[CONTRIBUTION FROM THE TRANSFORMER AND ALLIED PRODUCTS LABORATORY, GENERAL ELECTRIC COMPANY]

OXIDATION OF HINDERED PHENOLS. I. OXIDATION OF AND OXIDATION INHIBITION BY 2,6-DI-*tert*-BUTYL-4-METHYLPHENOL

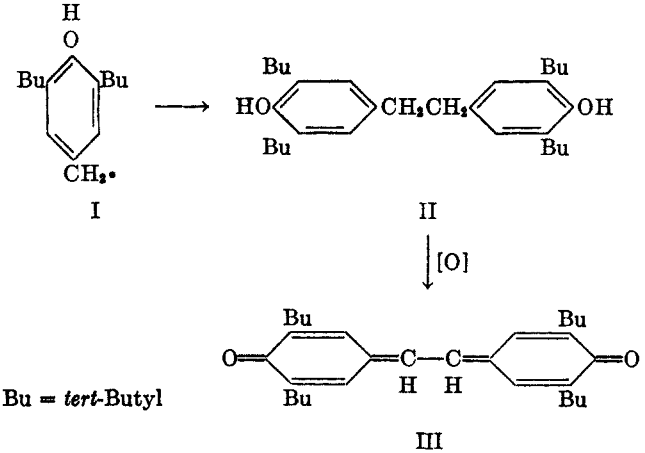
CLINTON D. COOK[1]

Received August 25, 1952

Numerous investigators have shown that the oxidation of hindered phenols frequently leads to dimeric products. Thus the oxidation of 1,3-dimethoxyphenol yields 3,5,3′,5′-tetramethoxy-4,4′-diphenoquinone (1). The oxidation of 2,6-di-*tert*-butylphenol gives 3,5,3′,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (2) and the oxidation of 2,4,6-trimethylphenol produces 3,5,3′,5′-tetramethylstilbene-4,4′-quinone (3, 4).

Recently, two papers have appeared concerning the oxidation of 2,6-di-*tert*-butyl-4-methylphenol, a problem of widespread interest due to the use of this compound as an antioxidant. One of these (5) reports the oxidation product formed by the action of chromic anhydride and acetic acid upon this compound to be a white aldehyde melting at about 185°. This is the 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde reported by Campbell and Coppinger (6). In the other work, Cosgrove and Waters (4) have reported the formation of 3,5,3′,5′-tetra-*tert*-butyl stilbene-4,4′-quinone (III) by the action of benzoyl peroxide upon 2,6-di-*tert*-butyl-4-methylphenol.

Cosgrove and Waters suggest that this dimeric product is formed *via* a 3,5-di-*tert*-butyl-4-hydroxybenzyl radical (I). If this were the case 1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethane (II) would be expected as an intermediate oxidation product prior to the formation of the stilbenequinone.



I

II

III

Bu = *tert*-Butyl

Recent work in this laboratory shows that this is very probably the case. Oxidation of 2,6-di-*tert*-butyl-4-methylphenol with limited amounts of oxygen,

---

[1] Present address: Chemistry Department, University of Vermont, Burlington, Vermont.

lead dioxide, alkaline ferricyanide, and hydrogen peroxide all led to the formation of mixtures of the red stilbenequinone (III) and a white compound which is very easily oxidized to III. This white compound has an infrared absorption at 2.7 μ characteristic of phenolic hydroxyl groups, is shown by molecular weight measurement to be a dimer of the starting compound, is unaffected by the action of zinc in boiling acetic acid, and is a fairly efficient antioxidant (Fig. 1).

