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Dehydrogenation of Phenols

I. Dehydrogenation of 2,6-Dimethylphenol with Silver Oxide

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The dimeric and polymeric products obtained by oxidation of 2,6-dimethylphenol with silver oxide were investigated. The results show that the phenoxyl radicals probably formed as intermediates mainly react to give diphenyl ether groups (Path A in Scheme 1).

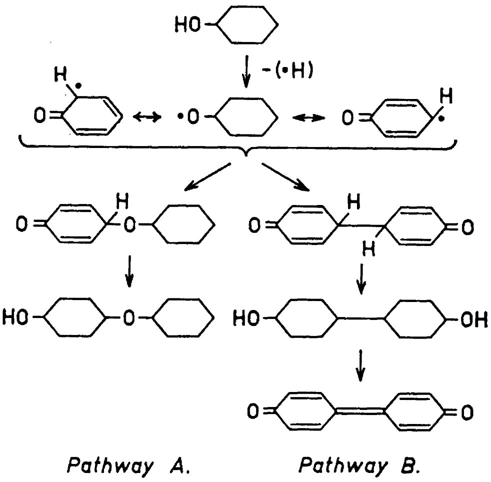
One electron oxidation of phenols (reviews [1,2]) affords phenoxyl radicals. Due to their different mesomeric forms they can pair to form stable products in various ways. They may react to form ether linkages (Path A in Scheme 1) or they may form carbon-carbon bonds (Path B). In the first case, quinol ethers and diphenyl ethers are obtained, in the second, bis-(*cyclo*hexadienone) derivatives, diphenyls and diphenoquinones.

Several examples of both types of oxidation products are known. The commonest types of dimers actually obtained are the diphenyls and diphenoquinones. The yields of these products are usually however rather low, the main products often being polymeric materials. It is therefore also necessary to study these polymers before deciding whether A or B represents the preferred reaction path.

These oxidation polymers have been studied only in the case of *o*-cresol. Pummerer [3] has briefly mentioned, without giving experimental details, that potassium ferricyanide oxidation gives a polymer with ether-linked phenolic units. According to Goldschmidt [4] *o*-cresol reacts with lead dioxide in acidified ether to give a trimer of the same type. His arguments are, however, not conclusive.

In some cases, high yields of diphenyls and diphenoquinones have been obtained by oxidation of phenols. For example, both benzoyl peroxide [5] and chromium trioxide in acetic acid [6] convert 2,6-dimethylphenol in high yield into the corresponding diphenoquinone. It is probable, however, that these reactions do not involve one electron mechanisms [7,8] but pass through cationic intermediates, as in the reactions of periodate [9] and lead tetracetate [10] with phenols.

On the other hand, reduction of ferric chloride and potassium ferricyanide involves only one electron and it seems likely therefore that their reactions with phenols involve



Scheme 1. The reaction pathways at dehydrogenation of phenols.

phenoxyl radicals. These reagents have also been used to prepare relatively stable phenoxyl radicals from sterically hindered phenols. It is of interest that in their reaction with 2,6-dimethylphenol the yields of the diphenyl and the diphenoquinone are much smaller than in the above mentioned cases[6].

Recently Ley, Müller and co-workers[11] have shown that labile quinol ethers are the initial products formed when phenols react with 2,4,6-tri-*tert.* butylphenoxyl-(1) and similar stable radicals. These may then split into radicals, which slowly form bis-(*cyclo*hexadienone) derivatives and diphenyls.

In the present investigation a study has been made of the oxidation of 2,6-dimethylphenol with silver oxide. The polymeric materials formed were examined as well as the dimeric products. This oxidation must be of the one electron type because the reduction of silver oxide, like that of ferric chloride and potassium ferricyanide, involves only one electron. Silver oxide was actually used by Pummerer[12] in some of his pioneer works to prepare stable phenoxyl radicals.

The oxidation was carried out by shaking a benzene solution of the phenol with silver oxide at room temperature. In some experiments sufficient silver oxide was added to abstract one hydrogen atom from each phenol molecule, in others, enough was used to abstract two hydrogen atoms (mole ratio silver oxide/phenol = 0.5 and 1, respectively).

In the first case a compound (I), the composition of which corresponded to $C_{16}H_{18}O_2$, was isolated in a yield of 15 %. The other substances obtained were 3,3',5,5'-tetramethyl-4,4'-diphenoquinone (yield 11 %) and small amounts of 3,3',5,5'-tetramethyl-4,4'-dihydroxy-diphenyl. The greater part of the residue was unreacted 2,6-dimethylphenol (yield 31 %) and undistillable, polymeric material.

