

Oxidation of Some 2,4,6-Trialkyl-substituted Phenols with Potassium Nitrosodisulfonate

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The 2,4,6-trialkylphenols I–V react with nitrosodisulfonate giving products with both one and two aromatic rings. Thus mesitol (I) gives the benzyl phenyl ether XVI, 3,5-dimethyl-4-hydroxybenzyl alcohol (XVIII) and 2,6-dimethyl-*p*-benzoquinone (XIX). With the *o*-*tert*-butylphenols II–V the *tert*-butyl group is removed with the formation of the *o*-benzoquinones XX–XXIII.

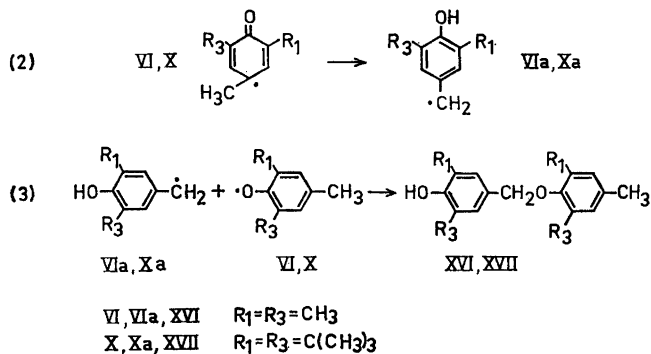
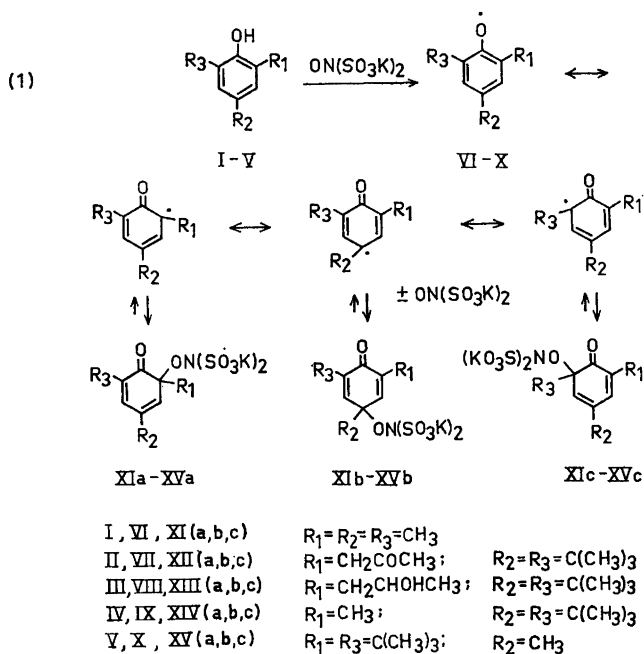
Oxidation of a phenol with potassium nitrosodisulfonate usually gives a *p*-quinone when the *p*-position is free¹ and an *o*-quinone when the phenol is *p*-substituted but has a free *o*-position.² Except for mesitol (I) which is reported to be unaffected,¹ the action of nitrosodisulfonate on 2,4,6-trialkyl-substituted phenols has not previously been examined.

