134. *Action of Alkali and Acid on Bishydroxydurylmethane.*

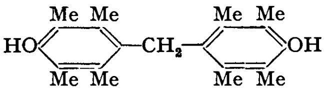
By A. Burawoy and J. T. Chamberlain.

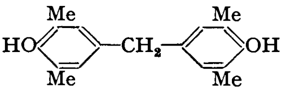
The steric repulsive interaction of the four methyl groups in the *o*-position to the methylene group in bishydroxydurylmethane (I) is responsible for a considerable weakening of the $C_{Ar}-CH_2-C_{Ar}$ linkages. In contrast to bis-4-hydroxy-3 : 5-dimethylphenylmethane (II) and bis-4-hydroxy-2 : 3 : 5-trimethylphenylmethane (III), bishydroxydurylmethane undergoes the following reactions. (i) Reduction by zinc dust and sodium hydroxide to pentamethylphenol and durenol. (ii) Hydrolysis below 100° by alkali with the formation of durenol and hydroxymethyl- (or alkoxymethyl)-durenol (VI). When heating is carried out with methanolic sodium methoxide at 220°, (VI) is subsequently reduced to pentamethylphenol. (iii) Hydrolysis below 100° by mineral acid, when the hydroxymethyl(or alkoxymethyl)-durenol formed is subsequently either recondensed to (I) or reduced to pentamethylphenol. This reduction is probably a property of the 4-hydroxy-2 : 3 : 5 : 6-tetramethylphenylmethyl ion (VIII) formed with mineral acid. It either involves disproportionation or is facilitated by a weak reducing agent added such as ethyl alcohol or formaldehyde, but not by methyl alcohol. These reactions afford convenient methods for the conversion of bishydroxydurylmethane into either durenol or pentamethylphenol and of durenol into pentamethylphenol, the original purpose of the investigation.

The exhaustive nuclear methylation of 3 : 5-dimethylphenol yields a mixture of durenol and pentamethylphenol, the amount of the latter increasing slowly with the number of dry distillations (cf. preceding paper). Our attempts to find a chemical method for the separation of these phenols or for the conversion of durenol into pentamethylphenol by an alternative route led to experiments of theoretical interest which are now reported. The original object has also been achieved.

If only pure pentamethylphenol is required, the mixture of the two phenols can be treated with formaldehyde and sodium hydroxide; durenol is then converted into bishydroxydurylmethane (I), and the unchanged pentamethylphenol can be separated by steam distillation (cf. preceding paper). It was not unreasonable to expect that the presence of four methyl groups in the *o*-position to the methylene group in bishydroxydurylmethane would be responsible for a considerable intramolecular steric hindrance of these groups (cf. below), and, as a result, an appreciable decrease of the $C_{Ar}-CH_2-C_{Ar}$ bond energies. We concentrated on the problem to convert (I) into either durenol or pentamethylphenol and investigated its reaction with zinc dust, alkali, and acid.

Action of Zinc Dust and Alkali.—Bis-4-hydroxyarylmethanes are, generally, not reduced to the corresponding phenols by heating with zinc dust and alkali. Thus, bis-4-hydroxy-3 : 5-dimethylphenylmethane (II) and bis-4-hydroxy-2 : 3 : 5-trimethylphenylmethane (III) remain unaffected. However, bishydroxydurylmethane (I) behaves like bis-2-hydroxy-1-naphthylmethane (Fries and Hübner, *Ber.*, 1906, **39**, 441; cf. also Robinson and Weygand, *J.*, 1941, 387) and is easily reduced to yield equal amounts of durenol and pentamethylphenol. The presence of four methyl groups in the *o*-position to the methylene group appears to be a necessary condition for the ease of reduction.


(I.)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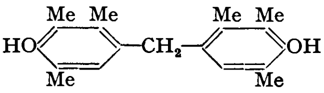
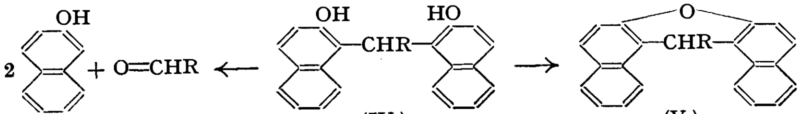

(III.)

