[Contribution from the Illinois State Geological Survey]

The Oxidation of 2,6-Di-*tert*-butyl-4-methylphenol[1]

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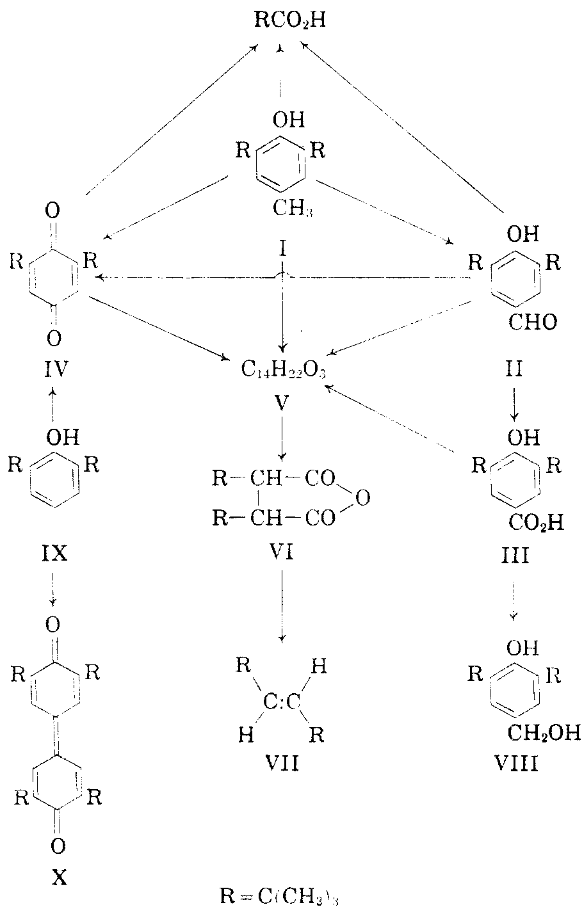
The products formed in the oxidation of 2,6-di-*tert*-butyl-4-methylphenol with oxygen and sodium hydroxide at about 100° are 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde, trimethylacetic acid, an acidic compound $C_{14}H_{22}O_3$, and probably 2,6-di-*tert*-butylbenzoquinone (which was actually isolated in the similar oxidation of the above-named benzaldehyde), in addition to compounds previously reported. Some of the properties of $C_{14}H_{22}O_3$ are given, and the oxidation of it to 2,3-di-*tert*-butylsuccinic anhydride is described, but assignment of structure is reserved pending the completion of more experimental work.

In a study of the initial stages of the oxidation of coal with oxygen gas in the presence of 5% aqueous sodium hydroxide and the effect of methylating the coal upon this oxidation,[3] the relatively mild temperature and pressure conditions of about 100° and about 150 mm. of mercury above atmospheric pressure were selected, as a similar oxidation under higher temperatures and pressures brings about a more far-reaching oxidative degradation than was desired.[4,5] A comparative study of the oxidation of a number of phenols under the same conditions was made subsequently. One of the phenols used was 2,6-di-*tert*-butyl-4-methylphenol; it was chosen because it was thought that the *tert*-alkyl groups in the 2- and 6-positions would protect these positions, resist oxidation themselves, and leave the methyl group in the 4-position open to attack.[6]

The oxidation of 2,6-di-*tert*-butyl-4-methylphenol under various conditions has been studied by a number of other investigators in recent years.[7-15] Many of these investigations were prompted by the fact that this phenol is an effective antioxidant· The current use of it as a food antioxidant[16] makes it highly desirable to identify as many as possible of its oxidation products.

The above-mentioned publication[6] from this laboratory reported the identification of the following oxidation products of this phenol: 3,5,3′,5′-tetra-*tert*-butyl-4,4′-dihydroxy-1,2-diphenylethane and 3,5,3′,5′-tetra-*tert*-butylstilbene-4,4′-quinone in the alkali-insoluble portion of the reaction mixture, and (by Duclaux constants) trimethylacetic acid.

Compounds isolated from the alkali-soluble por-



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[1] Published with permission of the Chief, Illinois State Geological Survey.

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tion are 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde[8,17] (II) and an acidic substance $C_{14}H_{22}O_3$ (V). The isolation and identification of trimethylacetic acid from oxidations of both aldehyde II and quinone IV substantiates the previous evidence (Duclaux constants) of its formation from the phenol I.

The identification of 2,6-di-*tert*-butylbenzoquinone (IV) in a similar oxidation of the aldehyde II suggests that it may be a minor product in this oxidation of the phenol, as well as in that described by Metro.[15]

DISCUSSION

The acidic compound V was prepared by the oxygen-sodium hydroxide oxidation of the aldehyde II, the acid III, and the quinone IV as well as the original phenol I. It is of considerable interest to note that the conversion of the quinone ($C_{14}H_{20}O_2$) to V should require only the addition of the elements of water. However, all attempts to effect this change with hot aqueous alkali alone failed, and when oxygen was also introduced, trimethylacetic acid was obtained as a co-product. Attempts to convert 2,6-di-*tert*-butylphenol (IX) directly to V by a similar alkaline oxidation were also unsuccessful, yielding only the diphenoquinone (X).

