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Oxidation of Hindered Phenols. X. Effect of 4-Substituents upon the Behavior of 2,6-Di-*t*-butylphenoxy Radicals

CLINTON D. COOK AND NILES D. GILMOUR

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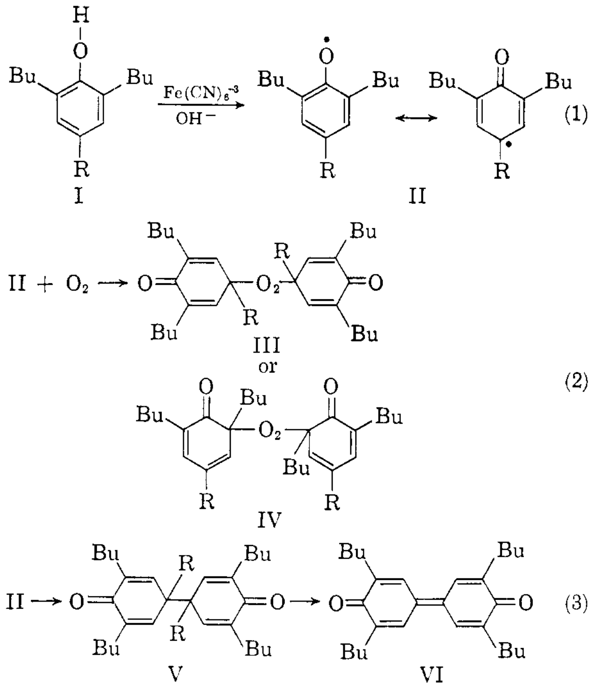
It is now established that the oxidation of trisubstituted phenols having bulky *ortho* substituents may produce phenoxy radicals of considerable stability.[1] As the reactions of such phenoxy radicals vary with the *para* substituent, it was of interest to prepare a series of 2,6-di-*t*-butylphenols having a variety of substituents in the 4-position and to study their behavior in the various reactions typical of phenoxy radicals (Equations 1–3).



Bu = *t*-butyl

Specific compounds are designated throughout the text by symbols after the number, indicating the nature of R. Substituents considered are phenyl, triphenylmethyl, benzhydryl, chloro, bromo, nitro, cyano, benzoyl, acetyl, α-methoxyethyl, and *t*-butyl.

As evidenced by the formation of an intense color on oxidation of the appropriate phenols with an alkaline ferricyanide solution and by subsequent reactions, the following radicals were of at least moderate stability (*i.e.*, capable of existence for at least a few minutes at room temperature): II-C_6H_5 (violet), II-$(C_6H_5)_3C$ (green), II-$(C_6H_5)_2CH$ (blue), II-CN (blue), II-C_6H_5CO (blue), II-CH_3CO (blue), and II-$CH(CH_3)OCH_3$ (blue).[2]

Radicals II-C_6H_5, II-$(C_6H_5)_3C$, II-CN, II-C_6H_5CO, and II-CH_3CO underwent reaction with oxygen much less readily than does 2,4,6-tri-*t*-butylphenoxy[7] (II-*t*-C_4H_9), the rates, as judged by loss of radical color, being in the order II-C_6H_5 > II-$(C_6H_5)_3$ > II-C_6H_5CO > II-CN. II-C_6H_5 reacted with oxygen at not more than one tenth the rate of II-*t*-C_4H_9, and II-CN at not more than one hundredth the rate of II-*t*-C_4H_9. Acceptable yields of peroxides III-C_6H_5 and IV-C_6H_5CO were obtained from the corresponding radicals. Radical II-$(C_6H_5)_3C$ gave an unidentified product which either was not a peroxide of type III or IV or which had a unique mode of decomposition as it did not initiate polymerization of acrylonitrile. The lowered reactivity of these radicals toward oxygen may be due to the increased opportunities for resonance stabilization[8] in the cases of II-C_6H_5, II-CN, and II-C_6H_5CO or in part to a lowered electron density on the *para* carbon. In this respect it is interesting to note that room temperature treatment of the silver salt of tribromophenol with benzene containing a trace of iodine, warming the salt with benzene, or treatment of 2,4,4,6-tetrabromo-2,5-

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(1) For leading references see (a) C. D. Cook and B. E. Norcross, *J. Am. Chem. Soc.* **81**, 1176 (1959); and (b) E. Müller, A. Shick, and K. Scheffler, *Ber.* **92**, 474 (1959).

