[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY, UNIVERSITY OF CHICAGO]

Reactions of Hindered Phenols. II. Base-Catalyzed Oxidations of Hindered Phenols*

M. S. KHARASCH AND B. S. JOSHI[1]

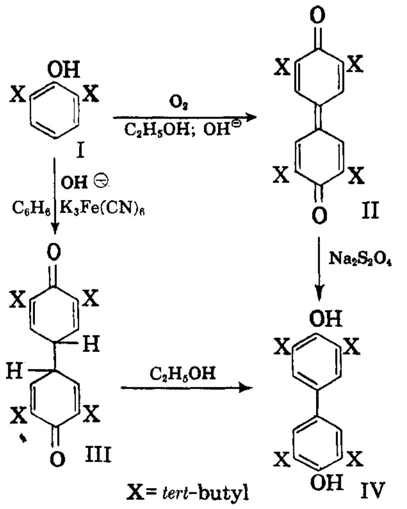
Received June 27, 1957

2,6-Di-*tert*-butylphenol (I) reacts with oxygen in the presence of a base to give 3,5,3′,5′-tetra-*tert*-butyl-4,4′-diphenoquinone. A stable keto tautomer of the phenol (IV) was obtained by oxidation of I with potassium ferricyanide. It has been established that a nearly quantitative yield of the hydroperoxide (XI) is formed upon treatment of V with oxygen in the presence of a base. The hydroperoxide (XI) is readily hydrolyzed to the alcohol (XII). The treatment of XVI with oxygen in the presence of a base gives X and IX along with a small amount of XVII. But a high yield of XVII is obtained when the free radical (XVIII) is allowed to stand for a few hours in the presence of a strong base. Mechanisms are suggested which account for many of the reactions here discussed.

There is an extensive literature dealing with the products formed upon oxidation of hindered phenols. These investigations may be classified as follows: (*a*) oxidations with so-called one electron oxidizing agents (ferricyanide, silver oxide, lead dioxide, etc.,[2–13] (*b*) oxidations with benzoyl peroxide;[14,15] (*c*) oxidations with alkyl hydroperoxides[16,17]; and (d) base-catalyzed oxidations with oxygen at elevated temperatures.[18,19]

The present investigation deals with the base-catalyzed oxidations of some hindered phenols by oxygen. The phenols were dissolved in hydroxylic solvents (ethanol or *tert*-butyl alcohol), the base was added, and the reaction mixture was vigorously agitated in the presence of oxygen. The pressure in the apparatus was only two or three centimeters above atmospheric pressure. The reaction was interrupted when the predetermined amount of oxygen was absorbed.

Oxidation of 2,6-di-tert-butylphenol. Under the experimental conditions previously cited, compound I absorbs one mole of oxygen to give a quantitative yield of 3,5,3′,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (II) and hydrogen peroxide (85% of calculated amount). The diphenoquinone has been prepared previously.[19,20] The product here obtained melted at 246°. The structure of II was confirmed by examination of the ultraviolet and visible ($\lambda_{max}^{iso-octane}$ 260, 270, and 418 mμ; ϵ_{max} 4300, 4300, and 84,000 respectively) and infrared spectra $\nu_{C=O}$ at 1635 cm.$^{-1}$ (medium) and 1605 cm.$^{-1}$ (strong).[cf. 21]



There are two mechanisms whereby II may be formed from I. The experimental evidence now available does not allow one to make an unequivocal

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[*] This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

(1) The authors are deeply indebted to Dr. N. C. Yang for many helpful discussions of the spectroscopic data here recorded.

(2) C. D. Cook, *J. Org. Chem.*, **18**, 260 (1953).

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

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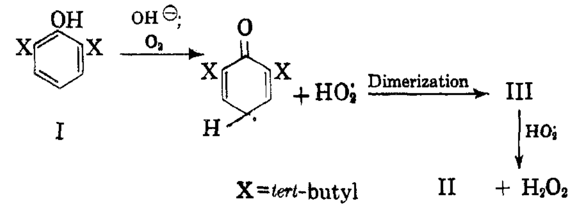
choice between them. However, it appears that II is formed from I by the following sequence of reactions.