Action of Alkali.—According to Cornforth, Cornforth, and Robinson (*J.*, 1942, 682), phenols such as 2-naphthol and resorcinol when treated with methanolic sodium methoxide at 220° are nuclear methylated, whereas others such as phenol and 1-naphthol remain unchanged. Moreover, bis-2-hydroxy-1-naphthylmethane yields 75% of 1-methyl-2-naphthol. It is reduced to 1-methyl-2-naphthol and 2-naphthol which subsequently undergoes further methylation.

We have found that bishydroxyarylmethanes such as (II) and (III) as well as bis-2-hydroxy-1-naphthylmethane remain unchanged when refluxed with strongly alkaline aqueous, methanolic, or ethanolic solutions, whereas bishydroxydurylmethane decomposes readily under these relatively mild conditions with the formation of about 50% of durenol. Hydrolysis (alcoholysis) has taken place to durenol and 4-hydroxymethyl- (or alkoxymethyl)-durenol. Again, the presence of four methyl groups in the *o*-position to the methylene group is responsible for the remarkable ease of hydrolysis (or alcoholysis).

When heated at 220° with methanolic sodium methoxide, bis-4-hydroxy-3 : 5-dimethylmethane (II) again remains unchanged, but bishydroxydurylmethane (I) yields a mixture of durenol and pentamethylphenol. Bis-4-hydroxy-2 : 3 : 5-trimethylphenylmethane (III) behaves like bis-2-hydroxy-1-naphthylmethane (*loc. cit.*) and under these more vigorous conditions also yields a mixture of 2 : 3 : 6-tri- and 2 : 3 : 4 : 6-tetra-methylphenol. These experiments indicate that the reductive fission of these bishydroxyarylmethanes is initiated by hydrolysis (or alcoholysis) followed by reduction of the hydroxymethyl (or alkoxymethyl)-phenols formed. It is probable that the nuclear methylation of 2-naphthol and resorcinol (*loc. cit.*) is also initiated by the intermediate formation at some stage of an alkoxymethylphenol (involving formaldehyde or formic acid as reactive agents). Durenol itself yields only traces of pentamethylphenol under these conditions.

Action of Mineral Acid.—Kharasch and Porsche (*J. Org. Chem.*, 1936—1937, **1**, 265) have shown that bis-2-hydroxy-1-naphthylmethanes (IV; R = H, Ph, etc.), when heated with a mixture of concentrated hydrochloric acid and glacial acetic acid (1 : 50) for a few minutes, undergo hydrolysis with the formation of 2-naphthol. When R = H and Ph, 5 and 50% respectively of 2-naphthol are obtained. Dibenzoxanthens (V) are also formed in varying amounts.


(IV.) (V.)

We have found that bishydroxyarylmethanes such as (II) and (III) remain unchanged under these conditions, whereas (I) yields 10% of steam-volatile product which consists of durenol and pentamethylphenol. The reaction is more complicated than in the case of bis-2-hydroxy-1-naphthylmethane. Reduction has taken place in addition to hydrolysis. Following up this result, heating was carried out with mixtures of concentrated hydrochloric acid and glacial acetic acid, methyl alcohol, and ethyl alcohol respectively, temperature and reaction time being also varied.

The apparently conflicting results (Table I) are accounted for as follows: Bishydroxydurylmethane (I) is first hydrolysed to yield durenol and hydroxymethyldurenol (VI). The latter [probably after preceding dehydration to the corresponding anhydro-derivative (VII) or formation of the 4-hydroxy-2 : 3 : 5 : 6-tetramethylphenylmethyl ion (VIII)] may undergo two competitive reactions : (*a*) condensation to the starting material, (*b*) reduction to pentamethylphenol. This either involves disproportionation, *i.e.*, another molecule of hydroxymethyldurenol, bishydroxydurylmethane or durenol serves as source of hydrogen, or it is facilitated by another hydrogen-supplying substance added such as ethyl alcohol or formaldehyde.

