Sodium Nitrite–Sodium Hydrogen Phthalate Filter Solution.—A solution of 1 g of 2,6-di-*t*-butyl-*p*-benzoquinone in 100 ml of ethanol was irradiated through a sodium nitrite–sodium hydrogen phthalate filter solution (λ >400 mμ) for 48 hr with a 275-W G.E. sun lamp. Evaporation of the solvent gave an orange oil which when triturated with hexane afforded a solid. This solid upon recrystallization from benzene–hexane gave 2-(2-ethoxy-2-methyl-1-propyl)-6-*t*-butylhydroquinone,[1] 0.277 g (23%), mp 125–127°.

Registry No.—IVa, 137-18-8; IVb, 4754-26-1; ethylhydroquinone dimethyl ether, 1199-08-2; β-methoxyhydroquinone dimethyl ether, 16162-59-7; IVc, 4197-79-9; IVe, 16162-61-1; dimethyl-2-(2-methoxy-1-propyl)-5-*n*-propylhydroquinone, 16162-62-2; dimethylbis-2,5-(2-methoxy-1-propylhydroquinone, 16203-63-7; IVf, 490-91-5; dimethyl-2-(2-methoxy-1-propyl)-5-methylhydroquinone, 14753-10-7; 2,6-dimethyl-5-methoxybenzofuran, 14753-09-4; 2-(2-methoxy-1-propyl)5-methylhydroquinone, 16162-65-5; 2,6-dimethyl-5-hydroxybenzofuran, 16162-66-6; 2,6-di-*t*-butyl-*p*-benzoquinone, 719-22-2.

Notes

The Cuprous Chloride–Amine Catalyzed Oxidation of 2,6-Di-*t*-butyl-*p*-cresol with Oxygen

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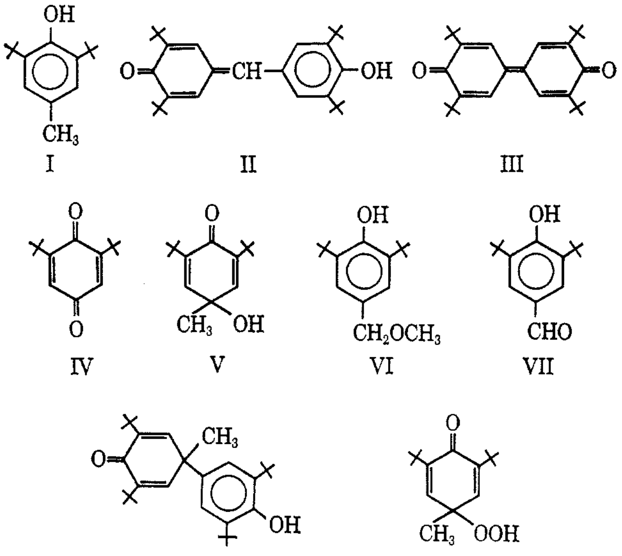
Received February 2, 1968

Recently, the air oxidation of 2,6-di-*t*-butyl-*p*-cresol (I) in alkaline ethanol was reported to give the demethylated dimers 2,6-di-*t*-butyl-4-(4-hydroxy-3,5-di-*t*-butylbenzylidene)-2,5-cyclohexadien-1-one (II) and 3,5,3′,5′-tetra-*t*-butyldiphenoquinone (III) (Chart I).[1] We now describe the formation of III and a different demethylated dimer, 2,6-di-*t*-butyl-4-methyl-4-(3,5-di-*t*-butyl-4-hydroxyphenyl)-2,5-cyclohexadien-1-one (VIII), among six identifiable products in the cuprous chloride–amine catalyzed reaction of I with oxygen.[2a] Based upon the earlier work of Kharasch and Joshi[2b] and the data obtained in the present investigation, a reasonable mechanism has been proposed to account for the over-all oxidation reaction.

The oxygenation of I in methanol solution using a cuprous chloride–amine catalyst gave six identifiable products which constituted 73% (weight) of the total reaction mixture. These products were (1) 3,5,3′,5′-tetra-*t*-butyldiphenoquinone (III, 5%); (2) 2,6-di-*t*-butyl-*p*-benzoquinone (IV, 27%); (3) 2,6-di-*t*-butyl-4-methyl-4-hydroxy-2,5-cyclohexadien-1-one (V, 14%); (4) 3,5-di-*t*-butyl-4-hydroxybenzylmethyl ether (VI, 14%); (5) 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (VII, 12%); (6) 2,6-di-*t*-butyl-4-methyl-4-(3,5-di-*t*-butyl-4-hydroxyphenyl)-2,5-cyclohexadien-1-one (VIII, 2%) (see Chart I). All of these compounds have been previously described as low-yield oxidation products of I under varied conditions.[1,3] The hydroperoxide IX which was isolated in the reaction of I with oxygen in ethanolic potassium hydroxide was observed to decompose to V (45%) and an unknown compound, mp 159–160° (20%).[2] This latter compound was identical with the product VIII (mp 154–156°) isolated from the oxygenation described herein, based upon the identity of the infrared, ultraviolet, and nmr spectra.