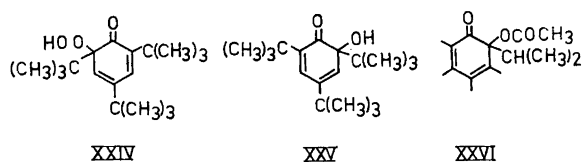
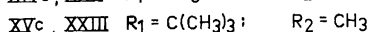
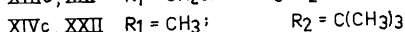
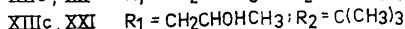
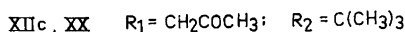
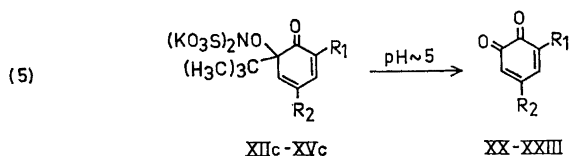
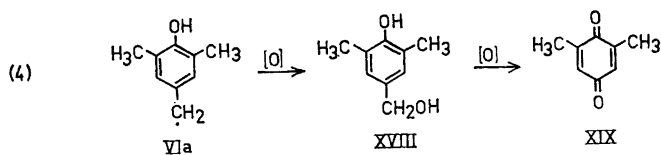
During work on the structures of some 2-acetylphenols it was found that 2-acetyl-4,6-di-*tert*-butylphenol (II) was oxidised by nitrosodisulfonate to an *o*-benzoquinone with the loss of a *tert*-butyl substituent.³ An examination was therefore made in the present investigation of the reaction of some 2,4,6-trialkyl-substituted phenols with nitrosodisulfonate.

When the phenols I–V were mixed with 2 moles of potassium nitrosodisulfonate in water or dilute acetone in the presence of sodium acetate or potassium dihydrogen phosphate, the violet colour of the oxidising agent disappeared relatively rapidly. The products formed in this reaction could not be extracted with chloroform but they were slowly converted to substances which could be extracted with organic solvents. Teuber and coworkers^{1,4,5} have shown that the oxidation of phenols with nitrosodisulfonate proceeds *via* cyclohexadienone derivatives. By analogy, the water-soluble, chloroform-insoluble primary products could be the salts XI–XV (a, b, c). Of these, only XIb–XVb can be colourless, whereas the compounds of structures a and c would be yellow like other 2,4-cyclohexadienone derivatives. In fact, ultraviolet absorption of the colourless reaction mixtures (Fig. 1) obtained with mesitol (I) and 4,6-di-*tert*-butyl-2-methylphenol (IV) was found to be very similar to that of 2,4,6-trimethyl-*p*-benzoquinol (a 2,5-cyclohexadienone derivative)⁶ but differed distinctly from that of *o*-benzoquinols (2,4-cyclohexadienone derivatives).^{3,6}

This shows that the 2,5-cyclohexadienones dominate; the presence of small amounts of the 2,4-isomers however cannot be excluded.

The reaction mixture obtained from mesitol (I) and nitrosodisulfonate in the ratio 1:2 became colourless within 5 min (see Exptl.), and, on evaporation, gave a colourless crystalline material which could not, however, be purified. The cyclohexadienone structure for the product was supported by its breakdown in the presence of dilute hydrochloric acid to form mesitol as would be expected from the results obtained by Teuber and Götz⁵ with analogous compounds. After a reaction time of several hours, a similar mixture of mesitol and nitrosodisulfonate gave starting material (I, 12 %), the benzyl





phenyl ether XVI (*ca.* 20 % as precipitate), 4-hydroxy-3,5-dimethylbenzyl alcohol (XVIII, 4 %) and 2,6-dimethyl-*p*-benzoquinone (XIX, 26 %).

When mesitol (I) was treated with a sufficiently large excess of nitrosodisulfonate (6 moles per mole of I), none of the benzyl phenyl ether XVI separated from the solution and the only extractable product was 2,6-dimethyl-*p*-quinone (XIX). The amount of the quinone XIX formed in this oxidation was, however, remarkably low — only 10 % yield was obtained after 24 h. That this was only to a lesser extent due to the instability of the quinone XIX in solution was shown by its half life of 5 days under similar conditions.

These results may be explained by the assumption that the cyclohexadienone XI b primarily formed is in equilibrium with small amounts of the mesomeric phenoxyl radical VI and nitrosodisulfonate, as shown in eqn. 1. The radical VI is converted to the final reaction products, the cyclohexadienone XIb thus being slowly consumed. In the presence of excess of nitrosodisulfonate the equilibrium would be displaced towards the cyclohexadienone. This would repress the secondary reactions of the radical VI, and the cyclohexadienone would be consumed at a lower rate than in the experiment with the molar ratio mesitol:nitrosodisulfonate 1:2. In fact, mesitol was liberated when the reaction mixture containing excess of the oxidant was acidified after 24 h.

