[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The Preparation and Properties of Some Higher Aliphatic *t*-Hydroperoxides

BY ROBERT W. FOREMAN AND HERMAN P. LANKELMA

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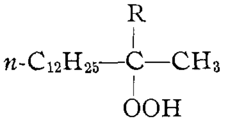
Three higher aliphatic tertiary hydroperoxides, 2-methyl-, 2-phenyl- and 2-cyclohexyltetradecyl hydroperoxides, have been prepared in pure form from the corresponding alcohols by oxidation with 90% hydrogen peroxide. Physical properties, including infrared absorption spectra, were determined for each. Autoxidation of 2-phenyltetradecane was shown to yield 2-phenyl-2-tetradecyl hydroperoxide.

Although many hydroperoxides have been described in the literature, no pure aliphatic hydroperoxides containing more than ten carbon atoms have been reported. For an initial study in this field, we selected *t*-hydroperoxides of the type



$n\text{-}C_{12}H_{25}\text{—}\overset{\displaystyle R}{\underset{\displaystyle OOH}{C}}\text{—}CH_3$ in which R was methyl, phenyl and cyclohexyl.

The three tertiary alcohols used as starting materials were prepared by the Grignard synthesis from dodecylmagnesium bromide and the appropriate ketone. Table I shows the properties of these alcohols. Attempts to oxidize them to the hydroperoxide by methods[1] which have been used for lower homologs were unsuccessful; the alcohols were recovered unchanged.

The oxidation was accomplished by treating the alcohol, dissolved in glacial acetic acid, with a large excess of 90% hydrogen peroxide and a little concentrated sulfuric acid at temperatures between 25 and 30°. This method failed to give 2-tetradecyl hydroperoxide from 2-tetradecanol, indicating that it is satisfactory for preparing tertiary hydroperoxides only.

The crude hydroperoxides were purified by chromatographic separation on activated alumina in conjunction with low-temperature crystallization from *n*-pentane or acetone. The 2-methyl- and 2-phenyl-2-tetradecyl hydroperoxides were isolated in high purity; the 2-cyclohexyl-2-tetradecyl hydroperoxide was obtained in about 90–95% purity. The yields ranged from 12–50%, as shown in Table II. The yield of the 2-methyl- and the 2-cyclohexyl-2-tetradecyl hydroperoxide could have been increased considerably by reworking of filtrates and chromatographic fractions.

Infrared Spectra.—The infrared spectra from 2.5 to 15.0 μ of each of the hydroperoxides and its corresponding alcohol were determined. The most significant absorption bands in the spectra of the 2-methyl compounds occur at 3.0, 8.67, 10.98 and 11.83 μ. The 3.0 μ bands are due to stretching vibrations of the OH and OOH groups. No distinction in position or intensity between the alcohol and hydroperoxide was found. The 8.67 μ bands are assigned to both the bending vibrations of the tertiary OH and to the terminal $C(CH_3)_2$ groups. The alcohol shows an expectedly intense absorption here. The 10.98 μ absorption is unique for the alcohol, while the 11.83 μ band is unique for the hydroperoxide. This latter is characteristic of tertiary hydroperoxides.[2]

The spectra of the 2-cyclohexyl compounds show the expected OH and OOH bands at 3.0 μ. The tertiary OH band at 8.75 μ is present only in the alcohol. The cyclohexyl group and long CH_2 chain give rise to absorptions common to both compounds at 11.20 and 13.87 μ, respectively. Unique for the alcohol is the strong absorption at 10.8 μ. The tertiary OOH band occurs at 11.63 μ and is expectedly less intense than that for the 2-methyl- hydroperoxide. Evidence for a slight carbonyl impurity in 2-cyclohexyl-2-tetradecyl hydroperoxide was observed at 5.84 μ. This impurity probably accounts for the lack of agreement in carbon, hydrogen analysis and low peroxide titration.