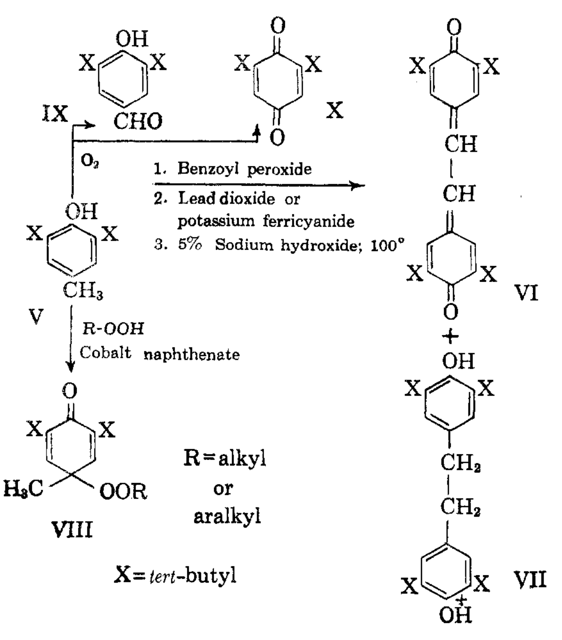


The formation of II from I by an ionic mechanism would involve a condensation reaction; but attempts to synthesize II from certain reasonable intermediates were of no avail.

When a solution of I in benzene was oxidized by alkaline ferricyanide, a different product (III) resulted. The ultraviolet (λ_{max} at 242 mμ; ϵ_{max} 15,000) and infrared spectra (characteristic dienone absorption at 1657 and 1638 cm.$^{-1}$, and no hydroxyl band) are in agreement with the structure assigned to III. Compound III is stable when dry, and in non-polar solvents. However, in polar solvents (ethanol) III is rapidly isomerized to IV (λ_{max} 265 mμ; ϵ_{max} 18,000).

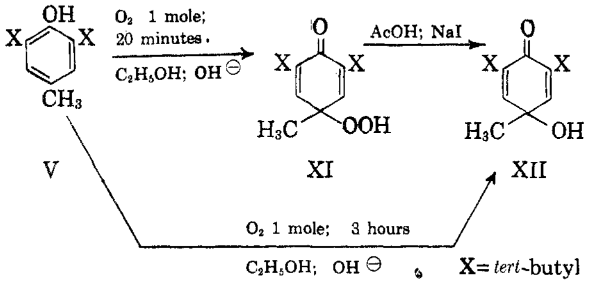
Compound III is unique—it is the keto tautomer of IV. As far as we are aware no such pair of keto-enol tautomers of phenolic compounds has ever been isolated. There is of course abundant evidence that, upon demand of a reagent, certain phenolic substances react as if they existed in equilibrium with the keto form.

Reaction of 2,6-di-tert-butyl-4-methylphenol (V) with oxidants and with oxygen. The oxidation of V by a variety of oxidants has been investigated previously. Thus, small quantities of VI and VII are formed when a solution of V in chloroform is heated with benzoyl peroxide for 70 hr.[15,18] The two compounds (VI) and (VII) have also been prepared by oxidation of V with lead dioxide or alkaline ferricyanide.[2,4] Treatment of V with alkyl or aralkylhydroperoxides and cobalt naphthenate gave 2,6-di-*tert*-butyl-4-methyl-4-alkyl(or aralkyl)peroxy-2,5-cyclohexadiene-1-one (VIII),[16,17]



Very low yields of identifiable products have been obtained from the reaction of V with oxygen in the presence or absence of alkali. Thus it is claimed that when a solution of V in a "petroleum base lubricating oil" is heated with oxygen at 110° in the presence of polished copper foil catalyst some amount of IX is formed.[22] When the temperature was maintained at 95° for 2–3 days and oxygen was bubbled in, (in the presence of a "copper-iron catalyst") about 8 percent of X was isolated.[23] Furthermore it is claimed[18] that small amounts of VI and VII are formed when a suspension of V in 5 percent alkali is heated with oxygen.

It seems fairly obvious, from the work thus far recorded, that the primary reaction product of V with oxygen is unstable and undergoes further changes when heated or upon prolonged standing in the presence of alkali. To overcome this difficulty, a solution of V in ethanolic potassium hydroxide was shaken with oxygen until one molar equivalent of the gas was absorbed and the reaction mixture worked up at once. Under these conditions the hydroperoxide XI was obtained in excellent yield (86%).[24] The oxygen absorption was very rapid – usually about 20 to 25 min.



