# 268. *Oxidation by Persulphate. Part III.** *Silver-catalysed Oxidation of the Six Dimethylphenols and of 2,4,6-Trimethylphenol.*

By R. G. R. Bacon and D. J. Munro.

On treatment in aqueous solution with the reagent $S_2O_8^{2-}$–$Ag^+$, dimethylphenols readily undergo nuclear oxidative coupling and oxygenation, while the *para*-methyl group of 2,4,6-trimethylphenol undergoes hydroxylation, coupling, and removal. The following crystalline products are obtained: 2,2′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl (from 2,4-dimethylphenol); 2,5-dimethyl-*p*-benzoquinone (from 2,5-dimethylphenol); 2,6-dimethyl-*p*-benzoquinone, 4,4′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl and the corresponding diphenoquinone (from 2,6-dimethylphenol); a tetrahydrotetramethyloxodibenzofuran (from 3,4-dimethylphenol); 4,4′-dihydroxy-3,3′,5,5′-tetramethyldiphenylmethane, 4-hydroxy-3,5-dimethylbenzyl alcohol, and the corresponding aldehyde (from 2,4,6-trimethylphenol); none from 2,3- and 3,5-dimethylphenol. The resins accompanying these products appear to be formed by oxidative coupling of 2—4 phenol molecules, with incorporation of some oxygen. Comparisons are made with results reported for dimethyl- and 2,4,6-trimethyl-phenols in other oxidation reactions of a presumed radical character.

On treatment with the aqueous "redox"-type oxidant $S_2O_8^{2-}$–$Ag^+$, phenol and *o*- and *m*-cresol yielded only resins, but *p*-cresol also gave crystalline fractions (~30%), comprising *ortho*-linked dimeric and trimeric cresol and the dimeric ketone (I).[1] Oxidations of the six dimethylphenols and of 2,4,6-trimethylphenol, carried out in a similar manner, are now reported. The phenols, sodium persulphate, and silver nitrate were in homogeneous aqueous solution (0·01—0·05M in phenol), at a molecular ratio of 1 : 1 : 0·1, and consumption of persulphate was complete in about a day at 40°. Resinous products were again prominent, but in the cases of 2,6-, 2,4-, and 3,4-dimethylphenol and 2,4,6-trimethylphenol crystalline products were isolated in yields of 70%, 18%, 12%, and 35% respectively. For these four phenols, the presence of *ortho*- and *para*-methyl groups had therefore somewhat simplified the usual complex course of oxidation. Some of the identified products were due to oxidative coupling, others to oxygenation processes.

The presumed radical character of oxidations by $S_2O_8^{2-}$–$Ag^+$, attributed to the species $Ag^{2+}$, $SO_4^{\cdot -}$, or $HO\cdot$, was discussed in the preceding paper. The powerful effect of the reagent in initiating the polymerisation of acrylonitrile[2] is in harmony with this view. As is shown below, the crystalline products from the phenols proved to be largely the same as those described for oxidations in aqueous media with a ferrous salt and hydrogen peroxide,[3] or with ferricyanide[4] or ferric chloride. The initial step in all cases appears to be removal of hydrogen from the phenol by a radical or multivalent metal ion: $RH + X\cdot \longrightarrow R\cdot + HX$; $RH + M^{n+} \longrightarrow R\cdot + H^+ + M^{(n-1)+}$. Coupling reactions of the resulting aryloxy-radicals R· have been discussed elsewhere.[3,5]

Oxidations of members of this group of phenols by lead tetra-acetate,[6,7] benzoyl peroxide,[8,9,10] acetyl peroxide,[10,11] and t-butyl hydroperoxide[12] have also been described.

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* Part II, preceding paper.

[1] Bacon, Grime, and Munro, *J.*, 1954, 2275.

[2] Bacon, *Quart. Rev.*, 1955, **9**, 287.

[3] Cosgrove and Waters, *J.*, 1951, 1726.

[4] Haynes, Turner, and Waters, *J.*, 1956, 2823.