The spectra of the 2-phenyl compounds are complicated by the many absorption bands characteristic of the phenyl group. The more prominent of these occur at 3.33, 6.28, 6.67, 9.7, 13.10 and 14.37 μ. The expected OH and OOH stretching bands were found at 2.97 μ, while the tertiary OH bending occurs in the alcohol at 8.72 μ. Unique absorptions for the alcohol appear at 10.6 and 10.75 μ. The characteristic tertiary OOH band occurs at 11.87 μ.

Thermal Stability.—Table III shows the thermal stabilities observed for these hydroperoxides, using the method of Mosher and Williams.[3]

Thermal decomposition is presumed to occur by simple release of O_2. The lower stability of the 2-phenyl- compound is probably traceable to the phenyl group which can stabilize the intermediate free radical.

Attempts to Prepare Salts and Esters.—Attempts to prepare sodium and potassium salts of the 2-methyl- and 2-phenyl-hydroperoxides by treatment with the aqueous or alcoholic hydroxides and with sodium ethylate were unsuccessful. This is similar to the behavior of 9-*trans*-decalyl and triphenylmethyl hydroperoxides but unlike the behavior of lower hydroperoxides.[4]

Attempts to prepare the *p*-nitrobenzoate of 2-methyl-2-tetradecyl hydroperoxide by the method used by Criegee and Dietrich[5] for lower molecular weight hydroperoxides were unsuccessful. Efforts to prepare a 3,5-dinitrobenzoate of 2-phenyl-2-tetradecyl hydroperoxide by the action of 3,5-dinitrobenzoyl chloride were also unsuccessful.

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[1] (a) R. Criegee and N. Dietrich, *Ann.*, **560**, 135 (1948); (b) N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 643 (1946).

[2] (a) A. R. Philpotts and W. Thain, *Anal. Chem.*, **24**, 639 (1952); (b) O. D. Shreve, *et al.*, *Anal. Chem.*, **23**, 282 (1951).

[3] H. R. Williams and H. S. Mosher, THIS JOURNAL, **76**, 2984 (1954).

[4] (a) R. Criegee, *Ber.*, **77**, 22 (1944); (b) R. Criegee and N. Dietrich, *Ann.*, **560**, 135 (1948).

[5] Criegee and Dietrich, reference 4b.

TABLE I

PROPERTIES OF STARTING -2-TETRADECANOLS

Substituent	B.p., °C. (1 mm.)	Refractive index, n^{20}_D	Density d^{20}_4	M.p., °C.	Analyses,[a] % Carbon		Hydrogen	
					Calcd.	Found	Calcd.	Found
2-Methyl	102	1.4438	0.838	21.5[b]				
2-Cyclohexyl	166–170	1.4708	.852	7–9	81.01	81.02	13.60	13.64
2-Phenyl	165–168	1.4918	.898	15–16.5	82.69	82.83	11.80	11.90

[a] Analysis by Huffman Microanalytical Laboratories, Wheatridge, Colorado. [b] H. J. Lunshof, *et al.*, *Rec. trav. chim.*, **66**, 348 (1947).

TABLE II

PROPERTIES OF 2-TETRADECYL HYDROPEROXIDES

Substituent	Yield, %	Refractive index n^{20}_D	Density d^{20}_4	M.p., °C.	Carbon, %		Hydrogen, %		Titer[b] (iodometric)
					Calcd.	Found	Calcd.	Found	
2-Methyl	16	1.4474	0.878	13–14	73.71	73.85	13.20	13.25	93.4
2-Cyclohexyl	12	1.4715	.868	21–23	76.86	76.06	12.90	12.35	89.1
2-Phenyl	50	1.4902[a]	.920	34	78.38	78.10	11.18	11.19	96.4

[a] For super-cooled liquid. [b] Determined by the method of Wagner, Smith and Peters, *Anal. Chem.*, **19**, 976 (1947).