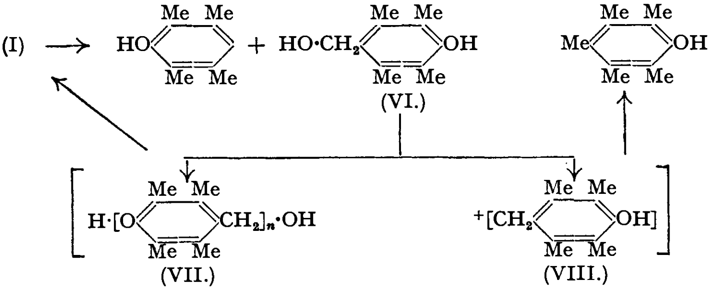
Heating with concentrated hydrochloric acid–glacial acetic acid at 96—97° yields a mixture of durenol and pentamethylphenol (i). The formation of the latter can only be explained by disproportionation which is indicated by the formation of a considerable amount of resinous

TABLE I.

Action of concentrated hydrochloric acid on bishydroxydurylmethane.

	Reagent.	Temp.	Time (hrs.).	Durenol, %.	Pentamethylphenol, %.
(i)	$CH_3{\cdot}CO_2H$–conc. HCl (1 : 1)	96—97°	6	15	24
(ii)	,,	70—80	6	25	trace
(iii)	$CH_3{\cdot}OH$–conc. HCl (1 : 1)	86—87	6	37	trace
(iv)	,,	86—87	15	83	trace
(v)	$C_2H_5{\cdot}OH$–conc. HCl (1 : 1)	93—94	6	33	42
(vi)	,,	70—80	6	25	25
(vii)	$C_2H_5{\cdot}OH$, saturated with HCl	80—85	6	40	40
(viii)	$CH_3{\cdot}OH$–conc. HCl–40% formaldehyde (2 : 2 : 1)...	82—83	6	—	52
(ix)	$C_2H_5{\cdot}OH$–conc. HCl–40% formaldehyde (2 : 2 : 1)	87—88	6	—	45
(x)	$CH_3{\cdot}CO_2H$–conc. HCl–40% formaldehyde (2 : 2 : 1)	95—96	6	—	62
(xi)	Conc. HCl–40% formaldehyde (4 : 1)	95	12	—	66
(xii)	As (ix), but durenol as starting material	87—88	6	—	70

material. At 70—80°, in addition to durenol only a trace of pentamethylphenol and resinous material is formed since at this lower temperature disproportionation is negligible (ii).



Durenol is also obtained with concentrated hydrochloric acid–methyl alcohol at 86—87° (iii, iv). The almost complete absence of pentamethylphenol and resinous material is again due to the lower temperature of the reaction. This affords a convenient method for the conversion of bishydroxydurylmethane into durenol.

It is remarkable that in contrast to the action of concentrated hydrochloric acid–methyl alcohol, concentrated hydrochloric acid–ethyl alcohol at 93—94° yields a mixture of similar amounts of durenol and pentamethylphenol in very good yield (v). Reduction is mainly caused by ethyl alcohol as indicated by the strong odour of acetaldehyde developed during the reaction, but to a small degree also by disproportionation, a small amount of resinous material in the non-volatile residue being present. At 70—80° the same result is obtained (vi). The yield is lower, but the non-volatile residue is almost pure starting material, indicating that at this lower temperature disproportionation has not contributed to the reduction. The different behaviour of methyl alcohol and ethyl alcohol is, obviously, due to a considerable difference in their reducing power. The action of absolute ethyl alcohol saturated with hydrogen chloride is similar (vii).

The only steam-volatile product obtained with formaldehyde is pentamethylphenol, since any durenol formed during the reaction would be reconverted into the starting material. Heating with a mixture of concentrated hydrochloric acid, 40% formaldehyde, and methyl alcohol (2 : 1 : 2) yields over 50% of pentamethylphenol in addition to some starting material (viii). This establishes that formaldehyde acts as a reducing agent in this experiment since in its absence only a trace of pentamethylphenol is formed (cf. iii and iv). Methyl alcohol can be replaced by ethyl alcohol, glacial acetic acid, and water respectively in this experiment (ix, x, xi).

The above experiments suggested a convenient method for the conversion of durenol into pentamethylphenol. Thus, treatment of durenol with ethyl alcohol, concentrated hydrochloric acid, and 40% formaldehyde affords as much as 70% of pentamethylphenol (xii).

