dimethyl- and dichlorobenzhydryl carbonium ions are 0.04, 0.57, 1.00, 1.13, 1.32 and 1.54, respectively. This is the approximate order which one would predict, assuming the explanation of Gold and Tye[4] to be correct.

It is of interest to note that the spectra of benzhydryl and triphenylcarbonium ions are quite similar.[2] Newman suggests that the steric inhibition to resonance is so great in triphenylcarbonium ions that only two or possibly one ring is involved in resonance. The greater stability of the triphenylcarbonium ions is not attributed to increased resonance, but to greater steric and inductive effects.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF VERMONT]

# Oxidation of Hindered Phenols. III. The Rearrangement of the 2,6-Di-*t*-butyl-4-methylphenoxy Radical

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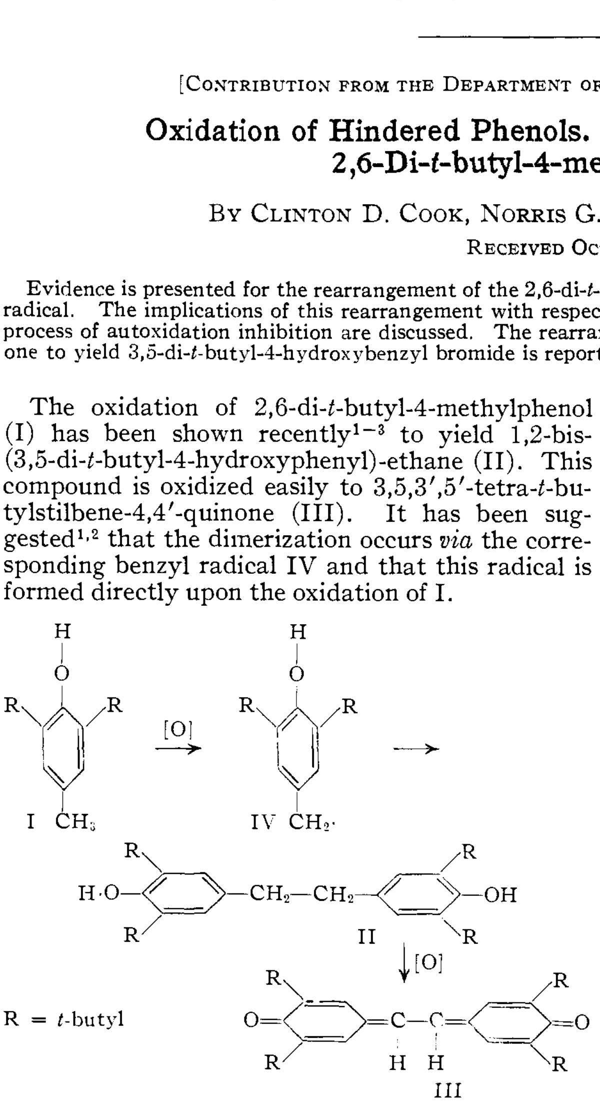
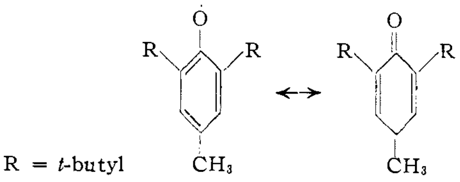
Evidence is presented for the rearrangement of the 2,6-di-*t*-butyl-4-methylphenoxy radical to give the 2,6-di-*t*-butylbenzyl radical. The implications of this rearrangement with respect to the stability of mononuclear phenoxy radicals and on the process of autoxidation inhibition are discussed. The rearrangement of 2,6-di-*t*-butyl-4-methyl-4-bromo-2,5-cyclohexadienone to yield 3,5-di-*t*-butyl-4-hydroxybenzyl bromide is reported.

The oxidation of 2,6-di-*t*-butyl-4-methylphenol (I) has been shown recently[1-3] to yield 1,2-bis-(3,5-di-*t*-butyl-4-hydroxyphenyl)-ethane (II). This compound is oxidized easily to 3,5,3′,5′-tetra-*t*-butylstilbene-4,4′-quinone (III). It has been suggested[1,2] that the dimerization occurs *via* the corresponding benzyl radical IV and that this radical is formed directly upon the oxidation of I.