TABLE III

THERMAL STABILITIES OF HYDROPEROXIDES

Hydroperoxide	First bubble temp., °C.	Steady decompn. temp., °C.
2-Methyl-2-tetradecyl	121	127
2-Cyclohexyl-2-tetradecyl	110	115
2-Phenyl-2-tetradecyl-	91	98

Autoxidation of 2-Phenyltetradecane.—An ultraviolet light-catalyzed autoxidation of 2-phenyltetradecane produced 2-phenyl-2-tetradecyl hydroperoxide in small yield. The method approximated that used by Ivanov and Savinova[6] for oxidizing *sec*-butylbenzene. A 6 to 7% concentrate of the hydroperoxide was separated from the oxidized hydrocarbon by chromatography. The presence of the hydroperoxide in the concentrate was established by infrared spectrometry and chemical titration. This result confirms the fact that at low temperatures oxygen attacks a tertiary C–H bond preferentially, even when a large number of secondary C–H groups are available.

Experimental

Density.—A 50-λ micropipet was used to measure sample volume. The samples and pipet were thermostated at 20° prior to measurement. The samples were rapidly pipetted into tared vials. Long draining times were used, but there was probably some error due to holdup on the walls of the pipet. The densities are therefore reported to only three significant figures.

Infrared Spectra.—Infrared spectra were determined using a Perkin–Elmer model 112 single-beam, double-pass, infrared spectrophotometer. This instrument is equipped with a recorder attachment which provides spectra plotted directly in transmittance.[7] Liquid samples were examined undiluted in 0.025-mm. fixed space absorption cells using a rock salt plate for reference. The 2-phenyl-2-tetradecanol was dissolved in 50 vol. % carbon disulfide and then examined in a 0.052-mm. fixed-space cell using a 0.025-mm. cell containing carbon disulfide for reference.

Thermal Stabilities.—A fine capillary eyedropper was used to transfer liquid or fused sample into the sealed end of a 1-mm. Pyrex capillary tube. The capillary tube was attached to a thermometer and then heated in an oil-bath at a rate of 2° per minute. The temperature at which the first bubble formed and rose to the surface was recorded together with the temperature at which a steady stream of bubbles was observed.

Chromatographic Separations.—A column of 48–100 mesh activated alumina in a tube 1 cm. in diameter and 30 cm. long was used. The samples were introduced to the column as 3–4% solutions in *n*-pentane. Effluent rate was maintained at 1.5 ml. per minute. The column was developed with 2 to 4% glacial acetic acid in *n*-pentane. Effluent was collected in successive fractions as determined by refractive index measurements. Experiments were terminated when appreciable acetic acid appeared in the effluent as detected by moist indicator paper. Fractions containing acetic acid were washed with aqueous sodium bicarbonate. *n*-Pentane was stripped off under N_2 at room temperature or slightly above.

Preparation of 2-Methyl-, 2-Cyclohexyl- and 2-Phenyl-2-tetradecanol.—These alcohols were prepared from *n*-dodecyl bromide and the appropriate ketones by the Grignard synthesis. Methyl cyclohexyl ketone was prepared by the method of Van Woerden.[8] The alcohols were purified by distillation under diminished pressure. Their physical properties and analyses are given in Table I.

2-Tetradecanol	Ketone	Yield, %
2-Methyl	Acetone	51
2-Cyclohexyl	Methyl cyclohexyl	25
2-Phenyl	Acetopheonone	54