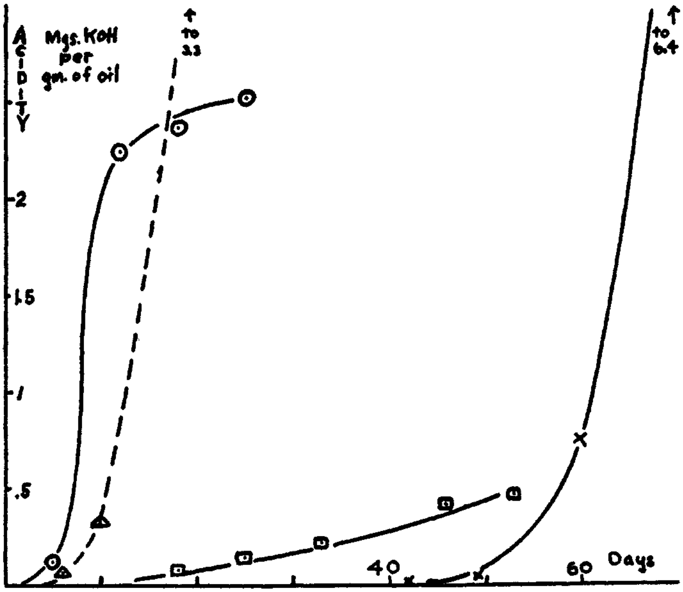
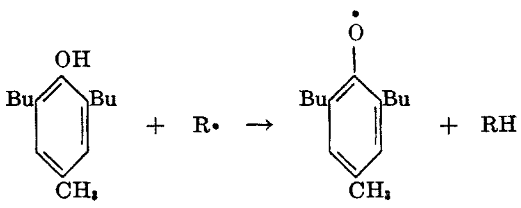


FIGURE 1. OXIDATION OF OILS AT 95° C. ⊙ = oil with no inhibitor; △ = oil + 0.3% 2,4,6-tri-*tert*-butylphenol; ⊡ = oil + 0.3% 1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-ethane; × = oil + 0.3% 2,6-di-*tert*-butyl-4-methylphenol.

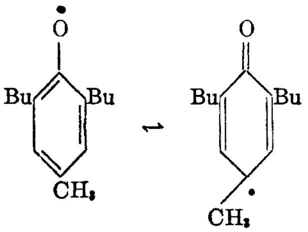
The above is suggestive of another (or additional) mode of inhibition to that proposed by Campbell and Coppinger (6). Assuming the usual scheme of oxidation,

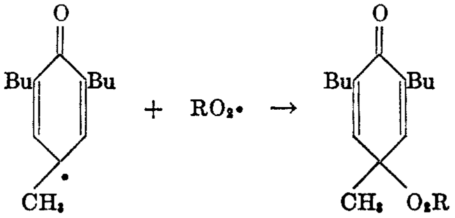
$$\begin{array}{rcccl} RH & + & O_2 & \rightarrow & R\cdot + HO_2\cdot \\ R\cdot & + & O_2 & \rightarrow & RO_2\cdot \\ RO_2\cdot & + & RH & \rightarrow & R\cdot + RO_2H \end{array}$$

these authors suggested that inhibition may occur by the following chain stopping reactions:



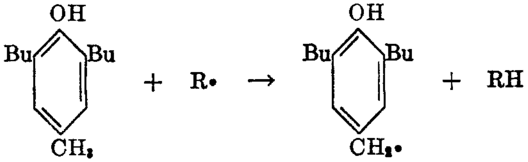
Eq. 1





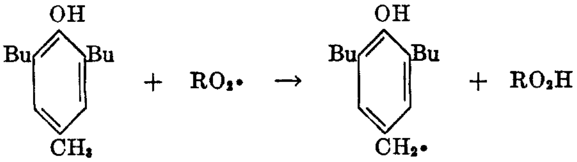
Eq. 1a

The apparent easy formation of substituted benzyl radicals from 2,6-di-*tert*-butyl-4-methylphenol introduces the possibility of the following scheme of inhibition:



Eq. 2

and, or



Eq. 2a

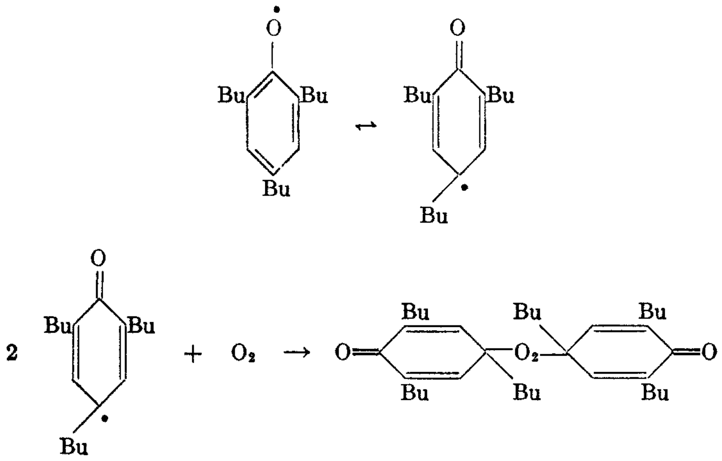
Bu = *tert*-Butyl

The dimeric product (II) formed from the 4-hydroxy-3,5-di-*tert*-butylbenzyl radicals could, of course, undergo similar reactions involving the *alpha* hydrogens in the ethane linkage.

There is a certain amount of evidence supporting a substituted benzyl radical intermediate in the antioxidation mechanism. Wasson and Smith (5) have shown that the 4-ethyl- and 4-*n*-butyl-2,6-di-*tert*-butylphenols are more effective inhibitors than the 4-methyl compound. This would be expected in the mechanism advanced above since the increased stability of the resulting secondary radical should make reactions 2 or 2a proceed more readily.

The same workers (see also 5a) found that 2,4,6-tri-*tert*-butylphenol is a relatively poor antioxidant, a fact confirmed by this work (Fig. 1). In this case, the substituted benzyl radical obviously cannot be formed.

When 2,4,6-tri-*tert*-butylphenol is oxidized (as, for example with PbO_2 in ether solution) an intense blue color immediately appears. Highly colored radicals have been observed from the oxidation of hindered phenols (7) and it seems likely that the blue color is due to the 2,4,6-tri-*tert*-butylphenoxy radical. Thus it would appear that the parent phenol should undergo reaction 1 as proposed by Campbell and Coppinger. The fact that this tri-*tert*-butylphenol is a poor antioxidant implies that reaction 1 is not alone responsible for inhibition. Reaction 1a might be precluded on a basis of steric hindrance. However, it has been found that the intense blue color here attributed to 2,4,6-tri-*tert*-butylphenoxy radical rapidly disappears in the presence of iodide ion or molecular oxygen. With iodide ion, the parent phenol is regenerated with the release of free iodine. With molecular oxygen preliminary work indicates the following reaction:



Bu = *tert*-Butyl

The slightly yellow crystalline product of this reaction decomposes at 148–149° with the evolution of gas, releases free iodine from iodide ion, and has a molecular weight consistent with the above formulation. Unfortunately, time has not permitted further elucidation of the structure of this compound. If the assigned structure is correct, it would seem rather unlikely that steric factors greatly hinder Campbell and Coppinger's reaction 1a.

Compounds II and III have been isolated from partially oxidized oil solutions. While they may have been formed by direct reaction with oxygen, their presence is at least consistent with the proposed mechanism. Unlike Wasson and Smith (5) no 4-hydroxy-3,5-di-*tert*-butylbenzaldehyde was isolated from oxidized oils.