CHART I



Conclusive evidence for the structural assignment VIII to the compound, mp 154–156°, was provided by several spectroscopic methods. The dimeric structure of VIII was evident on the basis of molecular weight determination [Calcd for $C_{29}H_{44}O_2$: mol wt, 424. Found: mol wt, 424 (mass spectrometry)]. The infrared spectrum possessed both a nonbonded hydroxyl absorption at 3640 cm^{-1} and a cross-conjugated dienone absorption at 1660 and 1640 cm^{-1}. The ultraviolet spectrum had absorption maxima at 237 mμ (ε 21,188) and 274 (2510) and is consistent

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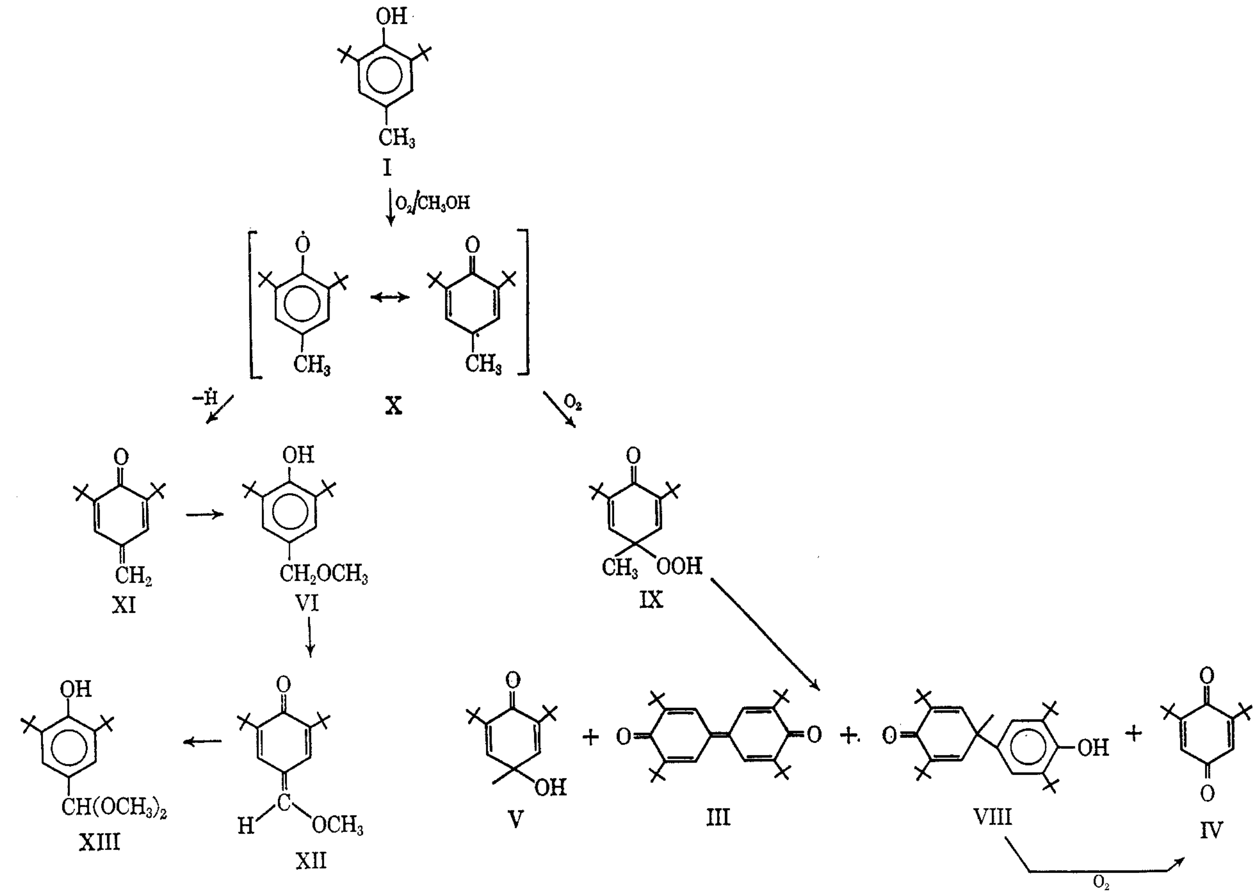
(1) C. H. Brieskorn and K. Ullmann, *Chem. Ber.*, **100**, 618 (1967).