(2) Since the completion of this work Müller and co-workers have published rather complete descriptions of radicals II-C_6H_5[1b] and II-CN[3a,3b] and have very briefly mentioned radicals II-$(C_6H_5)_3C$[4a] and II-C_6H_5CO.[4b] Radical II-C_6H_5 was first reported[5] in connection with an EMR study but its chemistry was not defined at that time. Reactions which almost certainly must involve radical II-C_6H_5 have also been reported recently but the radical was not observed directly.[6]

(3) (a) K. Ley, K. Scheffler, A. Rieker, and E. Müller *Z. Naturforsch.* **13b**, 460 (1958).

(3) (b) E. Müller, A. Rieker, K. Ley, R. Mayer, and K. Scheffler, *Ber.* **92**, 2278 (1959).

(4) (a) E. Müller, R. Mayer, and K. Ley, *Angew. Chem.* **76**, 73 (1958).

(4) (b) E. Müller, K. Ley, K. Scheffler, and R. Mayer, *Ber.* **91**, 2682 (1958).

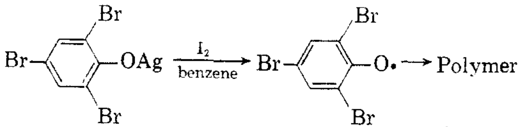
(5) J. E. Wertz, C. F. Koelsch, and J. L. Vivo, *J. Chem. Phys.* **23**, 2194 (1955).

(6) W. R. Hatchard, R. G. Lipscomb, and F. W. Stacy, *J. Am. Chem. Soc.* **80**, 3636 (1958).

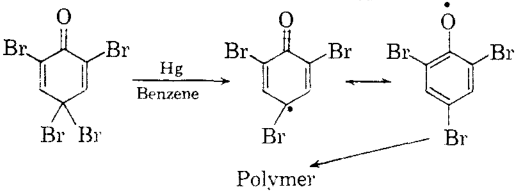
(7) C. D. Cook and R. G. Woodworth, *J. Am. Chem. Soc.* **75**, 6242 (1953).

(8) See G. M. Coppinger, *J. Am. Chem. Soc.* **79**, 501 (1957); K. Dimroth, F. Kalk, and G. Neubauer, *Ber.* **90**, 2058 (1957); and ref. 10.

cyclohexadiene-1-one with mercury yields a brilliant blue solution which over a period of an hour or so yields a polymeric material.[9–11] (See Eqs. 4 and 5.) Saturation of such solutions, which presumably contain the 2,4,6-tribromophenoxy radical, with oxygen does not produce a peroxide; nor is there any apparent diminution of the intensity of the blue color. Apparently the tribromophenoxy radical is also relatively unreactive toward oxygen.

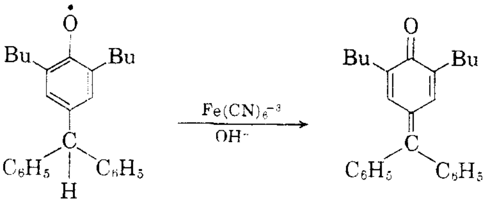


(4)



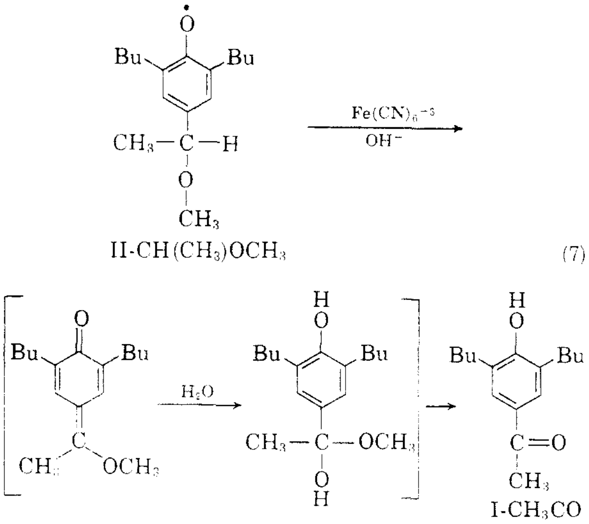
(5)

The phenoxy radicals II-$(C_6H_5)_2CH$ and II-$CH(CH_3)OCH_3$ underwent fairly rapid further oxidation either by disproportionation or with excess alkaline ferricyanide. Radical II-$(C_6H_5)_2CH$ gave the expected[1a] compound, 2,6-di-*t*-butyl-4-benzhydrylidine-2,5-cyclohexadiene-1-one (see Eq. 6), and II-$CH(CH_3)OCH_3$ gave 2,6-di-*t*-butyl-4-acetylphenol (I-CH_3CO), presumably by way of hydration of an intermediate quinonemethide and subsequent cleavage of the hemi ketal (Eq. 7). Further oxidation of I-CH_3CO produced a fairly stable phenoxy radical, II-CH_3CO.