The structure assigned to XI is based on the following considerations: (*a*) analyses, (*b*) the ultraviolet (characteristic dienone chromophore λ_{max} 234 mμ; ϵ_{max} 10,400) and (*c*) the infrared spectra (doublet at 1665 and 1645 cm.$^{-1}$ due to the conjugated carbonyl group, the hydroxyl stretching frequency at 3538 cm.$^{-1}$ and the peroxide linkage at 845 cm.$^{-1}$). The hydroperoxide XI, dissolved in acetic acid, liberates iodine from an acetic acid solution of sodium iodide and is converted into XII.[25]

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[22] J. I. Wasson and W. M. Smith, *Ind. Eng. Chem.*, **45**, 197 (1953).

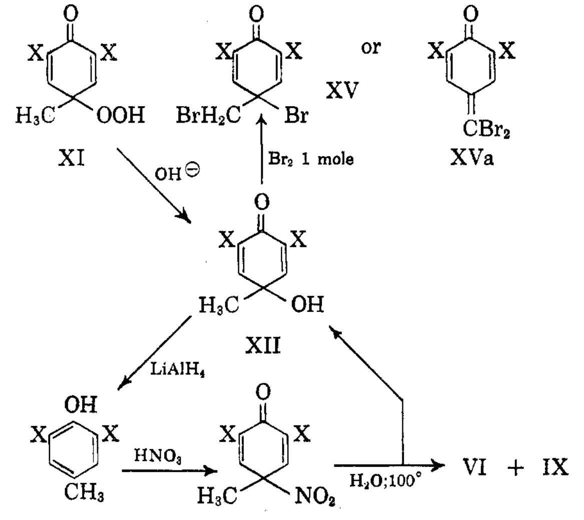
[23] S. J. Metro, *J. Am. Chem. Soc.*, **77**, 2901 (1955).

[24] Coppinger (private communication) prepared XI from V, hydrogen peroxide, and cobaltous, or other metal salts.

[25] Compound (XII) has been prepared by Coppinger (private communication) by reduction of (XI) with hydrogen gas in the presence of a platinum catalyst.

An ethanolic potassium hydroxide solution of XI (m.p. 115–116°) decomposes (complete loss of peroxide titer) within 2–3 hr. About 45 per cent of the hydroperoxide is converted into XII (m.p. 111–112°), about 20 per cent into a substance XIII melting at 159–160°. Compound (XIII) (mol. wt. 416) has the empirical formula $C_{30}H_{46}O_2$. Its ultraviolet (λ_{max} 237, 273 mμ; ϵ_{max} 20,000 and 2600 respectively) and infrared spectra (OH stretching at 3638 cm.$^{-1}$ and a doublet at 1658 and 1638 cm.$^{-1}$) were examined, but did not furnish sufficient information for assignment of a structure to XIII. Further work on this compound is contemplated.

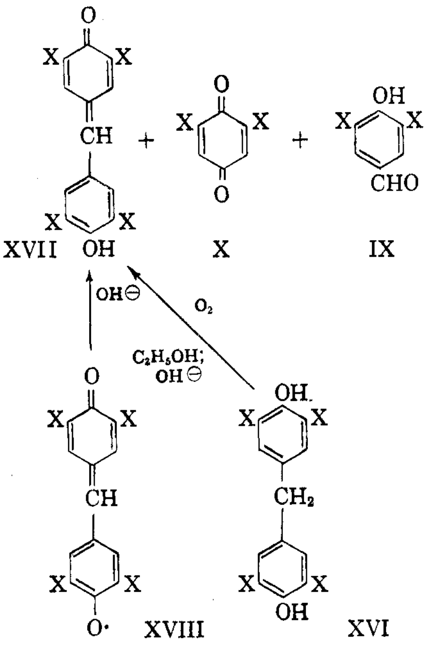
Structure (XII) is based on (*a*) analyses, (*b*) ultraviolet (λ_{max} 234 mμ; ϵ_{max} 10,400), and (*c*) infrared spectra (OH stretching at 3580 cm.$^{-1}$, twin band at 1665 and 1645 cm.$^{-1}$, and tertiary hydroxyl at 1045 cm.$^{-1}$). The alcohol (XII) undergoes a number of interesting transformations. These are in indicated below. Two items are of particular interest. First, the lithium aluminum hydride reduction of XII to V. Second, the transformation by bromine of XII into compound (XV). With one molar equivalent of bromine, a dibromide is formed which could be either XV or XVa. Structure (XV) is preferred for the dibromide over XVa. This conclusion is based on the ultraviolet spectrum of the compound (λ_{max} 250 mμ; ϵ_{max} 8300), and because compounds structurally similar to XVa have been shown to absorb at λ_{max} 220 mμ; ϵ_{max} 3600.[8]