The benzyl phenyl ether XVI mentioned above is probably formed by isomerisation of the phenoxyl radical VI to the benzyl radical VIa which couples with unchanged phenoxyl radical (eqns. 2 and 3). A similar rearrange-

ment of the phenoxy radical X to the benzyl radical Xa has been examined by Cook *et al.*⁷ That the latter isomerisation ($X \rightarrow Xa$) also takes place under the present conditions is indicated by the formation of 2,6-di-*tert*-butyl-4-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-4-methyl-2,5-cyclohexadienone on oxidation of 2,6-di-*tert*-butyl-4-methylphenol (V). The benzyl phenyl ether XVII was however not obtained; details will be given in a forthcoming communication.

3,5-Dimethyl-4-hydroxybenzyl alcohol (XVIII) has previously been obtained from mesitol by reaction with a variety of oxidising agents.⁸⁻¹¹ As already mentioned, it is obtained (in small amount) on oxidation with nitrosodisulfonate and can also be supposed to be formed *via* the benzyl radical VIa (eqn. 4).

4-Hydroxybenzyl alcohols are rapidly oxidised by nitrosodisulfonate to the corresponding *p*-quinones and formaldehyde.¹² The formation of 2,6-dimethyl-*p*-quinone (XIX) from a reaction mixture, which was colourless shortly after the start of the reaction and thus could not contain more than traces of unreacted nitrosodisulfonate, is assumed to occur by oxidation of the benzyl alcohol XVIII by nitrosodisulfonate continuously formed from the cyclohexadienone XIb due to the secondary reactions of the phenoxy radical.

When 2-acetylphenyl-di-*tert*-butylphenol II was treated with nitrosodisulfonate in KH_2PO_4 buffer for 8 h, a quinone (XX) with only one *tert*-butyl group was obtained. The red colour of the product indicated an *o*-quinonoid structure and this was confirmed by the formation of a phenazine derivative on treatment with *o*-phenylenediamine. The 2-(2-hydroxypropyl)-di-*tert*-butylphenol III obtained by reduction of the acetylphenol II with sodium borohydride, also gave a quinone (XXI) with simultaneous loss of a *tert*-butyl group. In view of the origin of these two phenols³ it was uncertain whether they had the 2,4-di-*tert*-butylphenol structures II and III or whether the *tert*-butyl groups rather were located in the 3- and 5-positions. That structures II and III are

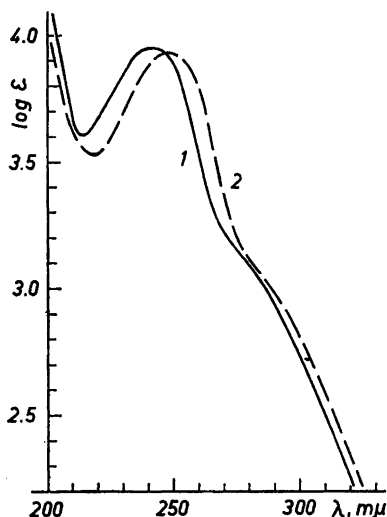


Fig. 1. Absorption spectra of reaction mixtures. A solution of 0.1 mmole of the phenol (see below) in 900 ml water was mixed with a solution of 0.2 mmole potassium nitrosodisulfonate and 1 mmole sodium acetate in 100 ml water. Spectra were recorded after stated times on a Perkin Elmer 4000 A Spectracord with water as reference. The molar extinction coefficients were calculated on the basis of the phenol concentration. 1. Mesitol (I). Reaction time 30 min. 2. 4,6-Di-*tert*-butyl-2-methylphenol (IV). Reaction time 12 h.