[5] Barton, Deflorin, and Edwards, *J.*, 1956, 530.

[6] Wessely and Sinwel, *Monatsh.*, 1950, **81**, 1055.

[7] Cavill, Cole, Gilham, and McHugh, *J.*, 1954, 2785.

[8] Cosgrove and Waters, *J.*, 1949, 3189.

[9] Cosgrove and Waters, *J.*, 1951, 388.

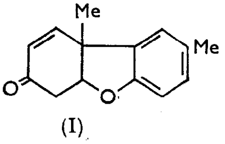
[10] Walling and Hodgdon, *J. Amer. Chem. Soc.*, 1958, **80**, 228.

[11] Wessely and Schinzel, *Monatsh.*, 1953, **84**, 425.

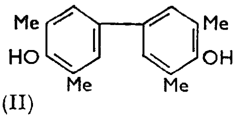
[12] Bickel and Kooyman, *J.*, 1953, 3211; cf. Campbell and Coppinger, *J. Amer. Chem. Soc.*, 1952, **74**, 1469; Cook, *J. Org. Chem.*, 1953, **18**, 261.

These oxidations are conducted in organic solvents, are generally assumed to involve radical mechanisms, and result, to some extent, in similar products to the aqueous oxidations, but they differ from the latter in yielding major amounts of 2- or 4-acyloxycyclohexadien-1-ones, incorporating acyloxy-groups from the reagents. A parallel to this in aqueous oxidations is found in Bamberger's report that permonosulphuric acid may cause incorporation of hydroxyl groups, giving 4-hydroxydien-1-ones (" quinols "), but the yields he recorded were very small, and indeed the effect described for 2,4,6-trimethylphenol[13] could not be confirmed when re-examined by Cosgrove and Waters.[9] So far as our own observations go, oxygenation effects between aromatic compounds and aqueous persulphate may take the form of phenol-formation (*e.g.*, from benzyl chloride; see Part II), quinone-formation (*e.g.*, from 2,6-dimethylphenol), and entry of oxygen into a side chain (*e.g.*, in 2,4,6-trimethylphenol and the compounds discussed in Part II); these reactions presumably involve participation of water at some stage.

With 2,6-dimethylphenol and $S_2O_8^{2-}$–$Ag^+$, the major reaction was nuclear coupling, giving a mixture (~60%) of 4,4'-dihydroxy-3,3',5,5'-tetramethylbiphenyl (II) and the corresponding 3,3',5,5'-tetramethyldiphenoquinone. The accompanying nuclear oxygenation gave 2,6-dimethyl-*p*-benzoquinone (~10%). The diphenoquinone, with or without the intermediate diphenol (II), has been reported from oxidations by $Fe^{2+}$–$H_2O_2$,[3] alkaline ferricyanide,[4] benzoyl or acetyl peroxide,[9,10] lead tetra-acetate,[7] chromic acid, and other oxidants.[14] 2,6-Dimethyl-*p*-benzoquinone is a minor product in the oxidation by $Fe^{2+}$–$H_2O_2$,[3] but is formed quantitatively with potassium nitrosodisulphonate.[15]



(I)



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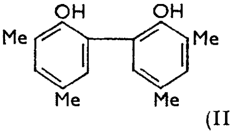

(III)

With 2,4-dimethylphenol and $S_2O_8^{2-}$–$Ag^+$, nuclear coupling was again the main identified mode of reaction, giving 2,2'-dihydroxy-3,3',5,5'-tetramethylbiphenyl (III). This is likewise produced in oxidations conducted electrolytically,[16] or with alkaline ferricyanide,[4] $Fe^{2+}$–$H_2O_2$,[3] air and ferric chloride,[17] sulphuryl chloride and zinc chloride,[18] or lead tetra-acetate.[7] About three-quarters of the alkali-soluble material obtained with $S_2O_8^{2-}$–$Ag^+$ was approximately trimeric in average composition and was oxygenated to the extent of about one atom per trimeric molecule. We did not obtain from the neutral portion of the product any of the ketonic dimer which Waters and his co-workers isolated in very low yield when using ferricyanide[4] or $Fe^{2+}$–$H_2O_2$[3] as oxidants, but we did obtain non-homogeneous, bright yellow, crystalline material (~2%); analysis of one fraction of it corresponded with the composition $C_{24}H_{24}O_4$.

