[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF VERMONT]

The Thermal Decomposition of Two Bis-(tri-alkylcyclohexadienone) Peroxides

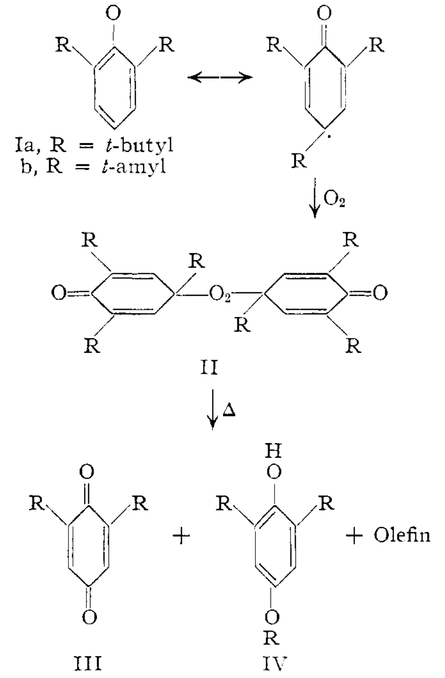
BY CLINTON D. COOK, ROBERT C. WOODWORTH AND PETER FIANU

RECEIVED APRIL 2, 1956

Thermal decomposition of bis-(1,3,5-tri-*t*-butyl-2,5-cyclohexadien-4-one) peroxide leads to the formation of 2,6-di-*t*-butyl-4-*t*-butoxyphenol, 2,6-di-*t*-butylquinone and isobutylene as the main products. Some isobutane is formed, implying the incursion of free *t*-butyl radicals. Similar results are obtained with bis-(1,3,5-tri-*t*-amyl-2,5-cyclohexadien-4-one) peroxide.

The formation of bis-cyclohexadienone peroxides (II) by the reaction of oxygen with 2,4,6-tri-*t*-alkylphenoxy radicals I has been discussed in recent papers.[1-4] It was reported[2] that bis-(1,3,5-tri-*t*-butyl-2,5-cyclohexadien-4-one) peroxide (IIa) undergoes thermal decomposition with the evolution of isobutylene. The course of the decomposition is of particular interest in view of the probable formation of unsymmetrical cyclohexadienone peroxides as the chain stopping reaction in autoxidation inhibition by phenols.[5-7]

Further study on bis-(1,3,5-tri-*t*-butyl-2,5-cyclohexadien-4-one) peroxide and on bis-(1,3,5-tri-*t*-amyl-2,5-cyclohexadien-4-one) peroxide has shown that at temperatures of around 200° the main products of decomposition were 2,6-di-*t*-alkylquinones (III), 2,6-di-*t*-alkyl-4-*t*-alkoxyphenols (IV) and the olefins derived from the *t*-alkyl groups (eq. 1).



(1)

The 2,6-di-*t*-butylquinone[6,8] was identified by conversion to 2,6-di-*t*-butyl-4-methoxyphenol[9] and by the fact that it formed only a monoxime, a characteristic of quinones with one hindered carbonyl group.[10] The product identified as 2,6-di-*t*-butyl-4-*t*-butoxyphenol was identical with a sample prepared by the addition of isobutylene to 2,6-di-*t*-butylhydroquinone. The behavior of this compound upon oxidation with alkaline ferricyanide was also consistent with this formulation (see Experimental). The identities of the products from the *t*-amyl substituted peroxide (IIb) were in the main shown by comparison of the infrared spectra with those of the corresponding *t*-butyl derivatives.

That the decomposition follows the expected free radical course was confirmed by the facts that the peroxides were effective catalysts for the polymerization of acrylonitrile and that the vivid blue color characteristic of 2,4,6-tri-*t*-butylphenoxy[1,2] appeared when the decomposition was conducted in molten 2,4,6-tri-*t*-butylphenol. Free *t*-alkyl radicals apparently intervene in the process since the gaseous product from the decomposition of the *t*-butyl substituted peroxide IIa contained 10–30% isobutane.

Since the bis-(1,3,5-tri-*t*-butyl-2,5-cyclohexadien-4-one) peroxide was the more readily obtainable, its decomposition was studied in more detail. It was found that the yield of gaseous products varied with the purity of the peroxide and with the temperature of decomposition. Thus at 207° carefully purified peroxide (m.p. 147–148°) consistently yielded a mole ratio of gas to peroxide of 0.86 ± 0.02 in a large number of trials. With impure peroxide (m.p. 130–136°) mole ratios of 1.01 and 0.99 were obtained in two trials. At 216° the mole ratio was 1.00 ± 0.02 for four trials. Unfortunately, the experiment cited in our original work[2] was at this temperature, implying a more precise stoichiometry than actually prevails. As the temperature was further increased, other reactions apparently became important. At 250° somewhat over two moles of gas was evolved per mole of peroxide. There was, however, a very sharp reduction in rate after a mole ratio of one was passed. The products formed at this temperature have not been investigated.