Compound V reacts as a monobasic acid; it is soluble in aqueous sodium bicarbonate and may be methylated with diazomethane or with methanol and hydrogen chloride. It gives a positive (red) enol test with ferric chloride and forms both acetyl and benzoyl derivatives. It fails to give a hydrazone with 2,4-dinitrophenylhydrazine, does not absorb bromine from a cold solution in carbon tetrachloride, does not hydrogenate readily with Adam's platinum oxide catalyst, does not give an aryloxyacetic acid with chloroacetic acid and sodium hydroxide, and gives a negative test for the phenolic function with Platkonskaya's phosphomolybdic acid reagent.[18] On oxidation with alkaline potassium permanganate it gives 2,3-di-*tert*-butylsuccinic anhydride (VI), the identity of which is shown by analysis, infrared absorption (Fig. 1), and by the lead dioxide degradation[19] to *trans*-1,2-di-*tert*-butylethylene (VII). The formation of VI indicates that a shift or rearrangement has occurred, bringing the *tert*-butyl groups from their original positions 1,3 to each other to the 1,2 positions. It is believed that the evidence at hand does not warrant drawing a conclusion as to whether such a shift occurs in the formation of V or in its subsequent oxidation to VI; for this reason no structure is now proposed for V.

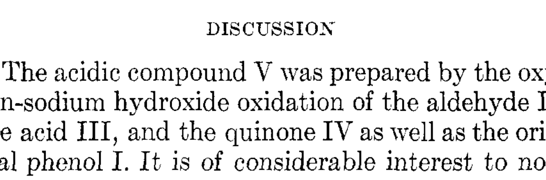

FIG. 1. INFRARED ABSORPTION SPECTRUM OF DI-*tert*-BUTYLSUCCINIC ANHYDRIDE.

EXPERIMENTAL[20]

3,5-Di-tert-butyl-4-hydroxybenzaldehyde (II) *and* $C_{14}H_{22}O_3$ (V) *from 2,6-di-tert-butyl-4-methylphenol* (I). The aqueous alkaline solution remaining after petroleum ether extraction of the large-batch oxidation of 2,6-di-*tert*-butyl-4-methylphenol with oxygen and sodium hydroxide[6] was treated with carbon dioxide until it reached *p*H 8.5; the precipitate was filtered out, digested with 5% hydrochloric acid, washed with water, and dried. This treatment gave 1.6 g. of crude product, thought at first to be an unhindered phenol but subsequently shown to be 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde.[8] After recrystallization from acetone, it melted at 187–189°; its *2,4-dinitrophenylhydrazone* melted at 235–236° corr. Previous investigators have reported 189° and 235–236°, respectively, for the melting points of these compounds.[8,10]

The filtrate from this carbon dioxide precipitation was acidified with 5 *N* sulfuric acid to about *p*H 2 and steam-distilled until about 7 liters of distillate had been collected. This distillate was made basic with sodium hydroxide, concentrated by evaporation to about 100 ml., and acidified again with sulfuric acid. This yielded about 2 g. of solid, which after recrystallization from ethanol melted at 132–133°. Sublimation at 85–100°/2.5 mm. gave a white product, m.p. 134–135° (V), shown by melting point of the mixture to be identical with that prepared from the aldehyde II, and subsequently from III and from IV.

Trimethylacetic acid was not actually isolated from the aqueous filtrate, but its presence was indicated by odor and by Duclaux constants.[6]

3,5-Di-tert-butyl-4-hydroxybenzaldehyde (II). Additional supplies of this aldehyde were prepared in about 70% yields by the bromine oxidation of I as described by Coppinger and Campbell.[9]

$C_{14}H_{22}O_3$ (V), *trimethylacetic acid, and 2,6-di-tert-butylbenzoquinone* (IV) *from the aldehyde* II. 3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde (20 g.) was placed in a flask fitted with two capillary tubes for oxygen inlets, and dissolved in 1 liter of 4 *N* sodium hydroxide. The solution was stirred and heated to 85–90° on a steam-cone and oxygen was introduced at a slow, uniform rate for 48 hours. The reaction mixture then was cooled and acidified to Congo Red with cold 5 *N* sulfuric acid, giving a cream-colored precipitate (A) and filtrate (B). A small amount of orange crystalline material (C) was scraped from the inside of the condenser.