consistent with the formation of an *o*-quinone was shown by the fact that 4,6-di-*tert*-butyl-2-methylphenol (IV) was oxidised to 5-*tert*-butyl-3-methyl-*o*-benzoquinone (XXII). Under similar conditions 2,6-di-*tert*-butyl-4-methylphenol (V) gave 3-*tert*-butyl-5-methyl-*o*-benzoquinone (XXIII) in low yield (20 %); obviously *para* oxidation products were also formed in this case. In solutions buffered with sodium acetate (instead of with dihydrogen phosphate) the butyl phenols II–IV reacted with nitrosodisulfonate but the colourless cyclohexadienones formed did not give *o*-quinones and the solutions remained almost colourless. This indicates the presence of the 2,5-cyclohexadienone derivatives XIIb–XIVb (see the ultraviolet absorption curve 2, Fig. 1). *o*-Quinone formation is thus catalysed by protons but this can be utilised only to a limited extent since at low pH there is also accelerated decomposition of the cyclohexadienones.⁵

Gersman and Bickel¹³ and Conradi and McLaren¹⁴ have shown that 2,4,6-tri-*tert*-butyl-6-hydroperoxy-2,4-cyclohexadienone (XXIV) decomposes into an *o*-quinone or an *o*-semiquinone and isobutylene. Ley and Müller¹⁵ have described evidence for a similar reaction, the formation of 3,5-di-*tert*-butyl-*o*-benzoquinone from 2,4,6-tri-*tert*-butyl-*o*-benzoquinol (XXV). By analogy with this the formation of the *o*-quinones XX–XXIII in the present experiments can be explained by decomposition of the 2,4-cyclohexadienone derivatives XIIc–XVc (eqn. 5). These may be present in small amounts in the primary oxidation mixture (eqn. 1), in which the 2,5-isomers XIIb–XVb predominate (see p. 760). The latter products would be converted into the 2,4-isomers XIIc–XVc as these undergo decomposition into the *o*-quinones. In the 2,4-isomers the electron attracting effect of the (protonised) carbonyl group should favour the loss of the 6-*tert*-butyl group as a carbonium ion.

Recently Zbiral¹⁶ has shown that 2-isopropyl-*o*-quinol acetates (XXVI) in the presence of boron trifluoride give pyrocatechols, a reaction that is related to that above. The action of the catalyst is explained as an electrophilic attack on the ring carbonyl group which is propagated through the conjugated system and leads to loss of the isopropyl group.

Becconsall, Clough and Scott¹⁷ considered that oxidation of phenols to diphenylethanes does not take place *via* benzyl radicals but through simultaneous dimerisation and rearrangement of phenoxyl radicals. Their theory is based on electron spin resonance measurements and on the absence of evidence for the formation of the benzyl phenyl ether XVII from 2,6-di-*tert*-butyl-4-methylphenol (V). Bennet¹⁸ has since shown that the phenoxyl radical X derived from this phenol (V) decays with first order kinetics which supports the theory of Cook *et al.*⁷ that the phenoxyl radical rearranges to the benzyl radical Xa before dimerisation. The formation of the benzyl phenyl ether XVI further supports the idea that the benzyl radicals may be intermediates in the oxidation of these phenols.

Becconsall *et al.*¹⁷ consider also that elimination of a *p*-methyl group — to give a diphenylmethane derivative — can occur in the reaction between phenoxyl radicals. They instance the isolation by Cosgrove and Waters⁹ of 4,4'-dihydroxy-3,5,3',5'-tetramethyldiphenylmethane on oxidation of mesitol (I); this result has also been reported by Bacon and Munro.¹¹ This diphenylmethane can however be a secondary product formed by condensation between

The diphenylmethane derivative XXVII is undoubtedly identical with a product of unknown structure obtained by Fries and Brandes²³ on hydrolysis of 4-bromo-2,4,6-trimethyl-2,5-cyclohexadienone (in the presence of mesitol) and later by Cosgrove and Waters⁹ on oxidation of mesitol with hydrogen peroxide in the presence of acidified ferrous sulfate (see Exptl., p. 767). In both cases, the benzyl alcohol (XVIII) formed initially seems to have undergone condensation with the mesitol.