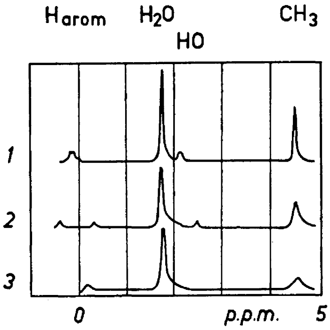


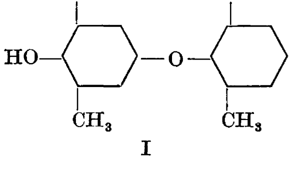
Fig. 1. NMR spectra of 1) 2,6-dimethylphenol, 2) compound (I), and 3) the solid polymer. Carbon tetrachloride solution. External standard: water.

The UV spectrum indicated that substance (I) was aromatic (λ_{max} 288 mμ, ε 7 400 in methanol). Acetylation showed that it contained one hydroxyl group which was found to be phenolic by the bathochromic shift[13] of the 288 mμ maximum in alkaline solution (λ_{max} 310 mμ, ε 9 000 in N methanolic KOH). The IR spectrum of the compound indicated the presence of both 1,2,3-trisubstituted (maxima at 715 and 780 cm^{-1})[14] and 1,2,3,5-tetrasubstituted (maximum at 850 cm^{-1})[15] benzene nuclei. (2,6-Dimethylphenol as a trisubstituted benzene derivative has peaks at 722 and 755 cm^{-1}). No carbonyl band was present. From this it was probable that the compound was 3,5,2′,6′-tetramethyl-4-hydroxydiphenyl ether (formula I), which can be obtained from the phenol by Pathway A, Scheme 1.

The NMR spectrum showed a single strong resonance peak at a chemical shift of 4.45 p.p.m. relative to benzene hydrogen (Fig. 1). This must be due to methyl groups in α-position to a benzene nucleus (reported values for methyl substituted benzenes about 4.7 p.p.m.)[16]. 2,6-Dimethylphenol has a strong peak at the same point. The 2.40 p.p.m. peak is probably caused by hydroxylic hydrogen (2.15 for 2,6-dimethylphenol) as it shifted to 2.20 p.p.m. on addition of dimethyl sulphoxide, which would form hydrogen bonds with the hydroxyl groups.

Two single resonance bands were obtained for aromatic hydrogen, one on each side of the peak for benzene hydrogen (—0.40 and 0.24 p.p.m., respectively). They may correspond to the coupled magnetic resonance for the hydrogen atoms in the phenolic benzene nucleus (—0.40 p.p.m.) and in the non-phenolic nucleus (0.24 p.p.m.).

The NMR showed the absence of aliphatic (except CH_3) and olefinic hydrogen. It is thus in agreement with the formula (I):



I

Structure (I) was confirmed by periodate degradation which gave 2,6-dimethyl-*p*-quinone. This reaction is analogous to the formation of phenol and *p*-quinone by periodate oxidation of *p*-hydroxy-diphenyl ether [9]. That 2,6-dimethyl-phenol was not obtained from (I) may be due to the fact that it reacts rapidly with periodate [17]. Unsubstituted phenol, on the other hand reacts very slowly with periodate [9].

When 2,6-dimethylphenol was treated with sufficient silver oxide to abstract two hydrogen atoms the diphenyl ether (I) was obtained in very low yield. A white amorphous material was isolated which had the elemental composition $C_8H_{8.12}O_{0.94}$ and must therefore have been formed from dimethylphenol by elimination of two hydrogen atoms.

Determination of the molecular weight of this material from the melting point depression of benzene solutions gave values of 1 300 and 1 900 (two samples), corresponding to 10—16 dimethylphenol units, respectively.

Heating with acetic anhydride and pyridine did not introduce any acetyl groups into the product and it therefore contained few or no hydroxyl groups. In agreement its IR spectrum (Fig. 2) showed only weak absorption in the vicinity of 3 500 cm^{-1}. There were two peaks in the carbonyl range, at 1 700 and 1 740 cm^{-1}. The extinction coefficients of these carbonyl peaks were, however, rather low and the occurrence of carbonyl groups was therefore regarded as small in the polymer. These groups have not been further examined.

The product did not oxidise potassium iodide and therefore did not contain any peroxide groups. Thus, the bulk of the oxygen atoms in the polymer must be present in ether groups.

