gave tetraphenylfuran (VIII, 47%) and the more soluble methyl ether Vc (34%), m.p. 129–131° (lit.,[7] 128°).

Anal. Calcd. for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98; OCH_3, 7.67. Found: C, 86.06; H, 6.10; OCH_3, 7.30.

No infrared absorption bands in the hydroxyl and carbonyl regions.

Treatment of the ethyl ether Vd with methanol to which saturated methanolic hydrogen chloride had been added (refluxing for 40 min.) gave VIII (59%) and Vc (32%).

Conversion of Vb into tetraphenylfuran (VIII) was effected in practically quantitative yield by refluxing glacial acetic acid (2 min.) (VIII was identified by mixture m.p. 174–176° and infrared absorption spectrum).

***cis*-1,1,2,4,4-Pentaphenyl-2-butene-1,4-diol (VI).**—Twenty grams (0.064 mole) of *cis*-dibenzoylstyrene (III) was added portionwise over 5 min. to a 200 ml. solution of 1.31 moles of phenyllithium (under nitrogen) with continued stirring for an additional 10 min. Hydrolysis with ammonium chloride solution and work-up with crystallization from methanol gave 10 g. (33%) of *cis*-glycol VI, m.p. 146–148°. It retained solvent of crystallization tenaciously, and it required drying under fusion for analysis.

Anal. Calcd. for $C_{34}H_{28}O_2$: C, 87.17; H, 5.97. Found: C, 87.06; H, 6.00.

Infrared absorption band (on sample dried by fusion): 3 μ, broad and strong; none for the carbonyl group. Ultraviolet absorption (in absolute ethanol): no maximum above 220 mμ; slight shoulder on the curve at 250 mμ, ε 5700. Crystallizations from solvent containing methanol gave material containing approximately 1 molecule of methanol. Samples carrying ethanol, methanol, or water of crystallization all showed strong broad absorption areas centering at *ca.* 3.1 μ. Crystallization from benzene–acetone mixture gave a product showing a strong carbonyl band at 5.9 μ (acetone of crystallization), and after drying under heating the sample showed complete absence of this carbonyl band.

The *cis*-glycol VI was also obtained by the action of phenyllithium exactly as above on the cyclic hemiketal Vb (total reaction time 18 min.); yield 15%, identified by melting point and infrared spectrum.

2,2,3,5,5-Pentaphenyldihydrofuran (VII).—A solution of 9.8 g. of the *cis*-glycol VI in 100 ml. of glacial acetic acid was refluxed for 3 min. Cooling precipitated the dihydrofuran VII, 5.9 g. (60%), recrystallized from methanol–benzene mixture; m.p. 199–200°.

Anal. Calcd. for $C_{34}H_{26}O$: C, 90.67; H, 5.77. Found: C, 90.28; H, 5.87. Infrared absorption: no hydroxyl or keto bands. Ultraviolet absorption (in absolute ethanol): λ_{max} 250 mμ, ε 14,500.

2,4,6-Trimethylbenzyl Hydroperoxide

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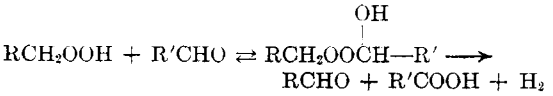
2,4,6-Trimethylbenzyl hydroperoxide has been synthesized and its thermal and acid-catalyzed decompositions examined. Acid-catalyzed decomposition products (mesitol and formaldehyde) complicate the thermal decomposition due to participation of formaldehyde in hydroxyperoxide formation. Mesityoxymethyl benzoate (III) is produced in good yield from decomposition of I with benzoic acid.

The decomposition of primary benzyl hydroperoxides has not been studied in detail, despite the importance of these compounds as intermediates in the autoxidation of the methylbenzenes. *p*-Methylbenzyl hydroperoxide has been shown to decompose to a limited extent *via* a hydroxyperoxide to give hydrogen as a product.[1] The involvement of the hydroxyperoxide and the yield of hydrogen are much less in this system than for the aliphatic primary hydroperoxides examined by Mosher,[2] a consequence of the lower reactivity of the aromatic aldehyde toward nucleophilic attack (equation 1). The importance of equation 1 in the overall decomposition can be further reduced if R′ is so substituted that attack on the aldehyde function is sterically hindered, such that the rate of formation of the hydroxyperoxide would be very much slower than the hydroperoxide decomposition. To test this viewpoint, 2,4,6-trimethylbenyl hydroperoxide (I), whose corresponding aldehyde is the highly hindered mesitaldehyde (R = R′ = 2,4,6-trimethylphenyl in equation 1) was synthesized and its decomposition examined.