X = *tert*-butyl

Reaction of 4,4'-dihydroxy-3,5,3',5'-tetra-tert-butyl diphenylmethane in the presence of base. A solution of XVI in ethanolic potassium hydroxide absorbs one molar equivalent of oxygen very rapidly. The second mole of oxygen is absorbed in about 40 min. During the absorption of oxygen, the reaction mixture acquires a dark purple color.

Examination of the visible spectrum of the alkaline solution indicates that the color is due to the anion of XVII (see previous paper). From the intensity of the color, it is estimated that this product is formed to the extent of about 2–4 per cent. Neutralization of the reaction mixture gives a yellow oil of average molecular weight 265, indicating that extensive cleavage had taken place. Two products (IX) and (X) were isolated when the oil was chromatographed on alumina.



X = *tert*-butyl

A solution of the free radical (XVIII) in ethanolic sodium hydroxide absorbs two molar equivalents of oxygen. The second mole of oxygen is absorbed rather slowly. A deep purple colored solution is thus obtained. Examination of the visible spectrum of the alkaline solution indicates that about half of the compound (XVIII) is transformed into the anion of XVII. Oxygen, however is not essential for this transformation, since a solution of XVIII in ethanolic sodium hydroxide (but in the absence of oxygen) gives the same yield of XVII. Examination of the other reaction products was not attempted, because the author of a recent communication[18] indicated that this work was underway in his laboratory.

EXPERIMENTAL

3,5,3',5'-Tetra-tert-butyl-4,4'-diphenoquinone (II). To a well agitated solution of 2,6-di-*tert*-butylphenol (2.06 g; 0.01 mole) in *tert*-butyl alcohol (25 ml.), potassium hydroxide (2 g. in 3 ml. water) was added and the flask was connected to an oxygen buret. It took 25 min. for the absorption of 224 ml. (0.01 mole) of oxygen. The brown colored reaction mixture was diluted with water (25 ml.) and the precipitate (2.0 g; 98%) was collected on a filter. Upon crystallization from ethanol red-brown plates with a purple reflex were obtained which melted at 246°. This material did not depress the melting point of an authentic sample of 3,5,3',5'-tetra-*tert*-butyl 4,4'-diphenoquinone (prepared by nitric acid oxidation of 2,6-di-*tert*-butylphenol[20]).

Anal. Calcd. for $C_{28}H_{40}O_2$: C, 82.4; H, 9.8. Found: C, 82.5; H, 9.8.

The alkaline filtrate after removal of II was acidified with acetic acid and the iodine liberated after addition of sodium iodide was estimated by titration with sodium thiosulfate.

In another experiment, a solution of 2,6-di-*tert*-butylphenol (1 g.) in *tert*-butyl alcohol (15 ml.) and water (1 ml.) was mixed with sodium hydroxide (0.3 g.) in an evacuated tube. The solution changed to a faint bluish green. No dimerized product was formed although the mixture was kept for 6 mo.

4,4'-Dihydroxy-3,5,3',5'-tetra-tert-butyl diphenyl (IV). The diphenoquinone (II; 0.2 g.) was dissolved in ethanol (50 ml.), sodium hydrosulfite added (1 g. in 10 ml. water), and the whole heated for 20 min. The precipitate which separated was collected on a filter and crystallized from ethanol. Pale yellow needles were thus obtained which melted at 185°.

Anal. Calcd. for $C_{28}H_{42}O_2$: C, 81.9; H, 10.3. Found: C, 81.5; H, 10.6.