There is, however, evidence suggesting that the oxidation of I may proceed through the isomeric phenoxy radical V.



V

Thus Campbell and Coppinger[4] have found that I reacts with *t*-butyl hydroperoxide to form 1-methyl-1-*t*-butylperoxy-3,5-di-*t*-butylcyclohexadienone-4. Cosgrove and Waters[5] obtained a similar result with 2,4,6-trimethylphenol and benzoyl peroxide. Finally, it has recently been shown[6] that the oxidation of 2,4,6-tri-*t*-butylphenol produces the corresponding phenoxy radical in excellent yields. Here, of course, the isomeric benzyl radical is an impossibility.

Since oxidative studies on I did not lead to any dimeric products suggestive of the phenoxy radical V, we were led to attempt its preparation by a different route. We have shown[6] that treatment of 2,4,6-tri-*t*-butyl-4-bromo-2,5-cyclohexadienone with alcoholic sodium iodide or with metallic mercury yields the 2,4,6-tri-*t*-butylphenoxy radical. It therefore was expected that similar treatment of 2,6-di-*t*-butyl-4-methyl-4-bromo-2,5-cyclohexadienone[7] (VI) would produce the corresponding phenoxy radical V and that the final product would be a dimer of this radical. When this reaction was performed, the main product was the substituted ethane II derived from the benzyl radical. In addition, I and III were formed. These latter products can best be explained by the oxidation of II by the benzyl radical

Quantitative measurements of the ratio of I to III confirm the stoichiometry indicated above. It therefore appears that the phenoxy radical V readily rearranges to the benzyl radical IV. This is not surprising in view of the advantage of obtaining the benzenoid configuration and the marked stability of the benzyl radical.

A number of cases of rearrangement of 4-bromocyclohexadienones have been reported. Thus, for example, Fries has shown that on gentle heating or long standing 2,5-dichloro-4-methyl-4-bromo-

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(1) C. D. Cook, *J. Org. Chem.*, **18**, 261 (1953).

(2) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 243 (1954).

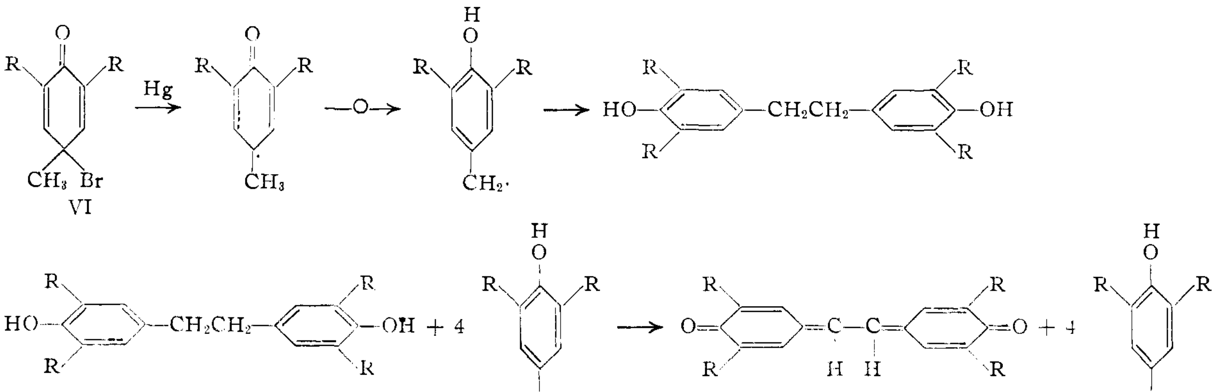
(3) G. R. Yohe, D. R. Hill, J. E. Dunbar and F. M. Scheidt, THIS JOURNAL, **75**, 2688 (1953).

(4) T. W. Campbell and G. M. Coppinger, *ibid.*, **74**, 1469 (1952).

(5) S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 388 (1951).

(6) C. D. Cook and R. C. Woodworth, THIS JOURNAL, **75**, 6242 (1953).

(7) G. M. Coppinger and T. W. Campbell, *ibid.*, **75**, 734 (1953).