II-$(C_6H_5)_2CH$

(6)



II-$CH(CH_3)OCH_3$

(7)

I-CH_3CO

Alkaline ferricyanide oxidation of the *p*-chloro (I-Cl) and *p*-bromo (I-Br) phenols gave dimeric products, V-Cl and V-Br, presumably by way of radicals II-Cl and II-Br.[12] The ultraviolet spectrum of V-Cl was almost identical with 1,1′-dihydro-3,5,3′5′ - tetra - *t* - butyl - 2,5,2′5′ - biscyclohexadiene-4,4′-one (V, R = H) produced from 2,6-di-*t*-butylphenol by Kharasch and Joshi.[13] Compound V-Br was an ill-defined, impure solid which evolved bromine on standing at room temperature, on warming, or on solution in ethanol, to produce the corresponding diphenoquinone (VI). Shaking either V-Cl or V-Br with mercury also gave VI. In view of the reversibility of the addition of bromine to 2,4,6-tri-*t*-butylphenoxy (II-t-C_4H_9)[7] these reactions are not surprising. Müller[4] has recently prepared the same compounds (V-Cl and V-Br) by oxidation of I-Cl and I-Br with II-*t*-C_4H_9, and reports identical behavior.

Oxidation of the *p*-nitrophenol (I-NO_2) with alkaline ferricyanide yields directly the diphenoquinone VI. This result is reminiscent of the loss of a carboxyl group on oxidation of 3,5-di-*t*-butyl-4-hydroxy benzoic acid.[14] The ready reversibility of addition of nitrogen dioxide to II-*t*-C_4H_9[7] makes a dimer of type V a very reasonable intermediate. However, all attempts to isolate such a product failed.

EXPERIMENTAL

A. *Preparation of the phenols.* Phenols I-C_6H_5,[15] I-Cl,[16] I-Br,[17] and I-CN[17] were prepared by known methods and had the properties cited in the original literature. Compound I-NO_2 was kindly supplied by H. Shapiro of the Ethyl Corporation, recrystallized from ethanol, m.p. 153–154°.

2,6-Di-t-butyl-4-triphenylmethylphenol (I-$(C_6H_5)_3C$). A solution of 20.6 g. (0.01 mole) of 2,6-di-*t*-butylphenol and 26.0 g. (0.01 mole) of triphenylcarbinol in 75 ml. of glacial acetic acid was treated with 5 ml. of concd. sulfuric acid at room temperature. After 5 hr. the crystals were filtered, washed with water, and recrystallized from ethanol to give 22 g. (50%) of colorless crystals, m.p. 179.5–180°; λ_{max} 284 mμ; ϵ_{max} 2650 (cyclohexane).

Anal. Calcd. for $C_{33}H_{36}O$: C, 88.15; H, 8.07. Found: C, 88.41; H, 8.09.

2,6-Di-t-butyl-4-diphenylmethylphenol (I-$(C_6H_5)_2CH$)—. A solution of 4.0 g. (0.02 mole) of 2,6-di-*t*-butylphenol and 3.6

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(9) Unpublished work with John A. Eberwein.

(10) See W. H. Hunter, A. O. Olson, and E. A. Daniels, *J. Am. Chem. Soc.* **38**, 1761 (1916); W. H. Hunter and G. H. Woolett, *J. Am. Chem. Soc.* **43**, 131 (1921).

(11) G. Staffin and C. C. Price have obtained similar polymers from 2,6-dimethyl-4-bromophenoxy. *Rubber World* **139**, 408 (1958). See also A. S. Hays, H. S. Blanchard, G. F. Endres, J. W. Eustance, *J. Am. Chem. Soc.* **81**, 6335 (1959).

(12) For evidence of the transient existence of a similar reactive phenoxy radical, 2,6-di-*t*-butylphenoxy, see E. Müller, K. Ley, and G. Schlehte, *Ber.* **91**, 2670 (1958).