Action of Acid on Ethoxymethyldurenol.—We have postulated that the first stage in the action of acid on bishydroxydurylmethane is hydrolysis to durenol and hydroxymethyldurenol. The latter [its anhydro-derivative (VII) or ion (VIII)] is either reduced to pentamethylphenol or condensed to the starting material as discussed. This has been experimentally confirmed by an investigation of the action of acid on the easily accessible ethoxymethyldurenol (for preparation, cf. preceding paper), which should behave like the alcohol (VII) itself (cf. Table II).

TABLE II.

Action of acid on ethoxymethyldurenol.

	Reagent.	Temp.	Time (mins.).	Durenol, %.	Penta-methyl-phenol, %.	Bishydroxy-duryl-methane, %.
(i)	$CH_3 \cdot CO_2H$–conc. HCl (1 : 1)......	96—97°	10		26*	65
(ii)	,, ...	96—97	60		40*	52
(iii)	$CH_3 \cdot OH$–conc. HCl (1 : 1).........	85—86	45	13	trace	80
(iv)	,, ...	60	120		trace*	93
(v)	$C_2H_5 \cdot OH$–conc. HCl (1 : 1)	93—95	45	—	76	10
(vi)	,, ...	60	120	—	50	40
(vii)	$C_2H_5 \cdot OH$–$CH_3 \cdot CO_2H$ (1 : 1)	90—100	45	—	—	100
(viii)	H_2O–$CH_3 \cdot CO_2H$ (1 : 1)	90—100	45	—	—	100
(ix)	$CH_3 \cdot OH$–conc. HCl–40% formaldehyde (2 : 2 : 1)	82	30	—	20	60

* Includes some durenol.

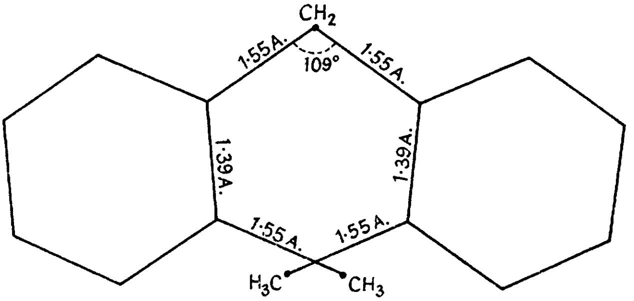
Heating with glacial acetic acid–concentrated hydrochloric acid at 96—97° for 10 minutes yields 26% of volatile phenols consisting mainly of pentamethylphenol formed by disproportionation, and a small amount of durenol formed by some hydrolysis of bishydroxydurylmethane formed in 65% yield (i). Prolonged heating increases the amount of durenol and pentamethylphenol at the expense of bishydroxydurylmethane (ii).

Methyl alcohol–concentrated hydrochloric acid at 60° yields quantitatively bishydroxydurylmethane, no reduction by methyl alcohol or disproportionation taking place (iv). At 85—86° a small amount of durenol is also obtained (iii). This is, obviously, due to the action of the acid on the bishydroxydurylmethane first formed.

In contrast, heating with ethyl alcohol–concentrated hydrochloric acid at 93—95° affords at least 76% of pentamethylphenol (v); again, the strong odour of acetaldehyde is observed during the reaction. A small amount of a resinous residue may indicate that disproportionation makes a small contribution to the reduction. At 60° the rate of reduction is considerably reduced (vi); 50% of pentamethylphenol and 40% of bishydroxydurylmethane are formed.

Again, formaldehyde acts as a reducing agent (ix). A mixture of methyl alcohol, concentrated hydrochloric acid and formaldehyde at 82—83° yields 20% of pentamethylphenol in addition to 60% of bishydroxydurylmethane.

FIG. 1.