Preparation of 2-Methyl-, 2-Cyclohexyl- and 2-Phenyl-2-tetradecyl Hydroperoxide.—The preparation from 2-methyl-2-tetradecanol is illustrative. A solution of 1 g. (4.4 millimoles) of 2-methyl-2-tetradecanol in 9 ml. of glacial acetic acid was placed in a 50-ml. round-bottom flask located behind a safety shield. Four grams of 90% hydrogen peroxide (106 millimoles) was added slowly with stirring, followed by 0.6 ml. of concentrated H_2SO_4. The flask was immersed in a 30° water-bath. After stirring for 1 hr., 50 ml. of water was added and the organic layer recovered by *n*-pentane extraction. The *n*-pentane extract was washed with aqueous sodium bicarbonate. A recrystallized product was recovered by chilling to −80° and filtering in a chilled suction funnel. This material titrated 55 to 60% hydroperoxide. A repeat of the foregoing reaction and recrystallization on combined products gave an over-all 48% yield of material titrating 75% hydroperoxide. This material was chromatographed on alumina to yield a fraction eluting just ahead of the acetic acid which titrated 88% hydroperoxide. A repeat chromatographic separation yielded pure 2-methyl-2-tetradecyl hydroperoxide. A total of 2.0 g. was prepared representing an over-all yield of 16% based on starting alcohol.

Autoxidation of 2-Phenyl-2-tetradecane.—Crude 2-phenyl-2-tetradecanol was dehydrated by heating with traces of sulfuric acid under diminished pressure, the crude product distilling over a range of 158–180° (1 mm.). It was purified by crystallization from acetone at −25° after removal of *n*-tetracosane impurity from an ether solution. A yield of 18.5 g. (38%) of mixed olefins was obtained from 74 g. of the alcohol.

Infrared analysis verified presence of mixed olefins and absence of alcohol or other impurities. Hydrogenation of 16 g. of the olefin mixture dissolved in 95% ethanol

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(6) K. I. Ivanov and V. K. Savinova, *et al.*, *Doklady Akademia Nauk, U.S.S.R.*, **59**, 905 (1948).

(7) R. W. Foreman and W. Jackson, *Instruments*, **22**, 497 (1949).

(8) S. Van Woerden, *Rec. trav. chim.*, **45**, 124 (1926).

was carried out in a Burgess–Parr low pressure apparatus using 0.8 g. of palladium–charcoal as the catalyst. A pressure drop of 4.9 p.s.i.g. from the initial 40 p.s.i.g. was measured (theoretical 4.85 p.s.i.g.). The product was recrystallized from 95 ml. of acetone at −25° to yield 9.7 g. of colorless liquid (65% yield from mixed olefins). The melting point, −3.0°, and $n^{20}{}_D$, 1.4810, agreed well with those reported by Cheltsova and Petrov.[9]

A 5-ml. cylindrical, fused-quartz test-tube was equipped with a capillary tube and vent tube extending through a two-hole cork. This was mounted at the geometric center of an ultraviolet exposure apparatus. The latter consisted of three General Electric germicidal lamps symmetrically located 4 inches apart and mounted in a cylinder of polished sheet aluminum. The quartz test-tube was filled with 2.83 g. of 2-phenyltetradecane. Pure O_2, at a flow rate of 4 to 5 ml. per minute, was passed into the hydrocarbon. The heat from the lamps maintained an air temperature of 50–55° throughout the oxidation. Extent of oxidation was determined periodically by infrared analysis and iodometric titration. The autoxidized hydrocarbon was removed after 17 days of continuous oxidation. A sample of this material titrated 1.4% peroxide calculated as 2-phenyl-2-tetradecyl hydroperoxide. Chromatographing of a 2-g. sample on alumina gave 0.27 g. titrating 6.4% hydroperoxide. The infrared spectrum of the peroxide fraction was determined. The most significant feature is an 11.84 μ absorption band. This is characteristic of tertiary hydroperoxides and is found at the same wave length in 2-phenyl-2-tetradecyl hydroperoxide. The presence of extensive oxygenated hydrocarbons other than the hydroperoxide is evidenced by strong —OH and C=O absorptions at 3.0 and 5.8–5.9 μ, respectively, and a strong 8–11 μ absorption. Retention of the long chain and phenyl groups is shown by a 13.89 and 13.15 plus 14.33 μ absorptions, respectively.