(2) (a) For a recent review of the cuprous chloride–amine–oxygen system in phenol oxidation see, A. S. Hay, *Adv. Polymer Sci.*, **4**, 496 (1967); (b) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957).

(3) (a) L. V. Gorbunova, N. S. Vasileiskaya, M. L. Khidekel, and B. A. Razuvaev, *J. Org. Chem. USSR*, **2**, No. 7, 1227 (1967); (b) J. I. Wasson and W. M. Smith, *Ind. Eng. Chem.*, **45**, 197 (1953); (c) S. J. Metro, *J. Amer. Chem. Soc.*, **77**, 2901 (1955); (d) E. Muller, A. Rieker, K. Ley, R. Mayer, and K. Scheffler, *Ber.*, **92**, 2278 (1959); (e) J. Sugita, *Nippon Kagaku Zasshi*, **87**, 1082 (1966) [*Chem. Abstr.*, **66**, 9477*w* (1967)].

CHART II



with a 4,4-arylalkylcyclohexadienone structure.[4] The evidence thus far indicates the compound to be a dimeric phenol-substituted cyclohexadienone. More conclusive data which indicated VIII to be the correct structure was obtained from nmr analysis[3e] ($CDCl_3$, τ): 8.77 (18 H, *t*-Bu quinoid ring), 8.60 (18 H, *t*-Bu aromatic ring), 8.41 (3 H, CH_3), 4.88 (1 H, -OH), 3.45 (2 H, quinoid ring H), and 2.95 (2 H, aromatic H).

The mechanism of the reactions of oxygen and hydroperoxides with I have been examined by several groups.[2,5,6] The products formed in these reactions have been explained on the basis of the intermediacy of corresponding resonance stabilized phenoxycyclohexadienone radical (X)[2,6,7] of I. The phenoxy radical of I has been demonstrated to decay to I and the corresponding quinone methide XI and the latter in turn formed the 1,2-bis(3,5-di-*t*-butyl-4-hydroxyphenyl)ethane and 3,3′,5,5′-tetra-*t*-butyl-4-4′-stilbenequinone.[7]

Formation of the products that we have obtained can be explained *via* the intermediacy of both the quinone methide XI and the cyclohexadienone radical (X) (see Chart II). The initially formed phenoxy radical could produce the quinone methide XI which in methanolic solution would lead to the benzyl methyl ether (VI) by a rapid 1,6 addition. Further oxidation of VI to the methoxyquinone methide XII and methanol addition to the latter would give the acetal (XIII).[8] The conditions under which the reaction was quenched would hydrolytically convert the acetal into the aldehyde VII. The absence of the stilbenequinone-type dimer in this reaction does not preclude the intermediacy of the quinone methide XI since the latter has been observed to undergo 1,6-type additions more rapidly than dimerization.[9]

The initially formed phenoxy radical can also react as the cyclohexadienone radical leading to the formation of the hydroperoxide IX. This hydroperoxide has been established as the source of the other products isolated. When IX was oxygenated under the same conditions as I, the following products were observed: (1) III, 5%; (2), IV, 2%; (3) V, 58%; (4) VIII, 2%. While a small yield of the *p*-benzoquinone IV was obtained from the oxygenation of the hydroperoxide, we have found that the quinone was also formed from the dimer VIII upon oxygenation with the cuprous chloride–amine system (22%). There was no evidence for the formation of the diphenoquinone III in the latter reaction. The oxygenation of V under the standard conditions resulted in a quantitative recovery of starting material. The demethylation of I to produce the dimers III and VIII presumably occurred *via* the loss of formaldehyde as has been observed previously in this system.[1]

Experimental Section

Melting points were taken on a Mel-Temp apparatus and were uncorrected. Infrared, ultraviolet, nmr, and mass spectra were

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[4] N. P. Neureiter, *J. Org. Chem.*, **28**, 3486 (1963).

[5] C. D. Cook, *ibid.*, **18**, 261 (1953).

[6] T. W. Campbell and G. M. Coppinger, *J. Amer. Chem. Soc.*, **74**, 1469 (1952).

[7] R. H. Bauer and G. M. Coppinger, *Tetrahedron Lett.*, **19**, 1201 (1963).