$$RCH_2OOH + R'CHO \rightleftharpoons RCH_2OO\overset{OH}{\overset{|}{C}}H{-}R' \longrightarrow RCHO + R'COOH + H_2 \quad (1)$$

Results and Discussion

The synthesis of I was achieved *via* oxidation of the appropriate Grignard reagent with oxygen at low temperatures.[3] Although some peroxidic material was formed, the yield was poor (*ca.* 30%) and the product contaminated with 2,4,6-trimethylbenzyl alcohol and dimesitylethane, the latter presumably formed during preparation of the Grignard reagent.[4] Base extraction improved the purity of the hydroperoxide somewhat, but removal of the remaining impurities by recrystallization was a wasteful process. Excellent purification of the base extract could be obtained by chromatography on Cellulose powder,[5] from which could be recovered, after a single recrystallization, hydro-

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(1) W. J. Farrissey, Jr., *J. Am. Chem. Soc.*, **84**, 1002 (1962).

(2) H. S. Mosher and C. F. Wurster, *ibid.*, **77**, 5451 (1955); C. F. Wurster, L. J. Durham, and H. S. Mosher, *ibid.*, **80**, 327 (1958); L. J. Durham, C. F. Wurster, and H. S. Mosher, *ibid.*, **80**, 332 (1958).

(3) C. Walling and S. A. Buckler, *ibid.*, **77**, 6032 (1955).

(4) L. I. Smith and J. Nichols, *J. Org. Chem.*, **6**, 489 (1941).

(5) N. Milas and A. Golubovic, *J. Am. Chem. Soc.*, **81**, 3361 (1959)

peroxide containing 98.5% of the theoretical active oxygen.

Decomposition of I was effected by heating to 100–130° in chlorobenzene solution in a helium atmosphere. Any evolved gas was collected and analyzed by gas chromatography. After removal of solvent, the product was analyzed by n.m.r. and mass spectrometry. Since many minor products were formed in addition to mesitoic acid, mesitaldehyde and 2,4,6-trimethylbenzyl alcohol, the n.m.r. and MS analyses were subject to considerable interference. Consequently, some of the runs were analyzed by separation of the mixture into its major constituents; acid was removed by carbonate extraction, aldehyde precipitated as the semicarbazone and the residue chromatographed on alumina to give the alcohol. This analysis involved rather large errors due to the small quantity of material handled, but in some instances it was the only procedure available.

The product distributions for a number of decomposition runs are shown in Table I. As expected, no hydrogen was produced, even for some runs to which mesitaldehyde was added initially. The more rapid decompositions with *n*-heptaldehyde were attended by considerable decarbonylation along with hydrogen evolution.

TABLE I

PRODUCT DISTRIBUTION FROM DECOMPOSITION OF I[a]

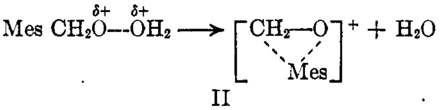
Products	C_6H_5Cl 130°	C_6H_5Cl 2.4 *n*-$C_6H_{13}CHO$ 130°	EtOH/H_2O HCl 26°
H_2	...[b]	0.01	
CO	...	.22[c]	
CO_2	...	.003	
Mes[h] COOH	0.06[d]	.002[d]	
Mes CH_2OH	.26[e]	.22[e]	
Mes CHO	.23[e]	.16[e]	0.03[f,g]
Mes OH	...	...	.8[d,f]
n-$C_6H_{13}COOH$		.01[g]	

[a] Expressed in moles per mole of hydroperoxide decomposed. Solutions were *ca.* 0.2 molar in hydroperoxide. [b] No gas evolved under these conditions. [c] Moles per mole of added *n*-heptaldehyde. [d] Analysis by MS. [e] Analysis by isolation procedure. [f] N.m.r. analysis. [g] Estimated by infrared analysis. [h] Mes = 2,4,6-trimethylphenyl.

That some of the *n*-heptaldehyde was involved in hydroxyperoxide formation is supported by the isolation of an equivalent of *n*-heptanoic acid. In addition to the products shown in the table, a number of other materials were present, but not in sufficient quantity for adequate identification. We were unable to detect any significant amount of product arising from intramolecular attack on the *ortho*-methyl substituents.[6]

At 100°, both with and without *n*-heptaldehyde added, hydrogen production was extensive. In addition to acid, aldehyde, and alcohol, mesitol, an acid-catalyzed decomposition product, was formed to an appreciable extent. Since very little mesitoic acid was found, it is likely that most of the hydrogen was not derived from a hydroxyperoxide involving I and mesitaldehyde. More probably, the hydrogen results from reaction of I with the formaldehyde produced along with mesitol. The relatively low activation energy for the acid-catalyzed process accounts for its increased importance at the lower temperature.