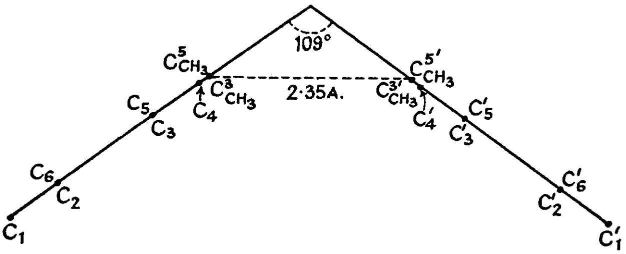


The reduction of ethoxymethyldurenol to pentamethylphenol requires the presence of a mineral acid. Boiling with 50% alcoholic or aqueous acetic acid affords quantitatively bishydroxydurylmethane (vii, viii): moreover, it is analogous to the known reduction of triphenylmethylcarbinol, benzhydrol, and similar alcohols to the corresponding methane derivatives by mineral acids and ethyl alcohol (Fosse, *Compt. rend.*, 1901, **133**, 100, 881; 1904, **139**, 601; Kauffmann *et al.*, *Ber.*, 1905, **38**, 2702; 1908, **41**, 4422; Schmidlin and Garcia-Banùs, *Ber.*, 1912, **45**, 3188). This suggests that it is a property of the 4-hydroxy-2 : 3 : 5 : 6-tetramethylphenylmethyl ion (VIII) formed with strong acids.

However, its analogy to the well-known reductive decomposition of diazo-compounds to the corresponding hydrocarbons is also noteworthy, although in the latter case the formation of aryl radicals might precede reduction to the hydrocarbons (Hey and Waters, *Chem. Reviews*, 1937, **21**, 169; cf. also *Ann. Reports*, 1937, **34**, 282; 1940, **37**, 278). Again, it is known that methyl alcohol is much less effective than ethyl alcohol (Hantzsch and Jochem, *Ber.*, 1901, **34**, 3337; Hodgson and Kershaw, *J.*, 1930, 2784), and that the alcohols can be replaced by formaldehyde (Brewster and Poje, *J. Amer. Chem. Soc.*, 1939, **61**, 2418).

Bishydroxyarylmethanes such as (II) and (III) remain unchanged when heated with hydrochloric acid under the various conditions discussed above. The ease of reduction with zinc dust and alkali and of hydrolysis with alkali or acid of bishydroxydurylmethane is, undoubtedly, due to the considerable steric repulsive interaction of the *o*-substituted methyl groups with the methylene group and the *o*-substituted methyl groups of the other benzene ring respectively which will be responsible for a considerable weakening of the $C_{Ar}-CH_2-C_{Ar}$ linkages. Repulsion of the methyl groups and the methylene group should already be considerable. This is supported by the known conversion of hexamethylbenzene and *iso*durene into mesitylene by the action of hydriodic acid at 180—200° (Klages, *Ber.*, 1904, **37**, 1715), and is comparable to the steric repulsive interaction of the halogen atoms in *o*-dichlorobenzene, indicated by the longer C–Cl distance (1·71—1·72 A.) as compared with that in chlorobenzene (1·69 A.) (Brockway, Beach, and Pauling, *J. Amer. Chem. Soc.*, 1935, **57**, 2693, 2705; Brockway and Palmer, *ibid.*, 1937, **59**, 2181; cf. Burawoy, *Trans. Faraday Soc.*, 1944, **40**, 537).

FIG. 2.



The steric repulsion of the methyl groups substituted in the 3, 3′, 5, and 5′ positions of the two benzene rings makes a considerable additional contribution to the weakening of the $C_{Ar}-CH_2-C_{Ar}$ linkages, since the 4-methyl group in pentamethylphenol is not removed when this phenol is heated with alkali or acid under the various conditions discussed. Figs. 1 and 2 show the dimensions of the molecule in the two possible extreme positions. (i) The benzene rings are coplanar, *i.e.*, lie in the plane of the paper. This can be excluded since the 3- and 3′-methyl C atoms would occupy almost the same position. (ii) Both rings are perpendicular to the plane of the paper. The $C^{3}_{CH_3}$ . . . . $C^{3'}_{CH_3}$ and $C^{5}_{CH_3}$ . . . . $C^{5'}_{CH_3}$ distances would be about 2·35 A.; the van der Waals radius of a methyl group being about 2·0 A., their interaction would be very considerable. An intermediate position may be the most stable one since it would involve the repulsive interaction of only one methyl group with the other benzene system, but it should still be larger. The C_{CH_3} . . . . benzene-plane distance would be about 2·0 A., whereas the half-thickness of the benzene ring alone is about 1·85 A.

An *X*-ray analysis of bishydroxydurylmethane should be of interest since one would also expect that, in addition to the observed weakening of the $C_{Ar}-CH_2-C_{Ar}$ linkages, their distances will be longer, the normal angle at the methylene C atom widened, and this atom probably will not lie in the plane of the benzene rings.