(13) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.* **22**, 1435, 1439 (1957).

(14) C. D. Cook, E. S. English, and B. J. Wilson, *J. Org. Chem.* **23**, 755 (1958).

(15) G. H. Stillson, D. W. Sawyer, and C. K. Hunt, *J. Am. Chem. Soc.* **67**, 303 (1945).

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

(17) L. A. Cohen, *J. Org. Chem.* **22**, 1333 (1957).

g. (0.02 mole) of benzhydrol in 50 ml. of glacial acetic acid was treated with 2.5 ml. of concd. sulfuric acid at room temperature. After 3 hr. the resulting crystals were filtered, washed with water, and recrystallized from *n*-hexane to give 7.5 g. (~100%) of colorless crystals, m.p. 134–134.5°, λ_{max} 284 mμ; ϵ_{max} 2980.

2,6-Di-butyl-4-benzoylphenol (I-C_6H_5CO)—. Aluminum chloride, 13.3 g. (0.1 mole), was added to 40 ml. (0.43 mole) of freshly distilled benzoyl chloride and the flask swirled until complex formation seemed to be complete. Using an ice bath to keep the temperature below 25°, 20.6 g. (0.1 mole) of 2,6-di-*t*-butylphenol was slowly added. The mixture was allowed to stand for an hour in an ice bath, then taken up in benzene, and washed with 4*M* sodium hydroxide. Evaporation of the benzene and recrystallization from petroleum ether (b.p. 90–120°) gave 17 g. (55%) of white crystals, m.p. 124–125°. A mixture melting point with an authentic specimen[18] gave no depression.

2,6-Di-t-butyl-4-acetylphenol (I-CH_3CO)—. At 0°, 3.5 g. (0.25 mole) of aluminum chloride was added to 25 ml. of acetyl chloride and, when solution was complete, 4.12 g. (0.02 mole) of 2,6-di-*t*-butylphenol was slowly added. After 45 minutes the mixture was poured into diluted hydrochloric acid containing cracked ice and then extracted with *n*-hexane. Evaporation of the excess hexane gave 3.2 g. (70%) of white crystals, m.p. 145–148°, recrystallized from *n*-hexane, m.p. 147–148°.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74; MW, 248.35; Found: C, 77.39; H, 9.87; MW, 255 (cryoscopic, benzene).

2,6-Di-t-butyl-4-(α-methoxyethyl)phenol (I-CH(CH_3*)OCH*$_3$) was prepared by the addition of methanol to 2,6-di-*t*-butyl-4-ethylidene-2,5-cyclohexadiene-1-one according to the method of Cook and Norcross.[1a] The material was obtained in essentially quantitative yields, m.p. 105–105.5° after recrystallization from acetonitrile-water solutions.

Anal. Calcd. for $C_{17}H_{28}O_2$: C, 77.22; H, 10.62; MW, 264.39; Found: C, 77.56; H, 10.18; MW, 261 (cryoscopic, benzene).

B. *Preparation of peroxides.* The peroxides were prepared by oxidizing the phenols with a twofold excess of alkaline potassium ferricyanide solution in oxygen-saturated benzene.[7]

Bis(1,5-di-t-butyl-3-benzoyl-2,4-cyclohexadiene-6-one) peroxide (IV-C_6H_5CO)—. Two grams of I-C_6H_5CO gave 0.22 g. (8%) of the above peroxide, m.p. 132–134° dec. after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{42}H_{50}O_6$: C, 77.51; H, 7.74. Found: C, 77.70; H, 7.68.

The ultraviolet spectrum λ_{max} 262 mμ, ϵ_{max} 23,000; λ_{max} 317 mμ, ϵ_{max} 5000 (cyclohexane) indicates that this peroxide has the structure IV-C_6H_5CO.[19] When 0.1% of the peroxide was added to acrylonitrile and the solution warmed to 70° under a nitrogen atmosphere, polymer started to precipitate within 2 min.

Bis(3,5-di-t-butyl-1-phenyl-2,5-cyclohexadiene-4-one) peroxide (III-$(C_6H_5)_3C$)—. Oxidation of 2 g. of I-C_6H_5 for 8 hr. gave 1.8 g. (87%) of light yellow crystals, m.p. 145–147° dec. after recrystallization from acetonitrile; reported,[1b] m.p. 146–148° dec.