3,5,3',5'-Tetra-tert-butyl-1,1'-dihydro-2,5,2',5'-bis-cyclohexadiene-4,4'-one (III). A benzene solution of 2,6-di-*tert*-butylphenol (4.12 g. in 50 ml.) was added dropwise under a current of nitrogen to a well stirred mixture of potassium ferricyanide (24 g.), water (100 ml.), benzene (200 ml.), and potassium hydroxide (4 g.). The red colored solution was poured onto crushed ice. The benzene layer was separated, washed with water, and dried over sodium sulfate. The solvent was removed at reduced pressure in a nitrogen atmosphere. The crude product thus obtained was washed with 35 ml. of petroleum ether. A colorless solid (2.6 g.) was thus obtained. Upon crystallization from iso-octane large colorless plates were obtained which melted at 151–152°.

Anal. Calcd. for $C_{28}H_{42}O_2$: C, 81.9; H, 10.3. Found: C, 81.8; H, 10.0.

The petroleum ether washings upon evaporation gave (1 g.) which melted at 245°.

2,6-Di-tert-butyl-4-methyl-4-hydroperoxy-2,5-cyclohexadiene-1-one (XI). 2,6-Di-*tert*-butyl-4-methylphenol (4.4 g; 0.02 mole) was dissolved in ethanol (50 ml.) and a solution of potassium hydroxide (2 g. in 5 ml. water) was added. The flask was quickly connected to an oxygen buret and the solution was vigorously agitated. In about 25 min., 450 ml. (0.02 mole) of oxygen was taken up. The solution which had become pale yellow, was immediately poured into ice water (700 ml.) and neutralized with acetic acid. The precipitate which separated was collected on a filter, washed with water, and dried (4.8 g.). Upon addition of sodium iodide to a solution of the crude hydroperoxide in glacial acetic acid, free iodine was liberated. Titration with sodium thiosulfate showed that the crude material was 90% pure. (Yield of pure XI calculated on the basis of the starting compound was 86%). Upon crystallization from *n*-hexane, colorless needles were obtained which melted at 115–116°.

Anal. Calcd. for $C_{15}H_{24}O_3$: C, 71.4; H, 9.6. Found: C, C, 71.3; H, 9.6.

Dilution of the acetic acid solution, after reaction of the pure hydroperoxide with sodium iodide, gave a solid which melted at 110°. This product was shown to be identical with an authentic sample of XII.

2,6-Di-tert-butyl-4-methyl-4-hydroxy-2,5-cyclohexadiene-1-one (XII). To a solution of 2,6-di-*tert*-butyl-4-methylphenol (22 g.; 0.1 mole) in ethanol (150 ml.), potassium hydroxide (15 g. in 15 ml. water) was added and the apparatus was connected to an oxygen buret. After about 20 min. the solution became dark brown. The temperature of the reaction mixture rose to 55°. At this point it was cooled externally with water. A total of 2250 ml. of oxygen (about 0.1 mole) was absorbed in 1 hr. The oxygen buret was then disconnected and the whole allowed to stand for two hours longer. The brown colored reaction mixture was then poured into ice water (800 ml.). It was neutralized by addition of acetic acid, and the pale yellow precipitate which separated was collected on a filter and thoroughly washed with water and dried over phosphorus pentoxide. The crude material (18.7 g.) (yield, 80% calculated) melted at 78–92°. The product did not liberate iodine when treated with an acetic acid solution of sodium iodide.

A part of the crude material (3 g.) was dissolved in benzene and chromatographed on a column (10 in. long) of alumina (70 g.) using benzene as solvent and eluent. The least adsorbed fraction (100 ml.) gave a solid (0.9 g.) which melted at 150–152°. Upon two crystallizations of this material from ethanol, colorless needles were obtained which melted at 160°.

Anal. Calcd. for $C_{30}H_{46}O_2$: C, 82.1; H, 10.5; mol. wt. 438. Found: C, 82.1, 82.0; H, 10.0, 10.1; mol. wt. 416.

The next fraction (300 ml.) gave a white solid (XII) (1.6 g.) which upon crystallization from *n*-hexane melted at 111–112°.

Anal. Calcd. for $C_{15}H_{24}O_2$: C, 76.2; H, 10.2. Found: C, 76.3; H, 10.1.

Reduction of XII *with lithium aluminum hydride.* A solution of compound (XII) (1 g.) in dry ether (30 ml.) was added to a well stirred suspension of lithium aluminum hydride (3 g.) in ether (50 ml.). The mixture was stirred for 3 hr. and allowed to stand overnight. The whole was then poured into dilute sulfuric acid and extracted with ether, and the layers separated. Upon removal of the ether colorless plates (0.6 g.) were obtained which melted at 66–67°. This product was identical with 2,6-di-*tert*-butyl-4-methylphenol.