For a very interesting related discussion of the configuration of diphenylmethane derivatives, cf. also Megson, *Brit. Plastics*, 1948, **20**, 27.

EXPERIMENTAL.

Action of Zinc and Sodium Hydroxide on Bishydroxydurylmethane.—Bishydroxydurylmethane (1·1 g.) was boiled under reflux with 10% sodium hydroxide (150 c.c.) and zinc dust (15 g.) for 6 hours. A mixture of durenol and pentamethylphenol (0·7 g.) was separated from unchanged starting material by steam distillation. After treatment with formaldehyde and sodium hydroxide, bishydroxydurylmethane (0·3 g.) and pentamethylphenol (0·3 g.) were separated by steam distillation. Extent of reduction, 64% of theory.

Action of Zinc and Sodium Hydroxide on Bis-4-hydroxy-3 : 5-dimethyl- and -2 : 3 : 5-trimethyl-phenylmethane.—The phenol (2 g.) was refluxed with zinc dust (15 g.) and 10% sodium hydroxide (150 c.c.) for 6 hours. The starting material was recovered quantitatively from the reaction mixture by extraction with ether.

Action of Alkali on Bishydroxydurylmethane.—(i) Bishydroxydurylmethane (2 g.) was heated under reflux for 10 hours with sodium (5 g.) dissolved in methyl alcohol or ethyl alcohol (100 c.c.). Steam distillation of the acidified mixture yielded durenol free from any pentamethylphenol (1·0 g.). The residue was almost pure starting material. A similar result was obtained when heating was carried out with a mixture of ethyl alcohol (40 c.c.) and 10% sodium hydroxide (40 c.c.). (ii) Bishydroxydurylmethane (2 g.) was heated for 7 hours with sodium (1 g.) dissolved in methyl alcohol (16 c.c.) in a Carius tube at 220°. Steam-distilled material consisting of durenol and pentamethylphenol (1·6 g.) yielded after treatment with formaldehyde and sodium hydroxide bishydroxydurylmethane (0·6 g.) and pentamethylphenol (0·9 g.).

Action of Alkali on Bis-4-hydroxy-3 : 5-dimethylphenylmethane.—(i) The phenol (2 g.) and sodium (5 g.) dissolved in ethyl alcohol (100 c.c.) were refluxed for 10 hours. Steam distillation yielded no volatile product, starting material being recovered unchanged. (ii) The phenol (2 g.) and sodium (1 g.) dissolved in methyl alcohol (16 c.c.) were heated for 10 hours in a Carius tube at 220°. Starting material was recovered unchanged.

Action of Alkali on Bis-4-hydroxy-2 : 3 : 5-trimethylphenylmethane.—(i) The phenol (2 g.) and sodium (5 g.) dissolved in ethyl alcohol (100 c.c.) were refluxed for 10 hours. The starting material was recovered unchanged. (ii) The phenol (0·5 g.) and sodium (0·3 g.) dissolved in methyl alcohol (6 c.c.) were heated for 10 hours at 220°. Steam-volatile material (0·4 g.) consisted of equal amounts of 2 : 3 : 6-trimethylphenol and 2 : 3 : 4 : 6-tetramethylphenol which were separated by treatment with formaldehyde and sodium hydroxide.

Action of Alkali on Bis-2-hydroxy-1-naphthylmethane.—(i) The phenol (2 g.) was refluxed with sodium (5 g.) dissolved in ethyl alcohol (100 c.c.) for 10 hours. The starting material was recovered unchanged. (ii) The phenol (2 g.) was heated with sodium (1 g.) dissolved in methyl alcohol (16 c.c.) for 10 hours at 220°. After dilution with water and acidification, a solid mixture (1·6 g.) was collected which consisted mainly of 1-methyl-2-naphthol (cf. Cornforth, Cornforth, and Robinson, *loc. cit.*).

Action of Sodium Methoxide on Durenol.—Durenol (2 g.) was treated with sodium (1 g.) dissolved in methyl alcohol (16 c.c.) for 10 hours at 220°. Steam-volatile material (1·6 g., m. p. 115—116°) consisted of durenol contaminated with traces of pentamethylphenol (0·05 g.).