With 3,4-dimethylphenol and $S_2O_8^{2-}$–$Ag^+$, 75% of the product was alkali-soluble but, apart from traces of unidentified crystals, it was resinous, approximately dimeric in average composition, and slightly oxygenated. The neutral fraction furnished in 13% yield a crystalline ketonic dimer, m. p. 157—158°, *i.e.*, a tetrahydrotetramethyloxodibenzofuran homologous with the well-known ketone obtained from *p*-cresol with $S_2O_8^{2-}$–$Ag^+$ and with several other oxidants,[1] and recently shown[5] to have the structure (I). After our experiments had been carried out, the same ketone was reported by Haynes, Turner, and Waters[4] from oxidation of 3,4-dimethylphenol with alkaline ferricyanide. As in our experiments, only one of the possible isomers was isolated. We found that the ketone

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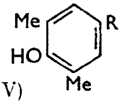
[13] Bamberger, *Ber.*, 1903, **36**, 2028.
[14] Auwers and von Markovits, *Ber.*, 1905, **38**, 226.
[15] Teuber and Rau, *Chem. Ber.*, 1953, **86**, 1036.
[16] Fichter and Meyer, *Helv. Chim. Acta*, 1925, **8**, 74.
[17] Erdtman, *Svensk Kem. Tidskr.*, 1935, **47**, 223.
[18] Bowden and Reece, *J.*, 1950, 1686.

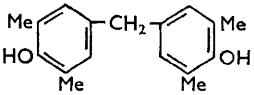
underwent change in m. p. on a column of alumina, though not on silica, gave an ultraviolet absorption spectrum almost coincident with that of the compound (I), and was converted by hydrobromic acid into a presumed dihydroxytetramethylbiphenyl.

Oxidation of 2,3-, 2,5-, and 3,5-dimethylphenol with $S_2O_8^{2-}$–$Ag^+$ gave resins, except that the product from the 2,5-isomer included 1% of 2,5-dimethyl-*p*-benzoquinone. The resins were mainly alkali-soluble and were mixtures of dimeric, trimeric, and higher dehydro-polymers, modified by a little oxygenation.

When 2,4,6-trimethylphenol (IV; R = Me) was treated with $S_2O_8^{2-}$–$Ag^+$, oxidation occurred in the *para*-methyl group, giving 4-hydroxy-3,5-dimethylbenzyl alcohol (IV; R = $CH_2$·OH) (22%) and 4,4′-dihydroxy-3,3′,5,5′-tetramethyldiphenylmethane (V) (13%). The products were identical with authentic samples prepared from 2,6-dimethylphenol and formaldehyde. The production of an alcohol, in appreciable yield, is noteworthy, since oxidation of a methyl substituent is rarely halted at the methylol stage (cf. Part II). Our observation supports Bamberger's claim [13] that traces of the alcohol are obtained when the oxidant for 2,4,6-trimethylphenol is permonosulphuric acid. There appears to be no other reported method for the conversion of (IV; R = Me) into (IV; R = $CH_2$·OH), but diacetyl peroxide [11] gives a high yield of the corresponding acetate (IV; R = $CH_2$·OAc). However, Haynes, Turner, and Waters [4] discovered a similar case of side-chain hydroxylation when they converted (IV; R = $CH_2$Ph) into (IV; R = CHPh·OH) with aqueous alkaline ferricyanide. Along with the alcohol we obtained a very small amount of the corresponding aldehyde (IV; R = CHO), which is the known product of oxidation of 2,4,6-trimethylphenol by ethyl nitrite [19] or by hydrogen peroxide and peroxidase.[20] The other main product (V) obtained with $S_2O_8^{2-}$–$Ag^+$ results from an oxidative coupling in which a *para*-methyl group is eliminated. The resulting diphenylmethane derivative had previously been reported [3] as a minor product (2%) in oxidation of 2,4,6-trimethylphenol with $Fe^{2+}$–$H_2O_2$, in which it was accompanied by an unidentified diphenol (15%). We did not isolate this diphenol from oxidation by $S_2O_8^{2-}$–$Ag^+$, nor did we observe the dibenzyl- and stilbene-type products of oxidative coupling which have been reported from reactions of 2,4,6-trimethylphenol with silver oxide,[21] benzoyl peroxide,[9] acetyl peroxide,[11] or t-butyl hydroperoxide.[12]