The UV spectrum of the polymer (Fig. 3) showed that it was made up largely of aromatic units. (Maxima at 238 mμ, ε 9 150; 278 mμ, ε 1 670; and 285 mμ, ε 1 640. Dioxan solution; ε-values calculated on a C_8-basis.) Its NMR spectrum (Fig. 1) supported this as it did not contain any resonance peak for aliphatic (except the CH_3 peak at 4.45 p.p.m.) or olefinic hydrogen. The aromatic hydrogen peak (0.22 p.p.m.) was above the benzene hydrogen peak.

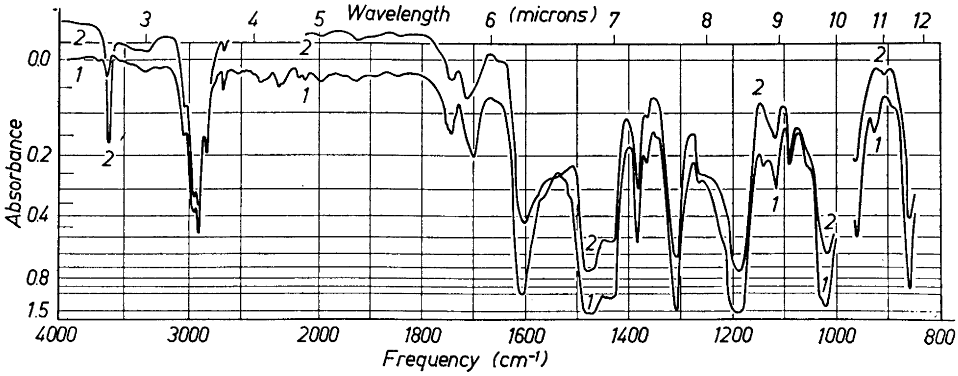


Fig. 2. IR spectra of 1) the solid polymer, and 2) the sirupy material from the mother liqour. Curve 2 displaced to lower absorbance for its separating from curve 1. Carbon tetrachloride solution.

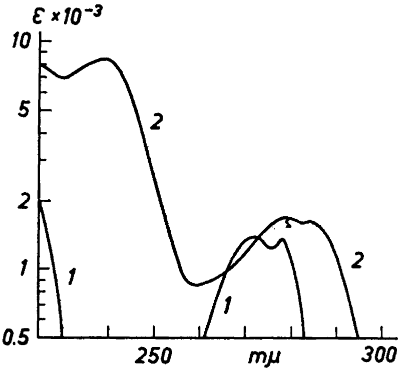


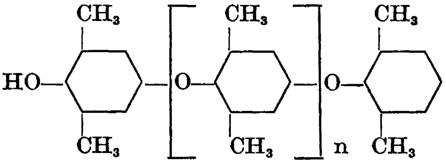
Fig. 3. UV spectra of 1) 2,6-dimethylphenol, and 2) the solid polymer. Methanol solution.

The IR spectrum gave an indication of the substitution in the benzene nucleus since it had a maximum at 850 cm^{-1} characteristic for 1,2,3,5-tetra-substituted benzene derivatives.

No trace of a maximum was present in the UV curve at 250—270 mμ, where diphenyl derivatives show strong absorption. (3,3′,5,5′-Tetramethyl-4,4′-dihydroxy-diphenyl: $\lambda_{\max}$ 267 mμ, ε 17 500 in methanol.)

These findings strongly indicated that the polymer is built up mainly according to formula (II). It also contained other structural features including a small percentage of carbonyl groups.

The polymeric material was obtained in a yield of about 40 %. From the mother liquor a semi-solid material was obtained, which gave essentially the same IR spectrum as the solid polymeric material (Fig. 2) but with the significant difference that the semi-solid material had a strong hydroxyl absorption peak. Its molecular weight was about 390, corresponding to 3.2 dimethylphenol units. These findings indicated that the material was of the same



II

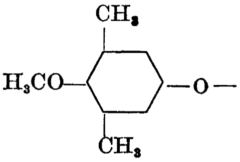
type as the solid polymer, but had a lower molecular weight. Distillation of the syrup gave a small amount of the diphenyl ether (I).

The yield of the syrup was about the same as the yield of the solid material (about 40 %). These experiments show therefore that on silver oxide oxidation in benzene the intermediate phenoxyl radicals mostly react according to Path A forming diphenyl ether groups.

The diphenyl ether (I) was obtained only in relatively low yield in these oxidations. Even when a theoretical amount of silver oxide was used the main products isolated were the starting material and the polymer. It is therefore probable that the dimer (I) is oxidised more easily than the dimethylphenol. This may be due to activation of the phenolic hydroxyl group of (I) by the phenoxy group in the *para*position.

When the oxidation was carried out in the more polar solvent dimethylformamide, the polymeric material was again obtained together with tetramethyl-diphenoquinone. The yield of the polymer was, however, low, at least in part due to difficulties in isolating the material. The similarity of the polymeric materials was shown by the IR spectra.