Action of Hydrochloric Acid on Bishydroxydurylmethane in Various Solvents.—(i) Bishydroxydurylmethane (2 g.) in glacial acetic acid (50 c.c.) and concentrated hydrochloric acid (2·5 c.c.) was boiled for 3 minutes and then steam distilled. Conditions were similar to those used for bis-2-hydroxy-1-naphthylmethane by Kharasch and Porsche (*loc. cit.*). The volatile material (0·2 g.) was shown by treatment with formaldehyde and alkali and separation as above to be a mixture of durenol and pentamethylphenol. The residue was impure starting material. (ii) Bishydroxydurylmethane (2 g.) was heated for 6 hours at 96—97° (in a boiling water-bath) with glacial acetic acid (40 c.c.) and concentrated hydrochloric acid (40 c.c.). Steam distillation yielded a phenolic mixture (0·8 g., m. p. 103—107°), from which after treatment with formaldehyde and alkali, pentamethylphenol (0·5 g.) and bishydroxydurylmethane (0·3 g.) were obtained. The residue was resinous (1·1 g.). (iii) The experiment was repeated, but the temperature was kept at 70—80°. Volatile material (0·5 g., m. p. 110—112°) was mainly durenol. The residue was almost pure starting material (1·4 g., m. p. 203—209°). (iv) Bishydroxydurylmethane (2 g.) was heated for 6 hours at 86—87° with methyl alcohol (40 c.c.) and concentrated hydrochloric acid (40 c.c.). Steam distillation yielded durenol (0·7 g., m. p. 114—116°) which was contaminated with a minute amount of pentamethylphenol. The residue was almost pure starting material. (v) Bishydroxydurylmethane (2 g.) was heated with methyl alcohol (40 c.c.) and concentrated hydrochloric acid (40 c.c.) for 6 hours as above. After further addition of methyl alcohol (40 c.c.) and concentrated hydrochloric acid (40 c.c.), heating was continued for another 9 hours. Steam distillation yielded almost pure durenol (1·6 g., m. p. 114—117°), contaminated by a trace of pentamethylphenol. There was a small resinous residue. (vi) Bishydroxydurylmethane (2 g.) was heated for 6 hours at 93—94° (in a boiling water-bath) with ethyl alcohol (40 c.c.) and concentrated hydrochloric acid (40 c.c.). The volatile phenolic mixture (1·5 g., m. p. 103—105°) afforded, after treatment with formaldehyde and sodium hydroxide, pentamethylphenol (0·8 g.) and bishydroxydurylmethane (0·6 g.). The residue was resinous (0·4 g.). (vii) The experiment was repeated at 70—80°. The volatile phenolic mixture (1 g., m. p. 102—105°) consisted of almost equal amounts of durenol and pentamethylphenol. The residue was mainly starting material (0·8 g.). (viii) Bishydroxydurylmethane (2 g.) and ethyl alcohol (100 c.c.) which was kept saturated with hydrogen chloride were refluxed for 6 hours. The phenolic mixture (1·6 g.; m. p. 100—103°), after treatment with formaldehyde and alkali, yielded bishydroxydurylmethane (0·8 g.) and pentamethylphenol (0·8 g.). The residue was tarry.

Action of Formaldehyde and Hydrochloric Acid on Bishydroxydurylmethane in Various Solvents. (i) Bishydroxydurylmethane (2 g.) was heated for 6 hours at 82—83° (in a boiling water-bath) with methyl alcohol (40 c.c.), 40% formaldehyde (20 c.c.), and concentrated hydrochloric acid (40 c.c.). Steam distillation afforded pure pentamethylphenol (1·1 g.). The residue (0·9 g.) yielded more steam-volatile material on further treatment. (ii) The experiment was repeated with ethyl alcohol instead of methyl alcohol at 87—88°. The yield of pentamethylphenol was 0·9 g.; the residue was tarry (1 g.). (iii) The experiment was repeated with glacial acetic acid instead of alcohol at 95—96°. The yield of pentamethylphenol was 1·3 g.; the residue was tarry (0·6 g.). (iv) Bishydroxydurylmethane (2 g.) was heated for 12 hours at 95° with 40% formaldehyde (20 c.c.) and concentrated hydrochloric acid (80 c.c.). The yield of pentamethylphenol was 1·4 g.