C. *Preparation of dimers.* A mixture of 10 g. of potassium ferricyanide, 2 g. of potassium hydroxide, 75 ml. of water, and 50 ml. of benzene was placed in a flask and flushed with oxygen-free nitrogen. A solution of 0.01 to 0.02 mole of the appropriate phenol (I-Cl, I-Br, I-NO_2) in 25 ml. of benzene was rapidly added and the mixture vigorously stirred for 2 to 5 min. The solutions were separated and the benzene layer dried and taken to dryness in a rotary vacuum drier.

1,1′-Dichloro-3,5,3′5′-tetra-t-butyl-bis-2,2′,5,5′-cyclohexadiene-4,4′-one (V-Cl)—. Oxidation of 2.6 g. (0.01 mole) of I-Cl as above gave 2.09 g. (77%) of the above dimer V-Cl, recrystallized from ethyl acetate to m.p. 148.5–150°; reported,[12] m.p. 150–151°; λ_{max} 242 mμ, ϵ_{max} 16,600 (cyclohexane).[20]

Anal. Calcd. for $C_{28}H_{40}O_2Cl_2$: C, 70.13; H, 8.41; Cl, 14.79; MW, 479.51; Found: C, 70.48; H, 8.49; Cl, 14.75; MW, 482 (cryoscopic, benzene). Attempted recrystallization from ethanol or shaking a benzene solution with mercury gave quantitative yields of diphenoquinone (VI) as identified by comparison of ultraviolet spectra and mixture melting points with an authentic specimen.[14]

Oxidation of 2.85 g. (0.01 mole) of I-Br as above gave 2.3 g. (81%) of impure yellow crystals which decomposed over a wide temperature range (110° up) and which decomposed on standing, on solution in polar solvents, or on shaking in benzene with mercury to give the diphenoquinone VI. The material showed an ultraviolet max at 242 mμ, ϵ_{max} = ~25,000 and gave a molecular weight (cryoscopic, benzene) of 538. Calculated for V-Br, 570.6.

Very rapid oxidation of I-NO_2 with limiting amounts of ferricyanide gave only the diphenoquinone VI and unchanged I-NO_2. Use of excess ferricyanide led to quantitative yields of VI.

D. *Other oxidations. 2,6-Di-t-butyl-4-benzhydrylidine-2,5-cyclohexadiene-1-one*—. A solution of 3 g. (0.08 mole) of I-$(C_6H_5)_2CH$ in 25 ml. of benzene was stirred with 20 g. (0.06 mole) of potassium ferricyanide and 10 g. (0.25 mole) of sodium hydroxide in 100 ml. water. The solution turned brilliant blue and gradually faded to deep orange. Removal of the benzene and recrystallization of the residue gave 2.6 g. (87%) of orange crystals, m.p. 178.5–179°, λ_{max} 261 mμ, ϵ_{max} 16,700 (cyclohexane).

Anal. Calcd. for $C_{27}H_{30}O$: C, 87.30; H, 8.15. Found: C, 87.40; H, 8.10.

Oxidation of 2,6-di-t-butyl-4-methylmethoxymethylphenol (I-CH(CH_3*)OCH*$_3$*) to 2,6-di-t-butyl-4-acetylphenol (I-CH*$_3$*CO)*—. A solution of 730 mg. (0.0027 mole) of I-CH-$(CH_3)OCH_3$ in 20 ml. benzene was oxidized with a solution of 5 g. (0.011 mole) potassium ferricyanide and 1 g. (0.025 mole) of sodium hydroxide in 25 ml. of water. The layers were separated and the benzene layer was washed with water and dried over sodium sulfate. After removal of the benzene 140 mg. (20%) of product was obtained, m.p. 144–147°. Mixed melting point and infrared spectrum showed the sample to be identical with I-CH_3CO.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF VERMONT
BURLINGTON, VT.

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[18] T. H. Coffield, A. H. Filbey, G. C. Ecke, and A. J. Kolka, *J. Am. Chem. Soc.* **79**, 5023 (1957).

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

[20] Reported for V, R = H, λ_{max} 242 mμ, ϵ_{max} = 15,000 ref. 13.

Hexachloroacetone as a Novel Source of Dichlorocarbene

PANKAJA K. KADABA AND JOHN O. EDWARDS

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Edwards, Evans, and Watson[1] carried out an electrometric study on dilute aqueous solutions of

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[1] E. G. Edwards, D. P. Evans, and H. B. Watson, *J. Chem. Soc.*, 1942 (1937).