EXPERIMENTAL

Preparation of 1,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)ethane. 2,6-Di-*tert*-butyl-4-methylphenol (30 g.) was dissolved in 300 ml. of ethyl ether and 16 g. of lead peroxide was added at room temperature. After stirring 30 minutes, the solution was filtered and evaporated to dryness. The unreacted phenol was removed from the residue by extraction with 100 ml. of ethanol and the remainder was recrystallized from ethanol and benzene. There resulted 5 g. of crude (m.p. 171–175°) light yellow material. By careful recrystallization from alcohol or acetic acid it was possible to obtain the material as white needles, m.p. 174–175°. This material showed a strong absorption at 2.7 μ characteristic of the phenolic hydroxyl group. Treatment with zinc dust and acetic acid had no effect. Oxidation with alkaline ferricyanide or lead dioxide resulted in the formation of the substituted stilbenequinone (III). This was a dimer of the starting compound; M.W. 429 (Benzene); calc'd for $C_{30}H_{46}O_2$, 438.7.

3,5,3'5' Tetra-tert-butylstilbene-4,4'-quinone. Evaporation of the mother liquor from the first crystallization described above gave a mass of orange-red crystals. Extraction of these with a small amount of glacial acetic acid gave 10 g. of red crystals melting at 296–301° (decomp). Recrystallization from ethanol containing a small amount of benzene raised the melting point to 314–315° (decomp). Reported (4) m.p. 300°.

Anal. Calc'd for $C_{30}H_{42}O_2$: C, 82.90; H, 9.74; M.W., 434.6.
Found: C, 82.88; H, 9.86; M.W. (benzene), 424.

The compound (4.70 mg.) released 2.77 mg. of iodine from sodium iodide in glacial acetic acid; calculated on the basis of 2 moles of hydrogen iodide per mole of quinone, 2.75 mg.

3,5,3',5'-Tetra-tert-butyl-4,4'-dihydroxystilbene. The stilbenequinone (1 g.) was heated for 10 minutes with 1 g. of zinc, 2 ml. of glacial acetic acid, 30 ml. of benzene, and 1 ml. of water. The orange-red color disappeared almost immediately. Upon filtering, partial evaporation of the solvent, and dilution with ligroin, 0.88 g. of white crystals, m.p. 235–237°, were recovered. Recrystallization from ligroin raised the melting point to 240–241° [reported (4) m.p. 230°]. Oxidation of this material with lead dioxide and benzene regenerated the stilbenequinone as evidenced by a mixture melting point of 314–315° of the resulting product with an authentic specimen.

Anal. Calc'd for $C_{30}H_{44}O_2$: C, 82.52; H, 10.16; M.W., 436.6.
Found: C, 82.43; H, 10.10; M.W., (benzene), 432.

The characteristic hydroxyl band at 2.7 μ was found. This was lacking with the stilbenequinone.

3,5-Di-tert-butyl-4-hydroxybenzaldehyde. Campbell and Coppinger's preparation of this compound (6) by the bromine oxidation of 2,6-di-*tert*-butyl-4-methylphenol in *tert*-butanol was duplicated. As they reported, the aldehyde melted at 189°, its 2,4-dinitrophenylhydrazone at 236°.

Oxidation of 1 g. of 2,6-di-*tert*-butyl-4-methylphenol with 1 g. of chromic anhydride in 50 ml. of acetic acid gave, upon dilution with water, 0.7 g. of an aldehyde. After one recrystallization from ligroin this aldehyde melted at 189°, its 2,4-dinitrophenythydrazone melted at 236°, and a mixture melting point with the bromine oxidation product showed no depression. This is the aldehyde reported by Wasson and Smith (5). A mixture melting point with this material and the dimeric material presumed to be 1,2-bis-(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethane showed a depression of 15°.

Oxidation of 2,4,6-tri-tert-butylphenol. 2,4,6-Tri-*tert*-butylphenol, m.p. 130–131°, was prepared from *tert*-butyl chloride and phenol by the method of Stillson, Sawyer, and Hunt (8). When lead dioxide or alkaline ferricyanide was added to an ethereal or benzene solution of this phenol a very intense blue color developed. Upon addition of sodium iodide in acetic acid, the blue color immediately disappeared and free iodine was produced. The resulting solution was treated with sodium thiosulphate, extracted with water, and evaporated nearly to dryness. There resulted white crystals which, after one recrystallization from ethanol, melted at 129–130°. A mixture melting point with 2,4,6-tri-*tert*-butylphenol was also 129–130°.