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[9] M. A. Cheltsova and A. D. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **12**, 87 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MAINE]

The Failure of the Darzens Reaction to Produce α-Aryl-Substituted Glycidic Esters[1]

BY HORTON H. MORRIS, RAYMOND H. YOUNG, JR., CAROL HESS AND THEODORE SOTTERY

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The preparation of glycidic esters containing a phenyl group in the α-position cannot be accomplished by means of the Darzens reaction if the carbonyl component of the reaction mixture contains an α-hydrogen atom. The products formed when an ethyl α-halophenylacetate and a carbonyl component containing an α-hydrogen atom are treated with potassium *t*-butoxide are ethyl phenylacetate, diethyl 2,3-diphenylsuccinate and diethyl 2,3-diphenylmaleate.

Previous reports[2] from this Laboratory have been concerned with the production of a number of α-aliphatic-substituted glycidic esters and with the nature of the decarboxylation products obtained from the corresponding glycidic acids. It seemed of interest to extend the work to include glycidic esters containing aryl groups as the α-substituent and to determine whether decarboxylation of the corresponding glycidic acids might cause migration of the α-substituent to yield aldehydes—a result not found when the α-substituent is aliphatic in nature.[2]

All but one attempt to prepare glycidic esters containing an aromatic group as α-substituent have failed. The failure seems to be related to the presence of an α-hydrogen atom in the carbonyl component of the reaction mixture, since only the use of benzaldehyde allowed the formation of a glycidic ester. The carbonyl compounds which have failed to yield a glycidic ester when allowed to react with ethyl α-bromophenylacetate or with ethyl α-chlorophenylacetate in the presence of potassium *t*-butoxide are acetone, cyclohexanone, pinacolone, acetophenone and isobutyrophenone.

In every case the products isolated were derived from the halo ester component of the reaction mixture and were ethyl phenylacetate, diethyl 2,3-diphenylsuccinate and diethyl 2,3-diphenylmaleate (isolated as 2,3-diphenylmaleic anhydride).

When ethyl α-bromophenylacetate was treated with potassium *t*-butoxide in the absence of a carbonyl compound, only diethyl 2,3-diphenylmaleate was formed. Ethyl α-chlorophenylacetate did not react with cyclohexanone in the absence of a condensing agent.

The amount of ethyl phenylacetate formed is dependent upon the nature of the carbonyl component used in the reaction. The reaction of acetone with ethyl α-bromophenylacetate gave a 35–40% yield of ethyl phenylacetate, acetophenone gave 28–32%, pinacolone gave about 20%, while the use of cyclohexanone gave a 50–65% yield of this ester. The reaction of isobutyrophenone with ethyl α-bromophenylacetate yielded no ethyl phenylacetate.

The use of an α-chloro ester in the reaction gave lower yields of ethyl phenylacetate than when an α-bromo ester was used. Thus, the reaction of acetone with ethyl α-chloroacetate gave ethyl phenylacetate in 29% yield while use of the α-bromo ester gave a 35–40% yield. The reaction of the α-chloro ester with cyclohexanone gave a 20–23% yield of ethyl phenylacetate while the α-bromo ester gave a 50–65% yield.

Diethyl 2,3-diphenylsuccinate and diethyl 2,3-diphenylmaleate were isolated in varying amounts from some of the runs.

Large amounts (30–80%) of unreacted ketone were recovered from every run. The unrecovered portion of the ketone had apparently undergone some type of polymerization, since extensive investigations failed to allow the isolation of any materials other than tars, derived from the ketone.

A re-examination of the low-boiling cuts obtained during the preparation of an α-decyl-substituted glycidic ester[3] showed the presence of ethyl laurate, which was formed in 17% yield from the reaction

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[1] Presented before the Division of Organic Chemistry at the 129th Meeting of the American Chemical Society, Dallas, Texas, April 13, 1956.

[2] H. H. Morris and Raymond H. Young, Jr., THIS JOURNAL, **77**, 6678 (1955), and previous papers.

[3] H. H. Morris and C. J. St. Lawrence, *ibid.*, **77**, 1692 (1955).