(IV)



(V)

## EXPERIMENTAL

The dimethylphenols were commercial samples, purified to constant m. p. The m. p.s of derived dimethylphenoxyacetic acids were essentially the same as those given in the literature. Samples of 2,4,6-trimethylphenol, synthesised from mesitylene, gave 2,4,6-trimethylphenoxyacetic acid, m. p. 152·5—153° (from benzene) (lit.,[22] 131·5°) (Found: C, 68·2; H, 7·3. Calc. for $C_{11}H_{14}O_3$: C, 68·0; H, 7·2%). The benzoate had m. p. 54·5—55·5° (from light petroleum) (lit.,[23] 61·5—62·5°) (Found: C, 80·1; H, 6·7. Calc. for $C_{16}H_{16}O_2$: C, 80·0; H, 6·7%). The derived phenylurethane had m. p. 142—143° (from light petroleum), in agreement with Auwers [24] and others (Found: C, 75·7; H, 6·7; N, 5·4. Calc. for $C_{16}H_{17}O_2N$: C, 75·3; H, 6·7; N, 5·5%). The rates of formation of the 2,6- and 2,4-dimethylphenoxyacetic acids were lower than those of the other isomers, and reaction was slower still with 2,4,6-trimethylphenol. These results are similar to those observed in the acetylation of these phenols.[25]

[19] Thiele and Eichwede, *Annalen*, 1900, **311**, 363.
[20] Booth and Saunders, *Nature*, 1950, **165**, 567.
[21] Goldschmidt and Bernard, *Ber.*, 1923, **56**, 1963.
[22] Steinkopf and Höpner, *J. prakt. Chem.*, 1926, **113**, 154.
[23] von Auwers and Mauss, *Annalen*, 1928, **464**, 293.
[24] Auwers, *Ber.*, 1899, **32**, 17.
[25] Bassett and O'Leary, *J.*, 1932, 2945.

All oxidations were carried out with thermostatic control at 40°. Aqueous solutions of the phenol, sodium persulphate, and silver nitrate, already at 40°, were mixed in the mol. ratio 1 : 1 : 0·1. To allow for differences in solubility, the concentration of the phenols in the mixed solution was varied as follows: 3,5-dimethylphenol, 0·05M; 2,6- and 3,4-dimethylphenol, 0·04M; 2,3- and 2,5-dimethylphenol, 0·033M; 2,4-dimethylphenol, 0·01M; 2,4,6-trimethylphenol, 0·008M. Some rate measurements were carried out by potentiometric titration of the acid liberated in the decomposition of the persulphate. 2,6-Dimethylphenol, 2,4,6-trimethylphenol, and 2,4-dimethylphenol showed 50% persulphate decomposition in 2, 4, and 5 hr., and substantially complete decomposition in 12, 20, and 30 hr., respectively. All oxidations were conducted for at least as long as was needed for complete consumption of persulphate. The oxidation products were mainly insoluble in water and their precipitation began almost immediately after mixing of the reagents. After isolation and drying, the precipitates were separated into neutral and alkali-soluble fractions and the filtrates were thoroughly extracted with ether.

