-*Diacetoxy*-3 : 3′-*di*-(2-*acetoxybenzyl*)*diphenylmethane* (VII).—The above halogen-free compound (1 g.) was refluxed with acetic anhydride (15 ml.) and concentrated sulphuric acid (2 drops) for 3 hr. Acetic anhydride was then removed under reduced pressure and the residue treated with aqueous methanol, then methanol. The insoluble material (1·03 g.), m. p. 110—112°, was recrystallised from ethanol (charcoal) and again from methanol to give a final m. p. of 126°. For analysis the *product* was dried over phosphoric oxide at 50°/0·15 mm. for 1 hr. (Found : C, 72·1; H, 5·6. $C_{35}H_{32}O_8$ requires C, 72·4; H, 5·5%).

6-*Chloro*-8-(3 : 5-*dichloro*-2-*hydroxybenzyl*)*benzo*-1 : 3-*dioxan* (IV).—3 : 5 : 5′-Trichloro-2 : 2′-dihydroxydiphenylmethane (10·2 g.) in glacial acetic acid (40 ml.) was stirred with trioxymethylene (2 g.) at 35—40°, and concentrated sulphuric acid (0·5 ml.) added. The temperature was raised to 50—55° for 1 hr., then to 90° for 2 hr. After cooling to room temperature, the crystalline magma was filtered and the solid (9·1 g.; m. p. 135°) washed with glacial acetic acid, then water. Recrystallisation from 1 : 1 benzene–light petroleum (b. p. 60—80°) yielded the *product* (5·5 g.), m. p. 141—147°, which after two recrystallisations from trichloroethylene had an unchanging m. p. 147—148° (Found : C, 52·5; H, 3·4; Cl, 30·5. $C_{15}H_{11}O_3Cl_3$ requires C, 52·1; H, 3·2; Cl, 30·8%).

8-2′-*Hydroxybenzylbenzo*-1 : 3-*dioxan* (VIII).—6-Chloro-8-(3 : 5-dichloro-2-hydroxybenzyl)-benzo-1 : 3-dioxan (4·1 g.) was treated with 10% aqueous sodium hydroxide (80 ml.) and water (160 ml.), a trace remaining undissolved. Raney alloy (8 g.) was added portionwise during an hour, with slight warming, and, after the mixture had been stirred overnight, the nickel was filtered off. The filtrate and washings were acidified with fairly concentrated hydrochloric acid, and the resulting precipitate (2·3 g.), m. p. 85—87°, was filtered off and washed with acid, then water. Recrystallisation of this chlorine-free material from 2 : 1 light petroleum (b. p. 60—80°)–trichloroethylene (charcoal) yielded the *product* (1·38 g.), m. p. 89—90° unchanged by further recrystallisation from 1 : 1 benzene–light petroleum (b. p. 60—80°) [Found : C, 74·3; H, 6·0%; *M* (in phenol), 236, 238. $C_{15}H_{14}O_3$ requires C, 74·8; H, 5·8%; *M*, 242].

The *acetoxy-derivative* (IX), after recrystallisation in turn from ethanol and methanol, had m. p. 60—62° (Found : C, 71·6; H, 5·6. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%).

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