The precipitate A was digested at room temperature in 1 liter of 5% sodium bicarbonate for 30 minutes and was filtered from the crude unreacted aldehyde, which was usually contaminated with silica. The bicarbonate solution was acidified with 5 *N* sulfuric acid, and the precipitate was filtered, dried, recrystallized from medium-boiling petroleum

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(17) The alkali solubility of this compound has been observed also by Dr. T. W. Campbell, private communication to G. R. Y., Oct., 1954.

(18) G. H. Stillson, D. W. Sawyer, and C. K. Hunt, *J. Am. Chem. Soc.*, **67**, 306 (1945).

(19) W. von E. Doering, M. Farber, and A. Sayigh, *J. Am. Chem. Soc.*, **74**, 4370 (1952).

(20) Unless otherwise specified, melting points are not corrected for stem exposure. Analyses by H. S. Clark and Donald Dickerson.

ether and sublimed at 90°/2 mm., which gave 12–30% yields of V, white crystals, m.p. 134–135°.

Anal. Calc'd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31; Mol. wt., 238.32. Found:[21] C, 70.58; H, 9.36; Mol. wt., 250; Neut. equiv., 241; Sapon. equiv. 244.

The acidic filtrate B was distilled until 30% of its volume had been collected as distillate, the distillate was extracted with ether, the ether evaporated, and the residual oily liquid distilled, giving about 2 g. of colorless liquid, b.p. 157–159°, n_D^{37} 1.400; its anilide melted at 128–129°. The literature records, respectively, 163–164,°[22] $n_D^{36.5}$ 1.3931,[23] and 132–133° (128°)[22] for these constants. The infrared absorption curve was identical with that of pure trimethylacetic acid.[24]

The crystals C from the condenser were recrystallized from dilute ethanol, giving less than 0.1 g. of IV, m.p. 62–66°; mixed with authentic 2,6-di-*tert*-butylbenzoquinone,[25] m.p. 63–68°. A similar product from a subsequent run melted at 67–68° and gave an infrared absorption curve identical with that of the authentic quinone.[24]

Recovery of unchanged aldehyde ranged from 60 to 20%.

Results of some qualitative tests on V are given above under DISCUSSION; descriptions of its derivatives will be presented in detail in a subsequent publication.

3,5-Di-tert-butyl-4-hydroxybenzoic acid (III). A mixture of 150 g. of potassium hydroxide, 150 g. of sodium hydroxide, and 40 ml. of water was placed in a 1200-ml. stainless steel beaker equipped with a chromel stirrer, heated to 190° on an electric hot plate, and 30 g. of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde was added slowly with stirring. Some aldehyde was lost by volatilization and the mixture became a lavender color. Heating was continued at 170–190° for 20 hours, the mixture was cooled to room temperature, and 2 liters of water were added. The resultant mixture was heated for 30 minutes, cooled again to 10°, filtered, and the filtrate acidified to Congo Red with 5 *N* sulfuric acid. The crude product was redissolved in sodium bicarbonate solution, filtered, reprecipitated, and recrystallized from 50% *tert*-butyl alcohol, giving 11.2 g. of the benzoic acid III, m.p. 217–218°.

Anal. Calc'd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86; Mol. wt., 250.33. Found: C, 72.23; H, 8.62; Neut. equiv., 254.2.

Lithium aluminum hydride reduction of the acid III, like the similar reduction of the aldehyde II,[9] gave 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol VIII; yield 79%, m.p. 135–136°. Coppinger and Campbell give 137.7–138.1° as the melting point of this compound.[9]

$C_{14}H_{22}O_3$ (V) *from 3,5-di-tert-butyl-4-hydroxybenzoic acid* (III). The oxidation of 1.5 g. of this acid in 300 ml. of 4 *N* sodium hydroxide by a procedure essentially like that applied to the corresponding aldehyde yielded 0.3 g. (21%) of V, m.p. 134–135°.

2,6-Di-tert-butylbenzoquinone (IV). This substance was prepared from 2,6-di-*tert*-butyl-4-methylphenol by the chromic anhydride oxidation of Allen and Burness[12] in 19% yield; m.p. 66.5–68°. A similar oxidation of 2 g. of 2,6-di-*tert*-butylphenol (IX) yielded 1.26 g. (60%) of the same material; in this case purification of the product was readily accomplished by diluting the reaction mixture with two volumes of ice-water, filtering, and recrystallizing from 50% ethanol.

$C_{14}H_{22}O_3$ (V) *from 2,6-di-tert-butylbenzoquinone* (IV). Two g. of this quinone in 100 ml. of 8 *N* sodium hydroxide was treated with oxygen as described above. After 12 hours it was found that much of the quinone had collected in the reflux condenser; this was washed back into the flask with 20 ml. of dioxane and the passage of oxygen was continued another 36 hours. This yielded 1 g. (47%) of V, m.p. 133.5–134.5°. Trimethylacetic acid, identified by isolation and conversion to the *anilide*, m.p. 129.5–131°, was formed also.[22]

Repeated attempts to effect this conversion in hot sodium hydroxide without introducing oxygen were not successful.