[8] Recent investigations in this laboratory have established the oxidative methoxylation of I under a variety of conditions to involve quinone methide intermediates. See also H. D. Becker, *J. Org. Chem.*, **30**, 982 (1965).

[9] L. J. Filar and S. Winstein, *Tetrahedron Lett.*, **25**, 9 (1960).

recorded on a Perkin-Elmer Model 337 spectrophotometer, a Cary Model 14 spectrophotometer, a Varian Model A-60 spectrometer, and a GE Monopole mass spectrometer (mass range 600), respectively. Gas chromatographic analyses were carried out on an F & M Model 700 vapor fractometer with a 4-ft 10% Apiezon L on Chromosorb W column.

Oxidation of 2,6-Di-*t*-butyl-*p*-cresol (I) in Methanol with Cuprous Chloride–Amine Catalyst. A. Conditions for the Isolation of III, IV, VII, and VIII.—A suspension of 0.544 g (0.0055 mol) of cuprous chloride and 6 g of anhydrous magnesium sulfate in a solution of 0.646 g (0.0055 mol) of tetramethylethylenediamine (TMEDA) and 0.59 g (0.01 mol, 7.5 ml of a solution of trimethylamine in toluene −0.078 g/ml) of trimethylamine in 125 ml of anhydrous methanol was prepared. A stream of oxygen (flow rate, 1 ft^3/hr) was bubbled through the stirred suspension for 10 min. While oxygen was continuously bubbled through the blue suspension, a solution of 22 g (0.1 mol) of I in 125 ml of methanol was then added to this mixture over a 0.5-hr period. The temperature of the reaction mixture was kept at 25° with cold-water bath. The reaction was continued for an additional 3.83 hr. The yellow-green reaction mixture was filtered and the filtrate evaporated to an oil. The oil was extracted with 200 ml of hot hexane and the hexane extract decanted from the residue. The volume of the extract was reduced to 50 ml and refrigeration of the resulting solution at 0° for 12 hr provided 0.66 g (3%) of VIII: mp 154–156°; $\lambda_{max}^{CCl_4}$ (cm^{-1}), 3640, 1660, and 1640; $\lambda_{max}^{C_2H_4OH}$ (mμ) 237 (ϵ 21,188), 274 (2150); nmr, τ (CCl_4) 8.77 (18 H), 8.60 (18 H), 8.41 (3 H), 4.88 (1 H, exchanged in D_2O), 3.45 (2 H), and 2.95 (2 H); mass spectrum, *m/e* 424 $(M)^+$.

A second crop of crystals was obtained upon cooling the filtrate, 0.012 g (0.05%) of III, mp 246° (lit.[2b] mp 246°). The infrared spectrum of this product was identical with that of authentic 3,5,3′,5′-tetra-*t*-butyl-4,4′-diphenoquinone.

Preparative thin layer chromatography of the filtrate from III on 1-mm thickness silica gel (Stahl GF 254) 8 × 8 in. plates using benzene–carbon tetrachloride (1.7:1) as solvent provided two isolable crystalline fractions: (1) 2,6-di-*t*-butyl-*p*-benzoquinone (IV), mp 55–58° (lit.[2b] mp 67°), and (2) 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (VII), mp 180–183° (lit.[2b] mp 187°). The infrared spectra of both of these products were identical with those of authentic samples.

B. Conditions for Quantitative Analysis of Products.—A suspension of 0.544 g (0.0054 mol) of cuprous chloride and 6 g of magnesium sulfate in 125 ml of methanol containing 0.646 g (0.0055 mol) of TMEDA and 0.59 g (0.01 mol) of trimethylamine (7.5 ml of a solution of trimethylamine in toluene, 0.078 g/ml) was stirred at 25° while a stream of oxygen was bubbled through the mixture (flow rate, 1 ft^3/hr) for 10 min. A solution of 22 g (0.1 mol) of I in 125 ml of methanol was then added dropwise during a 0.5-hr period to the blue reaction mixture maintaining the same oxygen flow rate. After the addition was complete, the mixture was oxygenated for an additional 3.83 hr. During the reaction, the temperature rose to 45° and gradually returned to 25°. The yellow-green reaction mixture was filtered and evaporated to a dark oil. This oil was dissolved in 250 ml of ethyl acetate and this solution was washed with 150 ml of cold 3% aqueous hydrochloric acid. The ethyl acetate layer was washed with water several times until the washings were neutral. The organic layer was dried ($MgSO_4$), filtered, and evaporated to a liquid which contained some solid. Filtration of the mixture gave 1.79 g of a solid, mp 180–183°, which was identical with 3,5-di-*t*-butyl-4-hydroxybenzaldehyde. The filtrate (21.2 g) was then analyzed by gas chromatography. This analysis provided the following percentage composition of this mixture: (1) III (5%); (2) IV (27%); (3) V (14%); (4) VI (14%); (5) VII (12%);[10] and (6) VIII (2%).