Added in proof. Müller *et al.* [*Z. Naturforsch.* **18 b** (1963) 1002] reported that both *o*- and *p*-*tert*-butyl groups may be removed on nitrosodisulfonate oxidation of phenols.

EXPERIMENTAL

Microanalyses were done by Alfred Bernhardt, Mülheim, Germany.

Materials. 2-Acetyl-4,6-di-*tert*-butylphenol (II) was prepared according to Ref.²⁴, 2-(2-hydroxypropyl)-4,6-di-*tert*-butyl phenol (III) according to Ref.²⁵ and 4,6-di-*tert*-butyl-2-methylphenol (IV) according to Ref.²⁶

Oxidation of mesitol (I) with 2 moles of potassium nitrosodisulfonate

A. *To cyclohexadienone XIb.* A solution of mesitol (540 mg, 4.0 mmoles) in acetone (5 ml) was mixed with a solution of potassium nitrosodisulfonate (2.07 g, 7.7 mmoles) in water (25 ml) and 1 N NaOAc (1 ml) at 45°. After 5 min the colourless mixture was cooled to -5° and the precipitate formed was filtered off (1.17 g). The presence of potassium hydroxylaminedisulfonate in the precipitate was shown by oxidation to nitrosodisulfonate with potassium permanganate in ammoniacal solution. The filtrate from the reaction mixture was taken to dryness under reduced pressure and the residue was slurried in ethanol and filtered. The colourless, crystalline precipitate was crude cyclohexadienone XIb (1.14 g), it slowly decomposed (turned brown) on heating and even on keeping at room temperature. A solution of the substance (156 mg) in water (1 ml) was made acid with a few drops of 5 N hydrochloric acid. After a short time a precipitate of mesitol (46 mg) formed.

B. *To 3,5-dimethyl-4-hydroxybenzyl 2,4,6-trimethylphenyl ether (XVI), 3,5-dimethyl-4-hydroxybenzyl alcohol (XVIII) and 2,6-dimethyl-p-benzoquinone (XIX).* A solution of mesitol (1.36 g, 10 mmoles) in acetone (50 ml) was added to a solution of potassium nitrosodisulfonate (5.4 g, 20 mmoles) in water (450 ml) and 1 N sodium acetate (50 ml). After 5 min the mixture was clear and colourless but then began to turn cloudy and yellow. After 4 h a pale brown precipitate (370 mg) was filtered off and recrystallised from ligroin and from methanol giving 3,5-dimethyl-4-hydroxybenzyl 2,4,6-trimethylphenyl ether (XVI) as colourless rods (180 mg), m.p. 122–123°. (Found: C 80.20; H 8.03. Calc. for C₁₈H₂₂O₂: C 79.96; H 8.20). The filtrate from the oxidation mixture was extracted with ether (3 × 100 ml) and the extract was dried (Na₂SO₄) and evaporated. The residue, a yellow oil (750 mg), was chromatographed on a silica gel column (40 × 2 cm). Elution with benzene/ethyl acetate (2:1) gave first a yellow fraction containing 2,6-dimethyl-*p*-quinone (XIX, 350 mg). This was followed by mesitol (I, 170 mg) and finally by 3,5-dimethyl-4-hydroxybenzyl alcohol (XVIII, 50 mg). The quinone was sublimed, m.p. and mixed melting point 72–73°. The benzyl alcohol XVIII was recrystallised from benzene, m.p. and mixed m.p. 103–104°.

Oxidation of mesitol (I) with excess nitrosodisulfonate

Mesitol (500 mg, 3.7 mmoles) in acetone (30 ml) was added to a solution of potassium nitrosodisulfonate (6 g, 22 mmoles) in water (200 ml) mixed with 1 N sodium acetate

solution (20 ml). After 24 h, the clear violet solution was extracted with ether (2×100 ml). The pale yellow ether solution on drying (Na_2SO_4) and evaporation gave a crystalline residue (50 mg) of 2,6-dimethyl-*p*-quinone (XIX). To the water phase was added conc. hydrochloric acid (50 ml). Extraction with ether (2×100 ml) after 30 min gave a yellow oil (400 mg) in which mesitol (I), 3,5-dimethyl-4-hydroxybenzyl alcohol (XVIII) and 2,6-dimethyl-*p*-quinone (XIX) were detected on thin layer chromatography (SiO_2 , CH_2Cl_2 , development with iodine). The main product, mesitol, was obtained as crystalline material on column chromatography in the same system.