Oxidation of 2,6-di-tert-butylphenol (IX). An attempt to oxidize this phenol to V by the oxygen-sodium hydroxide procedure used with the aldehyde II was unsuccessful. The phenol (4 g.) yielded 3.17 g. (80%) of 3,5,3′,5′-tetra-*tert*-butyldiphenoquinone (X), dark red crystals, m.p. 245–246.5°. Hart and Cassis[26] reported this compound, m.p. 245–247°.

Di-tert-butylsuccinic anhydride (VI). One g. of $C_{14}H_{22}O_3$ (V) was dissolved in 100 ml. of an aqueous solution containing 3.5 g. of potassium permanganate and 5 g. of potassium hydroxide and the mixture was stirred constantly at room temperature for 4 to 6 hours. The manganese dioxide was filtered out and washed with warm water and the excess permanganate in the combined filtrate and washings was destroyed with 10% hydrogen peroxide (or 90% formic acid) and 5 *N* sulfuric acid. The acidification resulted in the precipitation of white crystals, which were filtered out, dried, and recrystallized from medium-boiling petroleum ether or sublimed at 90°/2 mm., m.p. 114–115°. The yields varied from 20 to 60%; the higher yields were obtained in the shorter reaction times.

Anal. Calc'd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50; Mol. wt., 212.28. Found: C, 67.98; H, 9.53; Neut. equiv., not acidic; Sapon. equiv., 219. The infrared absorption spectrum is shown in Fig. 1.

Trans-2,2,5,5-tetramethyl-3-hexene (VII). Following a procedure essentially like that of Doering,[19] an intimate mixture of 1 g. of the succinic anhydride (VI), 5 g. of lead dioxide, and 10 g. of clean sand was placed in a 10-ml. distilling flask attached to a 3-ml. test tube cooled with Dry Ice as a receiver. The flask was heated with an oil-bath, the temperature of which was raised gradually to 170 ± 5°. During this heating some white crystals, presumably sublimed VI, appeared in the upper parts of the flask; these melted and ran back as the temperature reached about 125°. During the half-hour that the bath was kept at 170 ± 5°, about 6 drops of liquid distilled out at 118–121° and solidified in the receiver. On being melted, it showed contamination with a few fine crystals, probably of VI; the clear liquid was carefully removed with a pipet. It had a m.p. of (−6)—(−4°), n_D^{20} 1.4113, n_D^{25} 1.4087; it reduced dilute aqueous potassium permanganate and gave an infrared absorption spectrum corresponding to that of *trans*-2,2,5,5-tetramethyl-3-hexene.[27, 28]

The best values for the physical constants of *trans*-2,2,5,5-tetramethyl-3-hexene appear to be those of Howard, *et al.*[29]: b.p. (760 mm.) 125.013°, f.p. −4.75°, n_D^{20} 1.41148, n_D^{25} 1.40890, although Skvarchenko[30] gives n_D^{20} 1.4177.

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(21) C and H values are averages of three analyses.

(22) E. H. Huntress and S. P. Mulliken, *Identification of Pure Organic Compounds. Compounds of Order I*, p. 92. John Wiley and Sons, New York, N. Y., 1946.

(23) *Handbook of Chemistry and Physics*, 37th Edition, p. 1104. Chemical Rubber Publishing Co., Cleveland, Ohio, 1955–1956.

(24) Both curves run in this laboratory by Donald Dickerson.

(25) We are indebted to Dr. D. M. Burness of the Eastman Kodak Co. for the sample of quinone, m.p. 68°. See ref. 12.

(26) H. Hart and F. A. Cassis, Jr., *J. Am. Chem. Soc.*, **73**, 3179 (1951).

(27) American Petroleum Institute, Res. Proj. No. 44 at the Natl. Bur. Standards, *Infrared Absorption Spectrograms*, **Vol. III**, No. 717.

(28) N. Sheppard and D. M. Simpson, *Quart. Revs.* (*London*), **6**, 25 (1952).

(29) F. L. Howard, T. W. Mears, A. Fookson, and P. Pomerantz, *J. Am. Chem. Soc.*, **68**, 2121 (1946).

(30) V. R. Skvarchenko, *Uchenye Zapiski Moskov. Gosundarst. Univ. im. M. V. Lomonosova*, No. 131, 167–248 (1950); *Chem. Abstr.*, **47**, 9895^g (1953).

The constants for the *cis*-isomer of this hydrocarbon have been reported[29, 31] as follows: F.p. < −65°, b.p. 144.2–144.4°/748 mm., n^{20}_{D} 1.4271.

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(31) G. F. Hennion and T. F. Banigan, Jr., *J. Am. Chem. Soc.*, **68**, 1202 (1946).