Kuhn [18] has recently elaborated a new methylation technique for carbohydrates. The sugar, dissolved in dimethylformamide, is treated with silver oxide and methyl iodide. When 2,6-dimethylphenol is methylated in a corresponding way there is competition between the oxidation and the methylation reactions. From the reaction mixture a polymeric material was isolated the IR spectrum of which was identical with those of the above mentioned polymers. Analysis gave the empirical formula $C_8H_{8.03}O_{0.97}(OCH_3)_{0.065}$. The product thus contained one methoxyl group to 15 dimethylphenol units. Cryoscopic molecular weight determination gave a value corresponding to 14 units in the molecule. Probably the methoxyl groups were present as end groups (III) in the polymer.



III

EXPERIMENTAL

Oxidation of 2,6-dimethylphenol in benzene solution, mole ratio silver oxide/phenol = 0.5. Silver oxide (25 g) was added in portions to a solution of 2,6-dimethylphenol (25 g) in benzene (500 ml). The mixture was then shaken for 17 h at about 20° in the dark. Undissolved material was collected and extracted with boiling acetic acid. On cooling, red crystals (2.7 g) m.p. 208—210° (undepressed by admixture with 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone) were obtained.

The benzene filtrate was evaporated and the residue was dissolved in a small amount of benzene. Undissolved dark green crystals (0.2 g) were removed. These had m.p. 186—187°, undepressed on admixture with the quinhydrone from 3,3′,5,5′-tetramethyl-4,4′-dihydroxy-diphenyl and 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone. The benzene solution was again evaporated and the residue was distilled. The following fractions were collected: 1) b.p. 60—70° 0.3 mm Hg, 7.7 g of 2,6-dimethylphenol, m.p. 41.5—42°. 2) b.p. 140—150° 0.4 mm Hg, 3.9 g of substance (I), m.p. 101—105°.

The m.p. of substance (I) was raised to 105—108° by repeated recrystallisation from methanol — water. A small amount of crystalline material m.p. 223—225° (undepressed by admixture with 3,3′,5,5′-tetramethyl-4,4′-dihydroxy-diphenyl) was obtained from the mother liquor.

Compound (I). Found: C 78.9; H 7.3; O 14.0; OH 6.3. Calc. for $C_{16}H_{18}O_2$ (242): C 79.3; H 7.4; O 13.2; OH 7.0.

Oxidation with periodate. Sodium *para*periodate (3 g) dissolved in acetic acid — water (1:2 v/v, 100 ml) was added to a solution of substance (I) (0.6 g) in acetic acid (10 ml). The solution turned yellow. It was allowed to stand at room temperature for half an hour. The solution was then extracted with benzene, and the benzene solution was shaken with 5 % sodium hydroxide solution, dried (sodium sulphate) and evaporated. The residue (0.2 g) was sublimed at about 80° (bath temperature) and a pressure of 15 mm Hg to give yellow needles (0.11 g, yield 33 %) m.p. 55—58°. Recrystallisation from light petroleum increased the m.p. to 67—67.5°, undepressed by admixture with 2,6-dimethyl-*p*-quinone.

No 2,6-dimethylphenol was isolated from the sodium hydroxide solution. Similarly, no phenol was obtained when one mole of periodate was added to one mole of substance (I).

Oxidation of 2,6-dimethylphenol in benzene solution, mole ratio silver oxide/phenol = 1. Silver oxide (23 g) was added in portions to a solution of 2,6-dimethylphenol (12 g) in benzene (250 ml). The mixture was then shaken overnight at about 20°. Undissolved material was collected and extracted several times with boiling acetic acid. On cooling, 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone (1.0 g) crystallised from the acetic acid.

The benzene filtrate was extracted with 5 % sodium hydroxide solution (from which 0.17 g of 2,6-dimethylphenol could be recovered) and dried (sodium sulphate). The addition of light petroleum (b.p. 60−70°) to the benzene solution precipitated a white, amorphous material which was collected by centrifuging and washed with light petroleum. Weight after drying in a vacuum at room temperature, 2.1 g. Preparation A. (Found: C 80.4; H 6.7; O 12.6; mol. wt. 1 300). The IR and UV spectra are shown in Fig. 1 and Fig. 2, respectively.

The filtrate from material A was evaporated to dryness and the residue was dissolved in *iso*propyl ether. Ethanol was added to this solution and the white precipitate obtained was collected and washed with light petroleum. Weight 2.6 g. Preparation B. The IR and UV spectra were very similar to those of preparation A. (Found: C 80.5; H 6.8; O 12.5; mol. wt. 1 900).