Treatment of 2,6-dimethyl-p-quinone (XIX) with nitrosodisulfonate. The quinone XIX (327 mg) and potassium nitrosodisulfonate (1.53 g) were dissolved in water (145 ml) mixed with 1 N sodium acetate (5 ml). The violet colour had disappeared after 5 days. The solution was then extracted with ether (50 ml) and the ether phase was dried (Na_2SO_4) and evaporated. The residue (154 mg) was starting material (XIX).

General procedure for the oxidation of the phenols II–V to the o-quinones XX–XXIII. A solution of the phenol (10 mmoles) in acetone (500 ml) was poured into a solution of potassium nitrosodisulfonate (20 mmoles, 5.4 g) in water (400 ml) and 1/6 M KH_2PO_4 (100 ml). If drops of oil separated, the mixture was stirred until they dissolved. A further quantity of nitrosodisulfonate (5.4 g in 200 ml water) was added after 4 h for the oxidation of phenols II–IV and 12 h for phenol V. After a further 4 h for the phenols II–IV and 12 h for phenol V the filtered solution was extracted with chloroform (2×100 ml). The extract was evaporated and the residue was treated as described below.

The oxidation was carried out with 4 moles of nitrosodisulfonate per mole of phenol since it was found that a part of the phenol remained among the oxidation products when only two moles of nitrosodisulfonate were used. This was probably due to partial decomposition of the nitrosodisulfonate during the long reaction time.

Attempts to detect isobutylene by gas chromatography in the products of oxidation of IV failed, probably because the concentration was too low.

3-Acetyl-5-tert-butyl-o-benzoquinone (XX) from 2-acetyl-4,6-di-tert-butylphenol (II). The above procedure was followed and the crude crystalline product was recrystallised from hexane, red prisms, m.p. 78–79° (70 %). (Found: C 70.55; H 7.11. Calc. for $\text{C}_{13}\text{H}_{16}\text{O}_2$: C 70.88; H 7.32).

5-Acetyl-7-tert-butylphenazine from 3-acetyl-5-tert-butyl-o-benzoquinone (XX). The quinone XX (75 mg) in chloroform (5 ml) was mixed with *o*-phenylenediamine (75 mg) in chloroform (5 ml) and sodium sulfate (0.1 g). The mixture was kept overnight and then washed with 0.5 N sodium hydroxide solution, 0.5 N sulfuric acid and water. The material obtained on evaporation was recrystallised twice from light petroleum giving rosettes of yellow prisms, m.p. 88–89° (30 mg). (Found: C 78.16; H 6.75; N 9.65. Calc. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}$: C 78.06; H 8.00; N 9.58).

3-(2-Hydroxypropyl)-5-tert-butyl-o-benzoquinone (XXI) from 2-(2-hydroxypropyl)-4,6-di-tert-butylphenol (III). The oxidation was carried out as described above and the crude product was recrystallised from hexane giving the quinone XXI as red rectangular plates, m.p. 102–103.5° (60 %). (Found: C 70.22; H 8.27. Calc. for $\text{C}_{13}\text{H}_{18}\text{O}_3$: C 70.24; H 8.16).

5-tert-Butyl-3-methyl-o-benzoquinone (XXII) from 4,6-di-tert-butyl-2-methylphenol (IV). The oxidation product obtained by the above procedure was recrystallised from hexane, dark red prisms, m.p. 61–62° (65 %). (Found: C 73.96; H 7.96. Calc. for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C 74.13; H 7.92).