Action of Formaldehyde and Mineral Acid on Durenol.—(i) Durenol (5 g.), glacial acetic acid (150 c.c.), 40% formaldehyde (25 c.c.), and 10% sulphuric acid (30 c.c.) were heated on a water-bath for 4 hours. After addition of more formaldehyde (25 c.c.), heating was continued for another 4 hours. The yield of pentamethylphenol was 3 g. (ii) Durenol (2 g.), ethyl alcohol (100 c.c.), 40% formaldehyde (50 c.c.), and concentrated hydrochloric acid (100 c.c.) were heated at 87—88° for 6 hours. The yield of pentamethylphenol was 1·5 g.

Action of Hydrochloric Acid on Pentamethylphenol and Bis-4-hydroxy-3 : 5-dimethyl- and Bis-4-hydroxy-2 : 3 : 5-trimethyl-phenylmethane.—The phenol (1 g.), concentrated hydrochloric acid (20 c.c.), and glacial acetic acid or ethyl alcohol (20 c.c.) were boiled under reflux for 10 hours. The starting material was recovered unchanged.

Action of Hydrochloric acid on Ethoxymethyldurenol.—(i) Ethoxymethyldurenol (1 g.) was heated for 45 minutes at 93—95° with ethyl alcohol (25 c.c.) and concentrated hydrochloric acid (25 c.c.). Steam distillation afforded pure pentamethylphenol (0·6 g. ; 76% of theory). The residue was resinous (0·1 g.). (ii) The experiment was repeated, but the temperature was kept at 60°, and heating continued for 2 hours. Steam distillation afforded pentamethylphenol (0·4 g., 50% of theory). The residue was bishydroxydurylmethane (0·3 g. ; 40% of theory). The odour of acetaldehyde developed during the last two experiments. (iii) The ethyl ether (1 g.) was heated for 45 minutes at 85° with methyl alcohol (25 c.c.) and concentrated hydrochloric acid (25 c.c.). Steam-volatile material consisted of durenol (0·1 g.) contaminated with traces of pentamethylphenol. The residue was bishydroxdurylmethane (0·6 g. ; 80% of theory). (iv) The experiment was repeated, but the temperature was kept at 60° for 2 hours. There was a trace of steam-volatile product. The residue was pure bishydroxydurylmethane (0·7 g. ; 93% of theory). (v) The ethyl ether (1 g.) was heated for 10 minutes at 96—97° with glacial acetic acid (25 c.c.) and concentrated hydrochloric acid (25 c.c.). Steam distillation afforded pentamethylphenol contaminated with some durenol (0·2 g., m. p. 113—118°; 26% of theory). The residue was impure bishydroxydrurylmethane (0·5 g., m. p. 196—205°, 65% of theory). (vi) The experiment was repeated, but heating continued for 1 hour. The steam-volatile phenolic mixture consisted of roughly equal amounts of durenol and pentamethylphenol (0·3 g., m. p. 100—102°; 40% of theory). The residue was impure bishydroxydurylmethane (0·4 g. ; 52% of theory).

Action of Formaldehyde and Hydrochloric Acid on Ethoxymethyldurenol.—Ethoxymethyldurenol (1 g.), concentrated hydrochloric acid (60 c.c.), methyl alcohol (60 c.c.), and 40% formaldehyde (30 c.c.) were heated at 82—83° for 30 minutes. Steam distillation afforded pentamethylphenol (0·16 g. ; 20% of theory). The residue was impure bishydroxydurylmethane (0·5 g., m. p. 205—210°; 60% of theory).

Action of Hydrochloric Acid on Methoxymethyldurenol.—The methyl ether (1 g.) was heated for 45 minutes at 93—94° with ethyl alcohol (20 c.c.) and concentrated hydrochloric acid (20 c.c.). Steam distillation yielded pentamethylphenol (0·6 g. ; 71% of theory).

Action of Acetic Acid on Ethoxymethyldurenol.—The ethyl ether was boiled under reflux for 45 minutes with 50% aqueous or ethyl-alcoholic acetic acid. Bishydroxydurylmethane was obtained in quantitative yield.

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