2,6-Di-tert-butyl-4-methyl-4-nitro-2,5-cyclohexadiene-1-one (XIV). To a solution of 2,6-di-*tert*-butyl-4-methylphenol (3.3 g.) in glacial acetic acid (20 ml.), 70% nitric acid (2.4 ml.) was added gradually. The temperature of the reaction was maintained at 20° by cooling externally. Upon further cooling of the reaction mixture a crystalline white precipitate separated which was collected (3 g.) on a filter. Upon crystallization from methanol colorless needles were obtained which melted at 97° (dec.).

Anal. Calcd. for $C_{15}H_{23}O_3N$: C, 67.9; H, 8.7. Found: C, 67.9; H, 8.9.

The ultraviolet spectrum showed $\lambda_{max}^{ethanol}$ 233 mμ; ϵ_{max} 10,250.

Hydrolysis of XIV. The nitro compound XIV (1 g.) was dissolved in a small amount of ethanol, water (25 ml.) added, and the whole heated on a low flame for 20 min. The resulting dark-brown oil was extracted with ether, and the ether was removed. Upon standing for 2 days the oily material solidified. The crude product (0.8 g.) was dissolved in benzene, and chromatographed on alumina. The least adsorbed orange colored band gave a red solid (0.3 g.) which was crystallized from acetic acid. Orange-red needles of (VI) were thus obtained which melted at 314°. The light absorption spectrum in ethanol showed λ_{max} 442 mμ; ϵ_{max} 72,000.

On eluting the column with benzene containing 0.5% ethanol, and evaporation of the solvent a colorless compound (0.12 g.) was obtained which melted at 110° This product was shown to be identical with XII. Further elution of the column with benzene containing 2% ethanol gave a small amount of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde.

2,6-Di-tert-butyl-4-bromo-4-bromomethyl-2,5-cyclohexadiene-1-one (XV). To a solution of the tertiary alcohol (XII; 0.2 g.) in a mixture of acetic acid (2 ml.) and water (0.1 ml.), bromine (0.05 ml.) in acetic acid (1 ml.) was added. After 15 min. shining pale yellow plates (0.2 g.) separated which melted at 118°.

Anal Calcd for $C_{15}H_{22}OBr_2$: C, 47.6; H, 5.8; Br, 42.3. Found: C, 48.3; H, 6.0; Br, 41.7.

Concentration of the mother liquor gave 3,5-di-*tert*-butyl-4-hydroxy benzaldehyde (50 mg.).

Reaction of 4,4'-dihydroxy-3,5,3',5'-tetra-tert-butyl diphenylmethane (XVI) *with oxygen.* To a solution of the diphenylmethane (XVI; 2.1 g.) in ethanol (25 ml.), potassium hydroxide (0.5 g. in 0.5 ml. water) was added, and the flask quickly connected to an oxygen buret. The solution gradually turned deep purple and consumed about 124 ml. of oxygen in 8 min. The purple colored solution was poured into one liter of water and neutralized with acetic acid. The whole was then extracted with ether. Upon evaporation of the ether a yellow oil (2.0 g.) was obtained (mol. wt. 265). On chromatographing the oil (1.5 g.) over a column of alumina using benzene as solvent and eluent, the major fraction gave an orange-yellow crystalline product (0.3 g.) identified as 2,6-di-*tert*-butylbenzoquinone, melting at 67°.[17, 23] The infrared spectrum was identical with that reported by Müller and Ley.[10]

The absorption spectrum in isoöctane showed λ_{max} 252, 308, and 380 mμ; ϵ_{max} 15,800, 384, and 261 respectively.

On eluting the column with benzene containing 1% ethanol, a colorless fraction (0.43 g.) was obtained which melted at 187°. The product was shown to be identical with 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde.

Reaction of compound XVIII *with base.* Compound XVIII (0.04 g.) was suspended in a ethanolic (50 ml.) solution of sodium hydroxide (5%; 1 ml.). The air in the apparatus was replaced by nitrogen. The whole was then agitated vigorously. The color of the solution became intense purple in about 10 min. A small sample was withdrawn and its visible absorption measured at 575 mμ at different intervals. The extinction was found to be about ϵ_{max} 120,000 showing approximately half as much of XVII compared to the pure methylenequinone which has ϵ_{max} 220,000.