Bickel and Kooyman[6] noted the formation of 2,6-di-*t*-butylquinone during the reaction of 2,4,6-tri-*t*-butylphenol with 2,2,3,3-tetraphenylbutane and oxygen in the presence of α,α'-azodiisobutylnitrile. Metro[8] obtained the same quinone as a product of the autoxidation of a lubricating oil con-

---

(1) C. D. Cook, *J. Org. Chem.*, **18**, 262 (1953).

(2) C. D. Cook and R. C. Woodworth, THIS JOURNAL, **75**, 6242 (1953).

(3) C. D. Cook, D. A. Kuhn and P. Fianu, *ibid.*, **78**, 2002 (1956).

(4) Muller and Ley, *Ber.*, **87**, 922 (1954).

(5) T. W. Campbell and G. M. Coppinger, THIS JOURNAL, **74**, 1469 (1952).

(6) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 638 (1953).

(7) C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, THIS JOURNAL, **77**, 3233 (1955).

(8) S. J. Metro, *ibid.*, **77**, 2901 (1955).

(9) C. D. Cook, R. G. Inskeep, A. W. Rosenberg and E. C. Curtis, Jr., *ibid.*, **77**, 1672 (1955).

(10) G. W. Wheland, "Advanced Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., 1949, p. 381.

taining 2,6-di-*t*-butyl-4-methylphenol as an oxidation inhibitor. Finally, Swift, Mann and Fisher[11] isolated a red quinone, believed to be derived from γ-tocopherol, from autoxidized cottonseed oil. The present work suggests that these quinones are produced by decomposition of the corresponding cyclohexadienone peroxides.

Acknowledgments.—A Frederick Gardner Cottrell grant from the Research Corporation made this work possible. We are also indebted to Dr. Richard G. Inskeep for aid in the measurement of the infrared spectra.

Experimental

Preparation of Peroxides.—(a) Bis-(1,3,5-tri-*t*-butyl-2,5-cyclohexadien-4-one) peroxide (IIa) was prepared as previously reported.[2]

(b) **Bis-(1,3,5-tri-*t*-amyl-2,5-cyclohexadien-4-one) Peroxide (IIb).**—A solution of 9 g. (0.03 mole) of 2,4,6-tri-*t*-amylphenol[3] in 150 ml. of benzene was stirred with a solution of potassium ferricyanide (32 g., 0.1 mole) and 10 g. of potassium hydroxide in 100 ml. of water while oxygen was bubbled through the system. When all traces of blue color had disappeared, the benzene layer was separated, washed, dried and evaporated to dryness. The yellow solid was taken up in hot ethanol and quickly cooled. A yield of 8.5 g. (90%) of yellow crystals, m.p. 105–106° dec., was obtained. Further recrystallization raised the melting point to 106–108° dec. *Anal.* Calcd. for $C_{42}H_{70}O_4$: C, 78.94; H, 11.04. Found: C, 79.11; H, 11.20.

Decomposition of the Peroxides.—The peroxides, usually in approximately 1-g. quantities, were decomposed in bulbs fitted into the necks of standard taper flasks, refluxing liquids in the flasks maintaining the desired temperatures.

Isolation of Products.—The gaseous products were collected in a mercury filled gas buret or in a cold trap.

Cyclohexane solutions of the decomposition residues were reduced with zinc and acetic acid and the resulting hydroquinones removed by repeated extractions with 2% aqueous sodium hydroxide (containing a trace of sodium hydrosulfite). Acidification of the basic extract with hydrochloric acid gave the hydroquinones. Evaporation of the cyclohexane after extraction gave the 4-alkoxyphenols.

2,6-Di-*t*-butylquinone (IIIa) and 2,6-Di-*t*-butylhydroquinone.—When decomposed at 207°, the *t*-butyl substituted peroxide IIa gave yields of 85–95% (based on eq. 1) of crude hydroquinone. Recrystallization from ligroin gave white crystals, m.p. 115–116°; reported[6] 103.6°.

Oxidation of the hydroquinone with aqueous chromium trioxide gave 2,6-di-*t*-butylquinone, m.p. 67.5–68.5°, reported 68°,[6] 65–66°.[8] The oxime melted at 218.5–220°; reported 219–220°.

2,6-Di-*t*-amylbenzoquinone (IIIb) and 2,6-Di-*t*-amylhydroquinone.—The decomposition mixture from 2.2 g. of the *t*-amyl substituted peroxide IIb at 226° gave 0.8 g. (94%) of crude 2,6-di-*t*-amylhydroquinone, m.p. 109–110°; after recrystallization from ligroin, m.p. 111–112°. *Anal.* Calcd. for $C_{16}H_{26}O_2$: C, 76.74; H, 10.46. Found: C, 77.12; H, 9.72.

Oxidation of the hydroquinone with aqueous chromium trioxide gave orange 2,6-di-*t*-amylquinone which melted at room temperature. The quinone was converted to the monoxime, m.p. 133–134°. *Anal.* Calcd. for $C_{16}H_{25}O_2N$: C, 72.96; H, 9.56; N, 5.31. Found: C, 73.17; H, 9.35; N, 5.50.