*Oxidation of* 2,6-*Dimethylphenol.*—An aqueous solution (5 l.), containing 24·4 g. (0·2 mole) of the phenol yielded 17·6 g. of almost black precipitate (*A*), separated into an ether-insoluble fraction (*B*) (12·1 g.; ~50% yield), a semi-crystalline ether-soluble phenolic fraction (*C*) (3·2 g.), and a resinous ether-soluble neutral fraction (*D*) (2·4 g.). (*B*) contained a little free 3,3′,5,5′-tetramethyldiphenoquinone, but otherwise consisted of the quinhydrone of this compound, which crystallised from acetic acid in lustrous, dark blue-green plates, m. p. 200—210° (decomp.), varying with rate of heating (Found: C, 79·8; H, 7·1. Calc. for $C_{32}H_{34}O_4$: C, 79·7; H, 7·1%). The quinol moiety of the quinhydrone was separated with aqueous sodium hydroxide, leaving the diphenoquinone (6·3 g.), which crystallised from acetic acid in red needles, m. p. ~211° (decomp.) (Found: C, 79·9; H, 6·8. Calc. for $C_{16}H_{16}O_2$: C, 80·0; H, 6·7%). The fraction (*C*) was freed from 2,6-dimethylphenol (0·1 g.) and chromatographed on silica gel to yield 4,4′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl (II) (1·9 g., 8%). After recrystallisation from xylene and vacuum-sublimation this was obtained in pale yellow needles, m. p. and mixed m. p. 221·5—223°; the sample with which it was compared was prepared by reduction with zinc and acetic acid of the diphenoquinone made by the method of Auwers and von Markovits [14] (Found: C, 79·3; H, 7·7. Calc. for $C_{16}H_{18}O_2$: C, 79·3; H, 7·4%). The diacetate had m. p. 177·5—178° (lit.,[14] 174—175°) (Found: C, 73·2; H, 6·9. Calc. for $C_{20}H_{22}O_4$: C, 73·6; H, 6·8%). The fraction (*D*) appeared to contain lightly oxygenated polymers formed from three or more phenol units.

The deep yellow filtrate from (*A*) yielded a red semi-crystalline extract with ether. Its quinone content, determined by analysis,[26] corresponded with a 13% yield. After removal of unchanged phenol from the extract with aqueous alkali, 2,6-dimethyl-*p*-benzoquinone was obtained in yellow needles (1·3 g., 10%), m. p. 71—72°, not depressed by admixture with an authentic sample.[27] Reduction with sodium dithionite yielded 1,4-dihydroxy-2,6-dimethylbenzene, m. p. 153°.

*Oxidation of* 2,4-*Dimethylphenol.*—An aqueous solution (10 l.) containing 12·2 g. (0·1 mole) of the phenol yielded 9·5 g. of yellow precipitate. Ether-extraction of the filtrate yielded a red oil (2·2 g.), and the precipitate was separated into neutral (*A*) (2·0 g.) and alkali-soluble resin (*B*) (7·5 g.). Chromatography of (*B*) on silica gel with benzene containing increasing proportions of ether gave crystalline fractions (4·8 g.), which, when recrystallised from aqueous ethanol and then from benzene, yielded 2·1 g. (16%) of 2,2′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl (III) as needles, m. p. 136—136·5° after vacuum-sublimation (Found: C, 79·5; H, 7·5. Calc. for $C_{16}H_{18}O_2$: C, 79·3; H, 7·4%). It gave a diacetate, m. p. 110—110·5° (Found: C, 73·8; H, 6·8. Calc. for $C_{20}H_{22}O_4$: C, 73·6; H, 6·8%) (reported m. p.s vary from 134° to 138° for the phenol and from 107·5° to 109° for its diacetate). Further elution with benzene and ether gave non-crystalline material [Found for the mixture: C, 76·3; H, 6·8%; *M* (Rast method), 422. Trimers with one extra oxygen atom per mol., $C_{24}H_{26}O_4$, would require C, 76·1; H, 6·9%; *M*, 362].

