# Oxidation of Hindered Phenols. VI. Oxidative Decarboxylation of 3,5-Di-*t*-butyl-4-hydroxybenzoic Acid

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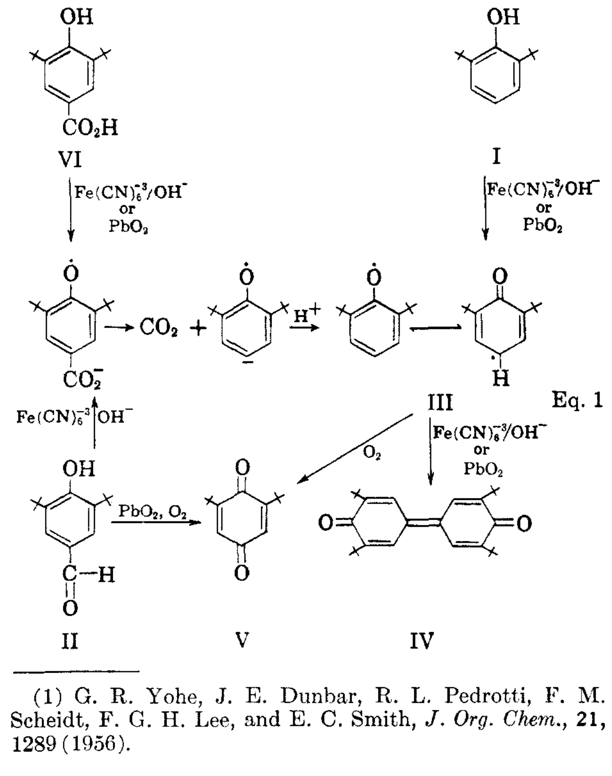
A recent paper by Yohe and co-workers[1] describes the formation of 2,6-di-*t*-butylquinone upon the oxidation of 2,6-di-*t*-butyl-4-methylphenol and 3,5-di-*t*-butyl-4-hydroxybenzaldehyde with molecular oxygen under alkaline conditions. Since work done in these laboratories has some bearing on this subject, we are led to the publication of this note.

We have found that oxidation of 2,6-di-*t*-butylphenol (I), 3,5-di-*t*-butyl-4-hydroxybenzaldehyde (II), and 3,5-di-*t*-butyl-4-hydroxybenzoic acid (VI) by alkaline ferricyanide in the absence of molecular oxygen produces 3,5,3′,5′-tetra-*t*-butyldiphenoquinone (IV) in essentially quantitative yield. If oxygen is present, moderate yields of 2,6-di-*t*-butylbenzoquinone (V) are also produced from the aldehyde. Under the latter conditions, 2,6-di-*t*-butylphenol gives small yields of the benzoquinone and 3,5-di-*t*-4-hydroxybenzoic acid forms only the diphenoquinone. When lead dioxide is used as the oxidizing agent, 2,6-di-*t*-butylphenol and 3,5-di-*t*-butyl-4-hydroxybenzoic acid both produce the diphenoquinone in excellent yield. In the presence of oxygen, lead dioxide reacts with the aldehyde to give some 2,6-di-*t*-butylbenzoquinone but no diphenoquinone is produced.



Eq. 1

These facts are consistent with an oxidatively induced decarboxylation of 3,5-di-*t*-butyl-4-hydroxybenzoic acid, presumably *via* the corresponding phenoxy radical (III). The failure of lead dioxide to produce diphenoquinone by reaction with the aldehyde is undoubtedly due to the inability of lead dioxide to oxidize the aldehyde to the acid. In this case the benzoquinone may perhaps be formed *via* an unstable peroxide. High molecular weight tars were also produced in this case. The proposed reaction scheme is outlined in Equation 1.

Since the acid does not decarboxylate in the absence of the oxidizing agents and since these oxidizing agents are known to react with phenolic hydroxyl groups to produce phenoxy radicals,[2] the proposed ion-radial (or, perhaps, an uncharged radical) is an attractive intermediate. The situation seems not unlike the alkaline decarboxylation of those acids which produce stable anions upon decarboxylation.[3] In the present case, the oxidative removal of the phenolic hydrogen permits the formation of a resonance-stabilized intermediate. A very intense green color during the initial stage of the oxidation of the aldehyde also suggests the incursion of a radical at this point. The variations in the ratio of benzoquinone to diphenoquinone are probably due to variations in the momentary concentration of phenoxy radical at the interface. Thus it is to be noted that maintaining a high dilution (dropwise addition) of the sparingly base-soluble aldehyde markedly increased the yield of the benzoquinone on oxidation with alkaline ferricyanide. This is the expected result since increasing the concentration should increase the rate of dimerization. Similarly, only the dimeric diphenoquinone was formed on oxidation of the acid which, of course, would tend to concentrate at the interface.

## EXPERIMENTAL

*Materials.* The method of Coppinger and Campbell,[4] oxidation of 2,6-di-*t*-butyl-4-methylphenol with bromine in *t*-butyl alcohol, was used to prepare 3,5-di-*t*-butyl-4-hydroxybenzaldehyde. A Cannizzaro reaction on the aldehyde according to the method of Yohe *et al.*,[1] gave 3,5-di-*t*-butyl-4-hydroxybenzoic acid. The Ethyl Corporation generously supplied the 2,6-di-*t*-butylphenol.