The great ease of rearrangement of the trimethylphenyl group was demonstrated by some decompositions in ethanol–water solution at room temperature with hydrochloric acid. Nearly complete rearrangement to mesitol and formaldehyde was observed, in stark contrast to other primary benzyl hydroperoxides which give considerable aryl aldehyde on acid-catalyzed decomposition.[7,8] The ability of the trimethylphenyl group to support an electron deficiency is reflected in its facile migration to the developing positive center (equation 2).



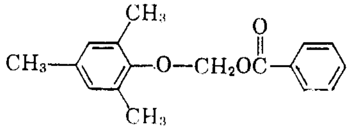
$$\text{Mes CH}_2\overset{\delta+}{\text{O}}\text{---}\overset{\delta+}{\text{O}}\text{H}_2 \longrightarrow \left[\begin{array}{c}\text{CH}_2\text{—O}\\ \text{Mes}\end{array}\right]^+ + \text{H}_2\text{O} \qquad (2)$$

II

$$\text{II} + \text{H}_2\text{O} \longrightarrow \text{H}_2\overset{+}{\text{O}}\text{—CH}_2\text{—O—Mes} \longrightarrow \text{Mes OH} + \text{CH}_2\text{O} + \text{H}^+ \qquad (3)$$

Reaction of intermediate II with water followed by decomposition of the resultant hemiacetal gives mesitol and formaldehyde.[7]

The effect of carboxylic acids on the decomposition was assessed by heating a mixture of the hydroperoxide with benzoic acid at 130°. The product, isolated in *ca.* 80% yield, was a benzoate ester. The n.m.r. and mass spectra, saponification equivalent, and elemental analyses were consistent with structure III. Saponification of the ester yielded



III

mesitol, benzoic acid, and formaldehyde (isolated as the dinitrophenylhydrazone) in accord with the hemiacetal ester structure.[9]

The isolation of III in high yield has some bearing on the mechanism of the acid-catalyzed rearrangement of hydroperoxides. Apparently, the rearranged ion II[10] need not react with the leaving

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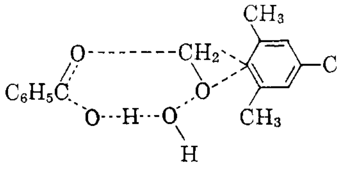
[6] F. D. Greene, G. R. Van Norman, J. C. Cantrill, and R. D. Gillion, *J. Org. Chem.*, **25**, 1790 (1960). The author is grateful to Professor Greene for pointing out this reference.

[7] A. W. de Ruyter van Steveninck and E. C. Kooyman, *Rec. trav. chim.*, **79**, 413 (1960); H. B. van Leeuwen, J. P. Wibaut, A. F. Bickel, and E. C. Kooyman, *ibid.*, **78**, 667 (1959).

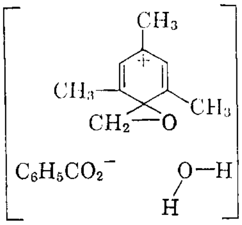
[8] M. S. Kharasch and J. G. Burt, *J. Org. Chem.*, **16**, 113, 128 (1951); A. D. Boggs, thesis, Ohio State University, 1954.

[9] H. Hock and H. Kropf, *Ber.*, **88**, 1544 (1955); R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948); H. J. Shine and R. H. Snyder, *J. Am. Chem. Soc.*, **80**, 3064 (1958).

[10] A referee has suggested that the free ion II need not be an intermediate and that either the cyclic transition state A or the ion pair B may be postulated.



A



B

water molecule (equation 3), but may react with other nucleophiles in the system, benzoic acid in this instance.

Also, formation of III precludes extensive participation of equation 4 as a chain propagation step[7,8]

$$\text{II} + \text{Mes CH}_2\text{OOH} \longrightarrow \text{Mes OCH}_2\text{OH} + \text{Mes CH}_2\text{O}^+ \quad (4)$$

in the decomposition.