When the blue solution was filtered from the lead dioxide and sealed from the atmosphere it maintained its color for several weeks. However, with ready access to oxygen the blue color rapidly disappeared. One gram of 2,4,6-tri-*tert*-butylphenol was dissolved in 50 ml. of benzene and approximately 5 g. of lead dioxide was added. After five minutes of vigorous shaking the solution was filtered and oxygen was bubbled through the filtrate until the blue color disappeared. Evaporation of the benzene nearly to dryness gave 1 g. of yellowish white crystals, m.p. 144–147° (decomp). A recrystallization from ligroin raised the decomposition temperature to 148–149°. The molecular weight was 560 (benzene); calc'd for $C_{36}H_{56}O_4$, 554.4.

Oxidation of oils. The oil used for determination of the inhibitory effect was a low viscosity naphthenic-based transformer oil. It had the following properties:

Boiling range, 760 mm.	280–370°
Viscosity, Saybolt Universal at 37.8°C.	55 sec.
Specific gravity	0.886
Aromatic carbon*, %	9–12
Naphthenic carbon*, %	40–50
Molecular weight (benzene)	280

The oils were oxidized by a modification of A.S.T.M. tentative method D 943 - 47 T (10). This test involves maintaining the sample of oil at 95° in the presence of oxygen, water, and a copper and iron catalyst. The oxidation of the oil was followed by determination of its acidity according to A.S.T.M. method D 188. The results of these tests are shown in Fig. 1.

To determine the oxidation products of the 2,6-di-*tert*-butyl-4-methylphenol in oil, a 20% solution of this compound in the oil described above was maintained at 120° in the presence of excess air. After one week 10 ml. of this oil was diluted to 100 ml. with ligroin and shaken with silica gel. The gel was eluted with methanol and upon evaporation of the methanol a few milligrams of II (m.p. 174–176°, mixture. m.p. 175–176°) were recovered. A similar sample after 6 weeks of oxidation gave a few milligrams of III. Methanol extraction of 100 ml. of an oil originally containing 0.3% by weight of the 2,6-di-*tert*-butylphenol and aged 40 days by the A.S.T.M. method mentioned above also gave a few milligrams of II. In contrast to Wasson and Smith (5), all attempts to isolate an aldehyde as, for example, through the 2,4-dinitrophenylhydrazone were unsuccessful.

PITTSFIELD, MASS.

REFERENCES

(1) HOFFMAN, *Ber.*, **11**, 329 (1878).
(2) HART AND CASSIS, *J. Am. Chem. Soc.*, **73**, 3179 (1951).
(3) PORTER AND THURBER, *J. Am. Chem. Soc.*, **43**, 1194 (1921).
(4) COSGROVE AND WATERS, *J. Chem. Soc.*, 388 (1951).
(5) WASSON AND SMITH, *Abstracts, 12th International Congress of Pure and Applied Chemistry*, 1951, P. 187. (The author is indebted to these authors for a preprint of this paper).
(5a) ROSENWALD, HOATSON, AND CHENICEK, *Ind. Eng. Chem.*, **42**, 162 (1950).
(6) CAMPBELL AND COPPINGER, *J. Am. Chem. Soc.*, **74**, 1469 (1952).
(7) GOLDSCHMIDT AND SCHMIDT, *Ber.*, **55**, 3197 (1922).
(8) STILLSON, SAWYER, AND HUNT, *J. Am. Chem. Soc.*, **67**, 303 (1945).
(9) VAN NES AND VAN WESTON, *Aspects of the Constitution of Mineral Oils*, Elsevier, Pp. 318–347.
(10) VON FUCHS, *A.S.T.M. Symposium on Insulating Oils*, Special Technical Publication #95, *Performance of Inhibited Transformer Oils*, 1949.

---

* By the n-D-M Method (9).