R = *t*-butyl

2,5-cyclohexadienone and 2-methyl-5-bromo-4-methyl-4-bromo-2,5-cyclohexadienone[8] rearrange to give the corresponding benzyl bromides. Similarly, we have found that 2,6-di-*t*-butyl-4-methyl-4-bromo-2,5-cyclohexadienone (VI) yields 4-hydroxy-3,5-di-*t*-butylbenzyl bromide. Since the corresponding tri-*t*-butyl compound has been shown to dissociate readily to give radicals,[6] we originally thought that this reaction might be the result of such a dissociation followed by rearrangement of radical V to radical IV and subsequent recombination with the bromine atom. This view was particularly attractive since (a) during rearrangement the reaction mixture was extremely sensitive to oxygen, (b) the rearrangement went rather readily in non-polar solvents, and (c) it has been shown that similar compounds readily effect the side chain bromination of toluene and ethylbenzene.[9] However, preliminary kinetic measurements indicate that this rearrangement is very likely polar in nature as suggested by Coppinger and Campbell.[7] Thus, while the rearrangement shows reasonably good first-order kinetics in non-polar solvents, the rate constant increases with increasing concentration of VI suggesting that the substance provides its own polar atmosphere. The reaction is profoundly sensitive to traces of acids or bases and the rate is markedly affected by solvent. Thus when 0.0125 *M* solutions were maintained at 59.5° for two hours, the extent of rearrangement of VI was 9% in cyclohexane, 44% in benzene and 87% in bromobenzene.

While a number of relatively stable polynuclear phenoxy radicals have been reported[10] there seems to be no record in the literature of a stable[11] mononuclear phenoxy radical other than 2,4,6-tri-*t*-butylphenoxy.[6] A review of the literature of phenolic oxidations coupled with our own work indicates two requirements for such a stable radical: (a) the *ortho* and *para* positions must be substituted to prevent nuclear dimerization, and (b) the substituents must not have $\alpha$-hydrogens. In this respect it is of interest to note that 2,6-di-*t*-butyl-4-methylphenol develops a transient deep blue color on oxidation with alkaline ferricyanide. This color is rapidly masked by the deep orange of III. Similarly, such compounds as 2,4-di-*t*-butyl-6-methylphenol,[2] 2,4,6-trimethylphenol[5] and 2,6-di-*t*-butylphenol[14] give dimeric products upon oxidation. It is impossible to say whether or not the first two dimers are formed *via* the corresponding phenoxy radical and its rearrangement. The present work, however, implies that there is a strong possibility of this being the case. On the other hand, 2,4,6-tri-alkyl phenols without $\alpha$-hydrogens such as 2,4,6-tri-*t*-amylphenol,[15] 2,6-di-*t*-butyl-4-methoxyphenol, 2,6-di-*t*-butyl-4-*t*-butoxyphenol and 2,6-di-*t*-butyl-4-ethoxyphenol[12] all yield stable radicals upon similar oxidation.

The rearrangement carries with it interesting implications concerning the mechanism of autoxidation inhibition. Thus, the fact that dimeric compounds similar to II can be isolated from oxidized hydrocarbon systems which originally contained these phenols does not necessarily mean, as has been suggested[1,3,16] that the reaction leading to these dimers *must* be the attack of a hydrocarbon or hydroperoxide radical upon an $\alpha$-hydrogen. These results indicate that the first step may well be removal of hydrogen from the phenolic hydroxyl.

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## Experimental

**Preparation of 1,2-Bis-(3,5-di-*t*-butyl-4-hydroxyphenyl)-ethane (II) and 3,5,3′,5′-Tetra-*t*-butylstilbene-4,4′-quinone (III).**—These compounds were prepared by the oxidation of 2,6-di-*t*-butyl-4-methylphenol with alkaline ferricyanide. In each case, 20 g. (0.09 mole) of the phenol (I) in 200 ml. of benzene was oxidized with a solution of 180 g. (0.55 mole) of potassium ferricyanide and 32 g. of potassium hydroxide in 300 ml. of water. After stirring at 60° the layers were separated and the volume of benzene reduced. The red stilbenequinone (III) precipitated first, and after recrystallization from benzene and ethanol melted at 315–316°, reported[1] 314–315°. When the oxidation period was 24

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[8] K. Fries and G. Oehmke, *Ann.*, **362**, 1 (1928).