Experimental

Decomposition Experiments.—The thermal decompositions of I were conducted in an inert atmosphere as previously described.[1] For the acid-catalyzed decomposition, 120 mg. of I in 5 ml. of aqueous ethanol was decomposed with 0.1 ml. of concentrated hydrochloric acid at room temperature for 16 hr. After dilution with water and solvent extraction, there was obtained 97 mg. of a white solid which was mainly mesitol.

2,4,6-Trimethylbenzyl Hydroperoxide (I).—The Grignard reagent was prepared in *ca.* 70% yield from the slow addition of 16.8 g. (0.1 mole) of 2,4,6-trimethylbenzyl chloride in 200 ml. of ether to 10.1 g. of magnesium and 100 ml. of ether at 0°. A portion of the Grignard solution (80 ml., *ca.* 0.019 mole) was added over a period of 2 hr. to 100 ml. of ether which was continuously saturated at −78° with a stream of dry oxygen. The mixture was warmed to 0°, poured into ice water and acidified to pH 8.5–9 with carbon dioxide gas. The ether layer was separated and extracted with ice-cold sodium hydroxide solution. After acidification with carbon dioxide, ether extraction, and solvent evaporation, there remained *ca.* 1 g. of a peroxidic solid. Two recrystallizations from methylcyclohexane gave 0.4 g. (0.0024 mole, 13% yield) of white solid,[11] melting at 84–89° with slight decomposition.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H. 8.49; active oxygen, 9.64%. Found: C, 72.6; H, 8.3; active oxygen, 9.5%.

Material of comparable purity was obtained in much higher yield by chromatography of the base extract on a Cellulose–dimethylformamide[5] column. One recrystallization from methylcyclohexane gave a 30% yield of material melting at 86–89°.

Mesitoxymethyl Benzoate (III).—A mixture of 0.46 g. of 2,4,6-trimethylbenzyl hydroperoxide and 1.24 g. of benzoic acid was heated to 134° for 3 hr. After the product was extracted with sodium carbonate solution, there remained 0.59 g. of an oil which solidified on standing. Recrystallization from pentane gave m.p. 71.5–71.7°.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71; sapon. equiv., 270. Found: C, 75.6; H, 6.9; sapon. equiv., 274.

From saponification of 0.12 g. of III, there were isolated 60 mg. of mesitol, m.p. 72.5–73.0°, mixture m.p. with authentic mesitol, 73.0–73.5°; and 40 mg. of benzoic acid, m.p. 118–123°. The acidified aqueous solution yielded a 2,4-dinitrophenylhydrazone, m.p. 165–166.5°, alone and mixed with authentic formaldehyde 2,4-dinitrophenylhydrazone.

Acknowledgment.—The author is indebted to L. C. Jennings for much of the experimental work, to N. F. Chamberlain and his associates for the n.m.r. spectra and their interpretation, and to Dr. F. C. Stehling and co-workers for the MS analyses.

[11] R. Hüttel, H. Schmid, and H. Ross, *Ber.*, **92**, 699 (1959), report the synthesis of an oil which is *ca.* 70% I.

The Free Radical Chemistry of Cyclic Ethers. III. A Free Radical Rearrangement Reaction[1]

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The mechanism of the *tert*-butyl peroxide-induced free radical addition of four-, five-, and six-membered cyclic ethers to 1-octene has been clarified. Ketones in addition to ethers were identified as the major products from all reactions studied. Thus, the chain transfer atom is the hydrogen atom alpha to the oxygen atom. The products also suggest that the intermediate alpha-ethereal radicals undergo decyclization. The infrared spectra show a trace of carbon-carbon unsaturation indicating that disproportionation is the chain termination step. The mechanistic implications of these results are discussed.

Previous work on the free radical chemistry of four-, five- and six-membered cyclic ethers has been limited to thermal decomposition and ultraviolet initiated reactions. In 1937, Kuchler and Lambert[3] demonstrated that the homogeneous thermal decomposition of *p*-dioxane proceeds mainly by a chain reaction. A similar study was carried out by Klute and Walters[4] on the thermal decomposition

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[1] Part II and a previous communication on this work have appeared, T. J. Wallace and R. J. Gritter, *J. Org. Chem.*, **26**, 5256 (1961).

[2] Present address: Esso Research & Engineering Company, Process Research Division, Linden, New Jersey. Abstracted from the Ph.D. dissertation of T. J. Wallace, June, 1960.

[3] L. Kuchler and J. Lambert, *Z. physik. Chem.* (Leipzig), **B37**, 285 (1937).

[4] C. H. Klute and W. Walters, *J. Am. Chem. Soc.*, **68**, 506 (1946).