Benzene solutions of (*A*) very slowly deposited yellow crystals (0·11 g., 1%). Duplicate oxidations at 20° or 40° gave rise to similar products (1—2%), isolated by chromatography on silica gel. When sublimed at 160—210°/0·05—0·001 mm., these products yielded yellow crystalline fractions of varying m. p., *e.g.*, 237—239° (Found: C, 76·4; H, 6·4%; *M*, 340) and

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[26] Willstätter and Majima, *Ber.*, 1910, **43**, 1171.

[27] Smith, Opie, Wawzonek, and Prichard, *J. Org. Chem.*, 1939, **4**, 318.

226—236° (Found: C, 78·0; H, 7·4%; *M*, 270). A typical ultraviolet absorption curve (in cyclohexane) showed maxima at 235 (log ε 4·27) and 308 mμ (log ε 3·69); reported maxima [28] for dimethyl-*p*-benzoquinones in n-hexane are ~250 (log ε 4·3), ~303 (log ε 2·5), and ~430 mμ (log ε 1·3).

*Oxidation of* 3,4-*Dimethylphenol*.—An aqueous solution (10 l.) containing 48·8 g. (0·4 mole) of the phenol yielded quantitatively a pale brown precipitate, from which a semi-crystalline neutral fraction (25—35% in various runs) was separated. When purified by recrystallisation from benzene, light petroleum, and ethanol, or by chromatography, a tetrahydrotetramethyloxodibenzofuran was obtained (yield ~12%) as needles, m. p. 155—157°. The purest sample, resulting from vacuum-sublimation, had m. p. 157—158° (Found: C, 79·3; H, 7·6. Calc. for $C_{16}H_{18}O_2$: C, 79·3; H, 7·5%); Haynes, Turner, and Waters [4] give m. p. 156°. The ketone was isolated in similar yield at 40° from oxidation of a 0·1M-solution in aqueous acetone (1 : 1 by vol.). The pure ketone was somewhat labile on chromatography on alumina, yielding a little resin and crystalline fractions, m. p. 137—152°; it was not significantly affected by silica gel. Besides the semicarbazone,[4] it formed an *oxime*, m. p. 209—211° (from methanol) (Found: C, 74·1; H, 7·4; N, 5·5. $C_{16}H_{19}O_2N$ requires C, 74·6; H, 7·4; N, 5·4%). The absorption spectrum of the ketone in cyclohexane showed sharp maxima at 223 and 300 mμ (log ε 4·40 and 3·72); the absorption curve for tetrahydrodimethyloxodibenzofuran (I) was practically identical and likewise showed maxima at 223 and 300 mμ (log ε 4·38 and 3·62). When refluxed with 48% hydrobromic acid, the tetramethyl ketone yielded a phenol which crystallised from aqueous methanol in needles, m. p. 149—151° (Haynes *et al.* give 152—154°), but it was difficult to purify, as were its derivatives.

The resinous alkali-soluble portion of the oxidation product (75%) was freed from unchanged phenol (2·5%) and chromatographed on silica gel or distilled at 0·05 mm. By either method only traces of crystalline material were obtained. Analysis and molecular weights of resulting resinous fractions indicated that they were dimeric or of higher complexity, and were slightly oxygenated.

*Oxidation of* 2,3-, 2,5-, *and* 3,5-*Dimethylphenols*.—The precipitates obtained in these oxidations amounted to 97—100% of the weight of the phenols. The neutral fractions from the 2,3-, 2,5-, and 3,5-isomer constituted 13, 18, and 4% respectively of the total products. Neither the neutral nor the alkali-soluble products of the oxidations yielded any pure crystalline compound when chromatographed on silica gel. Typical analyses were as follows (average compositions calc. on a $C_8$-basis):

| | C (%) | H (%) | *M* (Rast) | Average composition |
|---|---|---|---|---|
| Fraction from chromatography of alkali-soluble resin from 3,5-dimethylphenol | 72·1 | 7·1 | 314 | $(C_8H_{9\cdot3}O_{1\cdot7})_{2\cdot4}$ |
| Fraction from chromatography of neutral resin from 2,5-dimethylphenol | 78·1 | 7·0 | 381 | $(C_8H_{8\cdot6}O_{1\cdot15})_{3\cdot1}$ |
| Alkali-soluble resin from 2,5-dimethylphenol; fraction insoluble in benzene | 72·9 | 6·9 | 456 | $(C_8H_{9\cdot2}O_{1\cdot7})_{3\cdot5}$ |