*Oxidation and identification of products.* The solution of the aldehyde, phenol, or acid (.35*M* in benzene) was vigorously stirred with the oxidizing agent while nitrogen or oxygen was bubbled through the system. When ferricyanide was the oxidant, sufficient stock solution (175 g. potassium ferricyanide, 100 g. potassium hydroxide, 1 liter of water) was used to provide five moles of ferricyanide per mole of the reductant; with lead dioxide ten moles of oxidant per mole of reductant was used. The amount of reductant was between 1 and 5 grams in all runs. For the high-dilution runs, the reductant was dissolved in one half the solvent and added

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(1) G. R. Yohe, J. E. Dunbar, R. L. Pedrotti, F. M. Scheidt, F. G. H. Lee, and E. C. Smith, *J. Org. Chem.*, **21**, 1289 (1956).

(2) C. D. Cook, D. A. Kuhn, and P. Fianu, *J. Am. Chem. Soc.*, **78**, 2002 (1956).

(3) J. Hine, *Physical Organic Chemistry*, McGraw-Hill, New York, (1956), pp. 283–284.

(4) G. M. Coppinger and T. W. Campbell, *J. Am. Chem. Soc.*, **75**, 734 (1953).

TABLE I

| Substrate | Oxidant | Temp., °C. | Atm. | Rate of Addn. | Total Time, Hr. | Diphenoquinone | Benzoquinone | Remarks |
|---|---|---|---|---|---|---|---|---|
| Phenol | Ferricyanide | 25 ± 2 | $N_2$ | Immediate | 4 | 98%[a] | Trace[c] | |
| | | | $O_2$ | Dropwise | 43 | 71%[b] | 7% | |
| | Lead dioxide | | $O_2$ | Immediate | 12 | 96%[a] | None | |
| Aldehyde | Ferricyanide | | $N_2$ | Dropwise | 48 | 95%[a] | Trace[c] | |
| | | | $O_2$ | Immediate | 17 | 98%[a] | Trace[c] | |
| | | | $O_2$ | Dropwise | 36 | | 30% | Remainder diphenoquinone |
| | | 0 | $O_2$ | | 48 | | 58% | |
| | Lead dioxide | 25 ± 2 | $O_2$ | Immediate | 96 | None | 39% | Remainder tar |
| | Moist lead dioxide | | $O_2$ | | 72 | None | 26% | |
| Acid | Ferricyanide | | $N_2$ | Dropwise | 24 | 97%[a] | None | |
| | | | $O_2$ | | 44 | 96% | None | |
| | Lead dioxide | | $O_2$ | Immediate | 2 | 95%[a] | None | |
| Diphenoquinone | Ferricyanide | | $O_2$ | Immediate | 48 | | | No reaction |
| Aldehyde | $H_2O + O_2$ | | $O_2$ | | 75 | | | |
| | $H_2O/NaOH/O_2$ | | $O_2$ | | 72 | | | |

[a] Before recrystallization. [b] Loss in handling during recrystallization. [c] Less than 0.1%.

to the reaction mix containing the remainder of the solvent by means of a capillary dropping funnel. After reaction, the benzene layer was evaporated to dryness and the 2,6-di-*t*-butylbenzoquinone separated by sublimation at 65°. The diphenoquinone was recrystallized from ethanol, m.p. 240–241° (uncorr.), reported 245–247°,[5,6] and identified by the identity of the mixture melting point and ultraviolet spectrum with those of an authentic sample.[7]

In those cases where no benzoquinone was formed, the crude diphenoquinone melted within two degrees of the purified product.

*Anal.* Calcd. for $C_{28}H_{40}O_2$: C, 82.30; H, 9.87. Found: C, 82.35; H, 9.77.

The 2,6-di-*t*-butylbenzoquinone was recrystallized from methanol-water, m.p. 65–66°, reported 65–66°,[8] 67.5–68.5°.[9] A mixture melting point with a known sample showed no depression.

In several runs using the aldehyde, the aqueous layer was strongly acidified. Essentially quantitative (98%) evolution of carbon dioxide resulted.

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[6] W. J. Detroit and H. Hart, *J. Am. Chem. Soc.*, **74**, 5215 (1952).

[7] Kindly provided by Dr. Harold Hart.

[8] S. J. Metro, *J. Am. Chem. Soc.*, **77**, 2901 (1955).

[9] C. D. Cook, R. C. Woodworth, and P. Fianu, *J. Am. Chem. Soc.*, **78**, 4159 (1956).

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## Application of a Silicic Acid Chromatostrip Technique for Observing the Sequential Methylation of β-Resorcylic Acid and Related Reactions

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During recent work on the characterization of the naturally occurring estrogen, coumestrol,[2] it became necessary to prepare the 2,4-dimethoxy and 2-hydroxy-4-methoxybenzoic acids. We found that these acids, together with their methyl esters, form sequentially as discrete products during the methylation of β-resorcylic acid in alkaline solution. Utilization of a fluorescent silicic acid chromatostrip technique[3] permitted us to observe under ultraviolet light the sequence of formation of each intermediate compound during methylation. As a result, it was possible to stop the reaction at any time in order to obtain the desired derivative. Thus, from one methylation reaction mixture all the methylated derivatives of β-resorcylic acid could be readily isolated.

The chromatostrip technique used to follow the chemical reactions was originally developed by Kirchner *et al.*[3] and Miller and Kirchner[4] and has

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[2] E. M. Bickoff, A. N. Booth, R. L. Lyman, A. L. Livingston, C. R. Thompson, and F. DeEds, *Science*, **126**, 969 (1957).

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