[9] H. Goldhahn, *Österr. Chem. Z.*, **44**, 244 (1941); *C. A.*, **37**, $3745^2$ (1943).

[10] See, for example, W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, New York, N. Y., 1946, p. 72.

[11] By "stable" is meant that the radical be capable of independent existence for a period of at least a few hours. Blue crystals of solid 2,4,6-tri-*t*-butylphenoxy have been isolated[12] and in this state the material has been shown by paramagnetic resonance spectra to be extensively dissociated.[13] Both in the solid state and in solution, this radical does disproportionate slowly, the rate depending upon the concentration.[12]

[12] C. D. Cook and D. A. Kuhn, unpublished work.

[13] Personal communication from S. I. Weissman.

[14] H. Hart and F. A. Cassis, Jr., THIS JOURNAL, **73**, 3179 (1951).

[15] C. D. Cook and P. Fiann, unpublished work.

[16] A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

hours, 8.0 g. (40%) of **pure quinone** was obtained. With an oxidation period of **three hours, 3 g.** (15%) of pure quinone was recovered. On evaporation of the mother liquor from this run and several recrystallizations from glacial acetic acid, 4.0 g. (20%) of pure, nearly white II, m.p. 169–170° (reported 174–175°,[1] 169–170°[2]) was obtained.

A small sample of III was reduced with zinc and acetic acid to give 3,5,3′,5′-tetra-*t*-butyl-4,4′-dihydroxystilbene, m.p. 240–241° (reported 230°,[5] 236°,[2] 240–241°[1]). When equimolar quantities of this compound and III were mixed in diethyl ether a greenish-black quinhydrone, m.p. 276–280°, precipitated. It was not investigated further.

**Preparation of 2,6-Di-*t*-butyl-4-methyl-4-bromo-2,5-cyclohexadienone (VI).**—This compound was prepared by the method of Coppinger and Campbell; bromination of the phenol I in acetic acid and water. In order to obtain a pure product it was found necessary to add the bromine dropwise, and to filter the product and recrystallize it (from petroleum ether, Eastman Kodak P-950) immediately. Under these conditions, product having the reported melting point (91.0–91.3°) was easily obtained.

**Reaction of the Bromo Compound VI with Mercury.**—Five grams of the bromo compound VI was placed in a 300-ml. florence flask, 100 ml. of oxygen-free benzene added, and, after flushing with oxygen-free nitrogen,[17] 5 ml. of mercury was added and the flask sealed at the torch. On initial shaking the solution turned a bluish-green. This was soon replaced by the orange color characteristic of III. After shaking for one hour, the seal was broken, and the contents transferred through a filter to an evacuated flask where the benzene was evaporated, essentially by a process of flask distillation. The weight of orange-red solid recovered corresponded to the theoretical value (3.65 g.) after the loss of the bromine atom from VI.

The product contained 2,6-di-*t*-butyl-4-methylphenol (I), 1,2-bis-(3,5-di-*t*-butyl-4-hydroxyphenyl)-ethane (II) and 3,5,3′,5′-tetra-*t*-butylstilbene-4,4′-quinone (III). It was possible to separate I from II and III essentially quantitatively (±5%), by sublimation at 70° to constant weight. In one run 0.8164 g. of reaction product gave 0.0363 g. (4.45%) of I. The sublimed material melted at 68.5–69.5°, an authentic sample at 69.0–69.7° and the mixed melting point was 68.5–69.5°. Determination of the stilbenequinone III using a Bausch and Lomb monochromatic colorimeter with a 550 m$\mu$ interference filter gave a value of 2.38%. This gives a weight ratio of I to III of 1.87. For four moles of I per mole of III, theory gives a ratio of 2.03 (see eq. 2). A repeat run gave a value of 1.90. After removal of I by sublimation, recrystallization of the residue from glacial acetic acid gave an 80% yield of II which showed no depression in a mixture melting point with an authentic specimen.