When ether-extracted, the aqueous filtrates from the oxidation products of 2,3- or 3,5-dimethylphenol yielded small amounts of oils, but 2,5-dimethylphenol yielded a red, partly crystalline product (0·5 g., 4%), analysis of which [26] indicated a 30% content of quinone. Removal of phenol from the red product with aqueous alkali, followed by vacuum sublimation, gave pure 2,5-dimethyl-*p*-benzoquinone, m. p. 123·5—124°, not depressed by an authentic sample.[27]

*Oxidation of* 2,4,6-*Trimethylphenol*.—An aqueous solution (12 l.), containing 13·6 g. (0·1 mole) of the phenol, yielded 4·3 g. of a light brown precipitate (*A*) and a pale yellow filtrate, which, on exhaustive ether extraction, furnished 8·6 g. of a mixture (*B*) of brown oil and crystals. Practically all of (*A*) dissolved in aqueous alkali, and, when chromatographed on silica gel with benzene–ether (9 : 1), yielded mainly crystalline fractions. When recrystallised from ethanol, these fractions afforded 4,4′-dihydroxy-3,3′,5,5′-tetramethyldiphenylmethane (V) (1·7 g., 13%) in pale yellow needles, m. p. 175·5—176° (Found: C, 79·8; H, 7·9. Calc. for $C_{17}H_{20}O_2$: C, 79·7; H, 7·8%); the m. p. was undepressed by admixture with a sample prepared by Auwers's method.[29] The derived diacetate had m. p. 146°; Auwers [29] gives 142°, Cosgrove and Waters [3] 143°.

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[28] Braude, *J.*, 1945, 490.

[29] Auwers, *Ber.*, 1907, **40**, 2524.

Steam-distillation of (*B*) removed unchanged phenol (7%) and left a semi-solid product, from which 4-hydroxy-3,5-dimethylbenzyl alcohol (3·3 g., 22%) was obtained on recrystallisation from benzene and light petroleum. It showed m. p. 104—104·5° after a second recrystallisation [Found: C, 71·5; H, 8·0%; *M* (Rast method), 158. Calc. for $C_9H_{12}O_2$: C, 71·0; H, 7·9%; *M*, 152] and the m. p. was not depressed by admixture with an authentic sample prepared from 2,6-dimethylphenol and alkaline formaldehyde.[13] The fraction (*B*) from another oxidation of the phenol was absorbed on silica gel from benzene–light petroleum (3 : 1) and was eluted with benzene containing increasing proportions of ether. Only the earliest fractions (40% of the sample) were crystalline. Recrystallisation of these from benzene and then ethanol yielded two pure products, each ~2% of (*B*). One provided more (0·1 g.) of the dihydroxytetramethyldiphenylmethane, m. p. and mixed m. p. 175·5—176°, and the other a sample (<0·1 g.) of 4-hydroxy-3,5-dimethylbenzaldehyde (Found: C, 72·2; H, 6·8. Calc. for $C_9H_{10}O_2$: C, 72·0; H, 6·7%). The m. p. of the latter, 112—113·5°, was not depressed by a sample prepared by oxidation of 2,4,6-trimethylphenol with ethyl nitrite.[19]

We thank The Chemical Society for a grant from the Research Fund, and Monsanto Chemicals Ltd. for a gift of dimethylphenols.

QUEEN'S UNIVERSITY, BELFAST. [*Received, August 5th,* 1959.]