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Bromination of Octene-1 with *N*-Bromosuccinimide*

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Received June 27, 1957

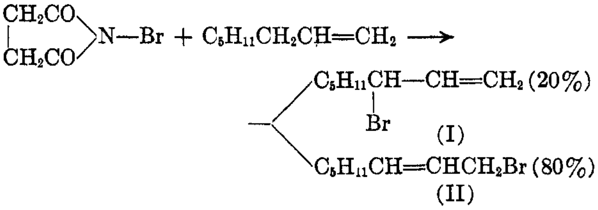
When *N*-bromosuccinimide reacts with octene-1 in light or in the presence of traces of peroxides, there is obtained a mixture consisting of 65% of monobrominated octenes, 15% of dibrominated octenes, and higher bromination products. The monobrominated octenes are *trans*-1-bromooctene-2 (80%; n_D^{20} 1.4760; b.p. 62–63°/6 mm) and 3-bromooctene-1 (20%; n_D^{20} 1.4669; b.p. 69–70°/14 mm). The dibrominated octenes contain one readily replaceable bromine atom per molecule. The reaction in question is retarded by oxygen and completely inhibited by small amounts of nitrosobenzene (0.5 mole %).

It has been claimed[1] that *N*-bromosuccinimide reacts with simple olefins containing a terminal double bond to give mixtures of allylic bromides of unknown composition. The composition of the mixture of the octenyl bromides resulting from the reaction of octene-1 with *N*-bromosuccinimide was investigated as part of an extensive study of the various mechanisms involved when *N*-bromosuccinimide reacts with a variety of organic compounds.

The bromination of octene-1 with *N*-bromosuccinimide was carried out in carbon tetrachloride in the presence of benzoyl peroxide (0.2 mole %) or in light. At 75°, in the absence of oxygen, the reaction is complete in about 1 hr. The reaction mixture was fractionated at low temperature and pressure. Two major fractions were thus obtained: (1) a mixture of monobrominated octenes (65 per cent); (2) a residue consisting of dibrominated octenes and higher bromination products.

Two fractionations of the monobrominated products through a 24-inch tantalum spiral column gave two fractions in the raio of one part to four.

Structures are assigned to these two materials (I and II) on the basis of their infrared spectra.[2] The lower boiling material (n_D^{20} 1.4670) has bands with maxima at 1635 cm.$^{-1}$, 985 cm.$^{-1}$, and 920 cm.$^{-1}$ (vinyl group) and therefore has structure I (3-bromooctene-1); the higher boiling material (n_D^{20} 1.4760) has bands with maxima at 1658 cm.$^{-1}$ and 962 cm.$^{-1}$ (*trans*-disubstituted double bond) and must therefore be compound II (1-bromooctene-2).



$$(CH_2CO)_2N{-}Br + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow \begin{cases} C_5H_{11}\underset{\displaystyle Br}{\underset{|}{C}}H{-}CH{=}CH_2\ (20\%) & \text{(I)} \\ C_5H_{11}CH{=}CHCH_2Br\ (80\%) & \text{(II)} \end{cases}$$

The dibrominated octenes, which form about 15 per cent of the reaction mixture, are extremely unstable; they could be distilled, without decomposition, from the higher bromination products only in a molecular still. Unfortunately, under these conditions small amounts of succinimide (formed in the reaction) are found in each fraction. Analyses, for total bromine and bromine removable by silver nitrate, indicate that only one of the bromine atoms in these dibromides is readily replaceable. Because of the large number of dibromides (each containing only one allylic bromine atom) which would result from bromination of compounds I and II, the dibromides were not examined in detail.

Whether products I and II formed in a ratio of 1 to 4 are primary reaction products, or whether formation of the large amounts of II is due (under

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* This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

[1] K. Ziegler, A. Späth, E. Schaaf, W. Schumann, and E. Winkelmann, *Ann.*, **551**, 93 (1942); Two excellent reviews are available (up to 1951) of the reactions of *N*-bromosuccinimide with many types of organic compounds [C. Djerassi, *Chem. Revs.*, **43**, 271 (1948); T. D. Waugh, *N-Bromosuccinimide, Its Reaction and Uses*, Arapahoe Chemicals, Inc., Boulder, Colorado, 1951].

[2] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1954.