2,6-Di-*t*-butyl-4-butoxyphenol (IVa). (a) **From the Peroxide (IIa).**—After extraction of the quinone (as hydroquinone) the residues from the peroxide decompositions at 207° were recrystallized from ligroin. After one such recrystallization yields in the order of 80% of 2,6-di-*t*-butyl-4-*t*-butoxyphenol were obtained. After several recrystallizations, white crystals, m.p. 99–100°, were obtained. This phenol was oxidized by alkaline ferricyanide to produce a brilliant red phenoxy radical, a reaction typical of such phenols.[3] *Anal.* Calcd. for $C_{18}H_{30}O_2$: C, 77.66; H, 10.86. Found: C, 77.50; H, 10.98.

(b) **From the Addition of Isobutylene to 2,6-Di-*t*-butylhydroquinone.**—One gram of the hydroquinone was dissolved in 20 ml. of benzene, a drop of sulfuric acid added and isobutylene passed through the solution at 20° until a 0.2-g. weight increase was achieved. The solution was washed with base, the benzene evaporated and the residue recrystallized from ligroin. A yield of 0.7 g. of 2,6-di-*t*-butyl-4-*t*-butoxyphenol resulted. The melting point, mixture melting point and infrared spectra were identical with the product isolated from the peroxide decomposition.

2,6-Di-*t*-butyl-4-*t*-amyloxyphenol.—After extraction of the quinone (as hydroquinone) from the *t*-amyl substituted peroxide IIb decomposition, the residue was vacuum distilled. A viscous, straw-colored liquid, b.p. 118–119° at 0.02 mm., was obtained. The infrared spectrum showed the presence of a highly hindered hydroxyl group. Oxidation with alkaline ferricyanide produced a brilliant red phenoxy radical which reacted with oxygen to form bis-(3,5-di-*t*-amyl-1-*t*-amyloxy-2,5-cyclohexadien-4-one) peroxide, m.p. 82–84° dec. The analysis of this peroxide and its ultraviolet spectra[3] indicate that the structure assigned the phenol is correct. *Anal.* Calcd. for $C_{42}H_{70}O_6$: C, 75.17; H, 10.51. Found: C, 75.14; H, 10.37.

2,6-Di-*t*-amyl-4-*t*-methoxyphenol.—Two ml. of dimethyl sulfate was added to a solution of 1.0 g. of 2,6-di-*t*-amylhydroquinone dissolved in 40 ml. of 5% sodium hydroxide. After 2 hr. of stirring under a nitrogen atmosphere, the system was extracted with cyclohexane. Evaporation of the cyclohexane gave a semi-solid. The infrared spectrum of this product showed the presence of only a hindered hydroxyl group and suggested a rather pure compound. Oxidation with alkaline ferricyanide gave a brilliant red phenoxy radical[3] which reacted with oxygen to give a solid peroxide. The reaction was not studied further.

Identification of the Gaseous Products. (a) **From Bis-(1,3,5-tri-*t*-butyl-2,5-cyclohexadien-4-one) Peroxide (IIa).**—Yields from the decomposition of this peroxide were determined by the volume of gas evolved. The isobutylene was identified by the formation of the dibromide[2] and from comparison of the infrared spectrum with that of a known sample. The infrared spectrum in the region 2700–3400 cm.$^{-1}$ was measured at a pressure of approximately 25 mm. in a 5-cm. cell using a lithium fluoride prism.

The presence of isobutane was shown by the fact that only 70–90% of the gas dissolved in fuming sulfuric acid and by comparison of the infrared spectra of the gaseous mixtures with those of known mixtures.

(b) **From Bis-(1,3,5-tri-*t*-amyl-2,5-cyclohexadien-4-one) Peroxide (IIb).**—A 6.3-g. (0.0098 mole) sample of this peroxide was decomposed at 230° and the low boiling product collected in a Dry Ice trap. After 110 min., 0.66 g. (0.0094 mole) of liquid, b.p. approx. 32°, was obtained. The liquid absorbed bromine very rapidly. A rough measurement of the density at 25° gave 0.69. The densities and boiling points of the branched amylenes are[12]: 3-methylbutene-1, 0.632; 20.1°; 2-methylbutene-1, 0.650, 31°; 2-methylbutane-2, 0.662; 38.4°. The infrared spectrum was very similar to but not identical with that of "trimethylethylene" produced by the dehydration of *t*-amyl alcohol.[13] Thus the data indicate that an amylene, or a mixture of amylenes, is produced but does not clearly characterize the specific one(s).

Polymerization of Acrylonitrile by the Peroxides.—Solutions (2%) of the peroxide in acrylonitrile were flushed with oxygen-free nitrogen and placed in a bath at 70°. Within 90 sec. the solutions became opalescent and by 150 sec. they were opaque. Curds of solid polymer were precipitating within 4 min. Blanks showed no polymerization after 15 min.

BURLINGTON, VERMONT

---

[11] C. E. Swift, G. E. Mann and G. S. Fisher, *Oil and Soap*, **21**, 317 (1944).

[12] M. L. Sherrill and G. F. Walker, THIS JOURNAL, **58**, 742 (1936).

[13] J. F. Norris and R. Raymond, *ibid.*, **49**, 2624 (1927).