The *iso*propyl ether — ethanol solution was evaporated to dryness, giving a semisolid residue (4.7 g). Preparation C. Mol. wt. 390. IR spectrum in Fig. 2.

Acetylation of preparations A and B. Samples of A and B (300 mg each) were heated with pyridine (3 ml) and acetic anhydride (3 ml) for 1 h at 100°. Water was added and the mixture was then extracted with benzene. The benzene solution was shaken with sodium bicarbonate solution and dried. Dissolved material was precipitated by adding methanol, filtered and washed with methanol. Both products gave 0 % acetyl.

Oxidation of 2,6-dimethylphenol in dimethyl formamide solution, mole ratio phenol/silver oxide = 1. Silver oxide (4 g) was added in portions to a solution of 2,6-dimethylphenol (2 g) dissolved in dimethylformamide (40 ml). The mixture was shaken overnight at room temperature. The solid material was then filtered off and extracted with boiling acetic acid. From the acetic acid solution 3,3′,4,4′-tetramethyl-4,4′-diphenoquinone (0.15 g) crystallised during cooling.

Chloroform and water were added to the dimethylformamide filtrate to give two phases. The upper layer was extracted several times with chloroform. The chloroform solutions were combined, shaken with water 6 times, dried and evaporated to dryness. The residue (0.67 g) was dissolved in benzene, and methanol added to the solution. The white precipitate obtained was collected (72 mg). The IR spectrum of this material agreed with those of preparations A and B above.

Oxidation of 2,6-dimethylphenol in dimethylformamide — methyl iodide solution. Silver oxide (7.5 g) was added in portions to a solution of 2,6-dimethylphenol (3 g) in dimethylformamide (15 ml) and methyl iodide (9 ml), and the mixture shaken overnight at room temperature. Undissolved material was removed and the filtrate was shaken with sodium thiosulphate solution and then with water. After drying, the solution was evaporated and the residue (1.35 g) was dissolved in *iso*propyl ether. Crystals of undissolved 3,3′,4,4′-tetramethyl-4,4′-diphenoquinone were removed (a few mg), the solution was poured into ethanol and the white precipitate (0.35 g) obtained was collected by centrifuging. (Found: C 79.5; H 6.8; O 13.6; OCH_3 1.66). The UV and IR spectra were identical with those of preparations A and B.

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REFERENCES

1. Barton, D. H. R. and Cohen, T. *Festschrift Arthur Stoll,* Basel 1957, p. 117.
2. Erdtman, H. and Wachtmeister, C. A. *Festschrift Arthur Stoll,* Basel 1957, p. 144.
3. Pummerer, R., Melamed, D. and Puttfarcken, H. *Ber.* **55** (1922) 3116.
4. Goldschmidt, S., Schultz, E. and Bernard, H. *Ann.* **478** (1930) 1.
5. Cosgrove, S. L. and Waters, W. A. *J. Chem. Soc.* **1951** 388.
6. Auwers, K. and v. Markovits, Th. *Ber.* **38** (1950) 226; **41** (1908) 2332; v. Auwers, K. and Wittig, G. *Ber.* **57** (1924) 1270.
7. Walling, C. and Hodgdon, R. B. Jr. *J. Am. Chem. Soc.* **80** (1958) 228.
8. Lewitt, L. *J. Org. Chem.* **20** (1955) 1297.
9. Adler, E. and Magnusson, R. *Acta Chem. Scand.* **13** (1959) 505.
10. Criegee, R. *Angew. Chem.* **70** (1958) 173.
11. Ley, K., Müller, E., Mayer, R. and Scheffler, K. *Chem. Ber.* **91** (1958) 2670.
12. Pummerer, R. and Frankfurter, F. *Ber.* **47** (1914); 1472; Pummerer, R. and Cherbuliez, E. *Ber.* **47** (1914) 2957.
13. Aulin-Erdtman, G. and Hegbom, L. *Svensk Papperstidn.* **60** (1957) 671.
14. McMurry, H. L. and Thornton, V. *Anal. Chem.* **24** (1952) 318; Colthup, N. B. *J. Optical Soc. Am.* **40** (1950) 397.
15. Connon, C. G. and Sutherland, G. B. B. M. *Spectrochim. Acta* **4** (1951) 373.
16. Chamberlain, N. F. *Anal. Chem.* **31** (1959) 56.
17. Adler, E. *Personal communication.*
18. Kuhn, R., Trischmann, H. and Löw, I. *Angew. Chem.* **67** (1955) 32.

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