Oxidation of VIII in Methanol with Cuprous Chloride–Amine Catalyst.—A mixture of 0.490 g (0.0011 mol) of VIII, 0.0059 g (5.9×10^{-5} mol) of cuprous chloride, 0.0071 g (6×10^{-5} mol) of TMEDA, 0.0065 g (1.1×10^{-4} mol) of trimethylamine, and 0.066 g of magnesium sulfate in 12 ml of methanol was oxygenated for 4.5 hr and worked up as previously described for I (part B). Gas chromatographic analysis of the reaction product (0.383 g) showed the following components: (1) VIII, 0.333 g (67% recovered); (2) 2,6-di-*t*-butyl-*p*-benzoquinone, (IV, 22%);[11] (3) 2,6-di-*t*-butyl-4-methyl-4-hydroxy-2,5-cyclohexadien-1-one (V, 0.9%).[11]

Oxidation of IX[12] in Methanol with Cuprous Chloride–Amine Catalyst.—A mixture of 1.0 g (0.004 mol) of IX, 0.022 g (2.2×10^{-4} mol) of cuprous chloride, 0.24 g of magnesium sulfate, 0.025 g (2.2×10^{-4} mol) of TMEDA, and 0.0236 g (4×10^{-4} mol) of trimethylamine was oxygenated for 4.5 hr and worked up as previously described. Gas chromatographic analysis of the reaction product (0.743 g) indicated the following components: (1) III, 5%; (2) IV, 2%; (3) V, 58%; (4) VIII, 2%.

Oxidation of V in Methanol with Cuprous Chloride–Amine Catalyst.—A mixture of 2.0 g (0.0084 mol) of V, 0.045 g (4.5×10^{-4} mol) of cuprous chloride, 0.054 g (4.6×10^{-4} mol) of TMEDA, and 0.049 g (8×10^{-4} mol) of trimethylamine in 21 ml of methanol was oxygenated for 4.5 hr and worked up as previously described. A quantitative recovery of V was obtained.

Registry No.—I, 128-37-0; VIII, 14387-13-4; oxygen, 7782-44-7.

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[10] This per cent yield includes the 1.79 g of VII which was isolated.

[11] Yield based upon the number of moles of VIII which reacted (3.7×10^{-4}).

[12] Prepared according to the method described in ref 2.

The Photolysis of Perfluoro-2,3-diazabuta-1,3-diene and Perfluoroacyl Fluorides

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Received November 29, 1967

The generation of the difluoromethylenimino radical from the photolysis of perfluoro-2,3-diazabuta-1,3-diene has been reported recently.[1] The apparent stability of this radical and the ease with which it adds to fluoro olefins[2] suggested that the photolysis of perfluoro-2,3-diazabuta-1,3-diene in the presence of photolytic sources of fluoroalkyl radicals would be a convenient route to the synthesis of azomethines. Heretofore, the only method of preparing these compounds was from the pyrolysis of oxazetidines[3] since it has recently been shown that the pyrolysis of tertiary perfluoroamines produces isomers of azomethines.[4,5]

Although several photolytic sources of fluoroalkyl radicals are available it was decided to use perfluoroacyl fluorides in this study. These materials were readily available and have been shown to produce both fluoroalkyl and fluoroformyl radicals upon photolysis.[6] Few reactions of the fluoroformyl radical have been described previously although the formation of difluoramino carbonyl fluoride, $NF_2C(O)F$, from the photolysis of tetrafluorohydrazine and carbon monoxide, is thought to involve a combination of difluoramino and fluoroformyl radicals.[7]

Results and Discussion

The photolysis of monofunctional perfluoroacyl fluorides in the presence of perfluoro-2,3-diazabuta-1,3-

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[2] P. H. Ogden and R. A. Mitsch, *J. Amer. Chem. Soc.*, **89**, 3868 (1967).

[3] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1881 (1955); 3461 (1955). D. A. Barr, R. N. Haszeldine, and C. J. Willis, *ibid.*, 1351 (1961).

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[5] R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, *J. Chem. Soc.*, 7203 (1965).

[6] J. F. Harris, *J. Org. Chem.*, **30**, 2182 (1965).

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