**Reaction of the Bromo Compound VI with Sodium Iodide.**—Under a nitrogen atmosphere, 2 g. (0.015 mole) of sodium iodide was dissolved in hot acetone, and 2 g. (0.0067 mole) of the bromo compound VI was added. After ten minutes the iodine was removed by addition of sodium thiosulfate and the solution extracted with ether. The ether was evaporated and the red-orange product recrystallized from glacial acetic acid. The yield was 0.4 g. (27%) of pale yellow crystals of II, m.p. 167.5–169.0°. A mixture melting point with an authentic sample of II showed no depression. Similar results were obtained when isopropyl alcohol was used as the solvent.

**Rearrangement of the Bromo Compound VI.**—Rearrangement was carried out by heating in petroleum ether solution, by melting VI on a steam-bath, and by allowing the material to stand for several weeks in a sealed tube. During rearrangement the reaction mixture was extremely sensitive to oxygen, developing a deep orange-red color and becoming extremely difficult to purify.

The most convenient method was to melt the solid on a steam-bath under a nitrogen atmosphere. After a 10-g. sample was heated for five minutes on the steam-bath, 30 ml. of oxygen-free petroleum ether (Eastman Kodak P-950) was added and the resulting solution cooled with Dry Ice and acetone to cause crystallization. The white crystals were washed with cold petroleum ether and dried under a stream of nitrogen at the Dry Ice temperature. Ten grams of VI gave 7 g. (70%) of product (m.p. 51–53°) after three such recrystallizations. *Anal.* Calcd. for $C_{15}H_{23}OBr$: C, 60.20; H, 7.75; Br, 26.70. Found: C, 60.02; H, 7.41; Br, 26.57. The product did not react with alcoholic sodium iodide to produce iodine as did the starting compound nor did it react with mercury. A 20% carbon tetrachloride solution showed the characteristic infrared hydroxyl adsorption at 3650 ± 5 cm.$^{-1}$ and there was no indication of hydrogen bonding in the region from 3300–3500 cm.$^{-1}$ (We wish to thank Mr. Earl C. Curtis, Jr., for making this measurement.)

A 0.2-g. sample of the benzyl bromide was dissolved in 50 ml. of acetone and 0.5 ml. of water added. After standing several hours, the solvent was evaporated and the residue recrystallized from ligroin (Eastman Kodak P-1628) to give a 70% yield of 3,5-di-*t*-butyl-4-hydroxybenzyl alcohol, m.p. 139–141° (uncor.). This alcohol was synthesized by reduction of the corresponding benzaldehyde with lithium aluminum hydride according to the method of Coppinger and Campbell. The product melted at 139–141° (uncor.), reported 137.7–138.1°. The mixture melting point was also 139–141°.

**Kinetic Measurements.**[18]—Freshly prepared bromo compound VI was weighed out and dissolved in the appropriate amount of solvent. Ten-milliliter aliquots were placed in separate, ground-glass stoppered test-tubes, flushed with carbon dioxide, wrapped with foil, and placed in the constant temperature bath. After the desired time interval, a tube was removed and its contents washed into a flask containing 50 ml. of isopropyl alcohol, 3 ml. of glacial acetic acid and about 3 g. of sodium iodide. During this transfer the flask was flushed with a stream of carbon dioxide. The sample was then heated on a boiling water-bath (reflux condenser) for ten minutes under a blanket of carbon dioxide and the iodine titrated with standard thiosulfate. Known samples gave results to within ±1% of theory. The cyclohexane and benzene were dried over sodium wire and the bromobenzene over calcium sulfate. All were distilled shortly before using. Runs were done in duplicate. While individual runs gave good first-order kinetics, the rate constant was extremely sensitive to conditions, being sensitive to acids and bases and to the purity of VI. Since VI is rather unstable, the purity of VI was probably the greatest obstacle to precise results. For four runs, each made from a separate batch of VI, the first-order rate constant was $3.92 \pm 0.28 \times 10^{-5}$ sec.$^{-1}$ at 59.50° in benzene solution with an initial concentration of 0.0125 *M*.

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[17] L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

[18] Work by Mr. Ronald C. Chisholm.