3-tert-Butyl-5-methyl-o-benzoquinone (XXIII) from 2,6-di-tert-butyl-4-methylphenol (V). The residue obtained by the above procedure crystallised from light petroleum. The product on recrystallisation from ethanol without heating the solution above 40° gave red prisms, which decomposed on heating, m.p. 115° (Kofler block). Yield about 20 %. (Found: C 74.14; H 7.76. Calc. for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C 74.13; H 7.92).

Treatment of 2,6-dimethylquinonemethide with mesitol (I). A solution of the quinonemethide in isooctane (50 ml) was prepared according to Filarand Winsten²⁷ by oxidation of phenol I (100 mg) with Ag_2O (4 g). After filtration an equal quantity of the phenol I was added and the mixture kept overnight at room temperature. By thin layer chromatography (SiO_2 , CH_2Cl_2 , development with iodine) none of the benzyl ether XVI could be detected in the solution.

4,4'-Dihydroxy-3,5,3',5'-tetramethyldiphenylmethane. A solution of 3,5-dimethyl-4-hydroxybenzyl alcohol (XVIII, 500 mg) in water (80 ml) was treated with 5 N hydrochloric

acid (20 ml). A white precipitate formed slowly; after 1 h 180 mg was filtered off and after 24 h a further 120 mg. The precipitate was identified by m.p. and mixed m.p. 175–176° and by the acetate m.p. 143–145°. ¹¹

Treatment of 3,5-dimethyl-4-hydroxybenzyl 2,4,6-trimethylphenyl ether (XVI) with hydrochloric acid. (a) A mixture of substance XVI (100 mg) and 5 N hydrochloric acid (10 ml) was refluxed for 10 min. Mesityl (I) separated from the water vapour condensate. (b) A mixture of substance XVI (127 mg) and 5 N hydrochloric acid (5 ml) was stirred for 24 h and then filtered. Crystallisation of the precipitate from 50 % acetic acid gave 4,3'-dihydroxy-3,5,2',4',6'-pentamethyldiphenylmethane (XXVII), rods (99 mg, 78 %), m.p. 158–160°. (Found: C 79.56; H 8.07. Calc. for C₁₈H₂₂O₂: C 79.96; H 8.20).

4,3'-Dihydroxy-3,5,2',4',6'-pentamethyldiphenylmethane (XXVII) from 3,5-dimethyl-4-hydroxybenzyl alcohol (XVIII) and mesitol (I). A mixture of mesitol (200 mg) and 5 N hydrochloric acid (50 ml) was stirred while a solution of 3,5-dimethyl-4-hydroxybenzyl alcohol (XVIII, 150 mg) in water (30 ml) was added dropwise over a period of 12 h. The solid material present in the reaction mixture after recrystallisation from dilute acetic acid gave 100 mg of XXVII, identical by m.p. and mixed m.p. (158–160°) with the product obtained from XVI (see above).

The diphenylmethane XXVII, on treatment with acetic anhydride in the presence of perchloric acid ²⁸ gave an acetyl derivative, m.p. 132–132.5°. It is obviously identical with the diacetate C₂₂H₂₆O₄ of m.p. 132° (Ref.⁹) and 133° (Ref.²⁸) obtained from a product C₁₈H₂₂O₂ (m.p. 152° and 153°) reported in Refs.^{9,28}

The identity of the latter product with XXVII was further supported in the following way. In analogy to the procedure described by Fries and Brandes,²⁹ a solution of mesitol (410 mg) in acetic acid (4.1 ml) was mixed with a solution of sodium acetate (0.5 g) in water (2 ml) and the mixture after cooling in ice was treated with a solution of bromine (480 mg) in acetic acid (1 ml). The bromine colour faded rapidly. Ice water was added immediately afterwards, precipitating a yellow oil. A thin layer chromatogram (SiO₂, methylene chloride, development with iodine) showed the presence of diphenylmethanes, *R_F* 0.28, and mesitol, *R_F* 0.55. There was also an unidentified spot, *R_F* 0.19.

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