was broken up by vigorous shaking with pentane and was carbonated.

The usual analysis[9] for *o*-anisic acid showed the amount of *o*-sodioanisole which had been present. The sodium halide was determined by means of silver nitrate with an aliquot and titration of the excess nitrate with potassium thiocyanate against ferric nitrate as an indicator. The alkyl or aryl chloride was determined by digesting an aliquot from the hydrocarbon layer with sodium sand and then analyzing for halide ion in the above way with silver nitrate.

In a few cases, the fines and coarse particles were scarcely distinguishable. The control experiment, no. 1, contained no true fines, but a few of the most finely divided particles were analyzed. The last two reactions listed in the table proceeded too rapidly for isolation of any especially reactive fraction.

**Adsorption of Amyl Chloride on Sodium Chloride and Potassium Isopropoxide.**—Wurtz sodium chloride (one mole) was prepared from amyl chloride and sodium metal in pentane. The mixture was centrifuged, the pentane layer was removed by decantation and the sodium chloride was transferred to a flask which contained heptane. Amyl chloride, one mole, was then added, the mixture was stirred together for 45 minutes with the high-speed stirring apparatus. The mixture was then centrifuged. The solid appeared homogeneous, but as much as possible of an upper portion was removed by swirling and was analyzed.

In a similar way, the adsorption of a mole of amyl chloride on a mole of potassium isopropoxide (from potassium metal and isopropyl alcohol) and the adsorption of two moles of amyl chloride on a mixture of a mole each of sodium chloride and potassium isopropoxide were measured.

In Table IV the adsorptions on the fines and the coarse particles are given but there was no differentiation in physical appearance possible between the two grades. The results show more adsorption on the alkoxide than on the chloride. In the mixture the halide salt appears to repress the adsorption on the alkoxide. All adsorption values are less than those on *o*-sodioanisole shown in Table I.

TABLE IV

ADSORPTION OF AMYL CHLORIDE ON SODIUM CHLORIDE AND POTASSIUM ISOPROPOXIDE

| Solid | Mole ratio of amyl chloride to solid, Fines | Coarse |
|---|---|---|
| Wurtz sodium chloride | 2.00/10.4 = 0.192 | 85.8/778 = 0.110 |
| Potassium isopropoxide | 21.4/41.3 = .518 | 127/390 = .328 |
| $NaCl + KOC_3H_7$-*i* | 23.4/72.4 = .323 | 93.0/849 = .109 |

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, STANFORD UNIVERSITY]

# Peroxides. I. *n*-Alkyl Hydroperoxides

BY HOMER R. WILLIAMS[1] AND HARRY S. MOSHER

RECEIVED JANUARY 8, 1954

A new and practical synthesis for the pure *n*-alkyl hydroperoxides (*n*-propyl through *n*-decyl) by the reaction of *n*-alkyl methane sulfonates with 30% hydrogen peroxide has been developed. These compounds are now readily available as analytically pure materials. These primary alkyl hydroperoxides exhibit the same order of stability as *t*-butyl hydroperoxide.

Although the tertiary alkyl hydroperoxides have been readily available by the reaction of the tertiary alcohol with hydrogen peroxide in the presence of strong acid,[2] and many allylic types are formed by air oxidation,[3] only the methyl, ethyl, *n*-propyl and *n*-butyl members of the normal saturated series have been described. These have been prepared in the past by the method of Baeyer and Villiger,[4,5] using the reaction of hydrogen peroxide with dialkyl sulfates; the yields were generally unsatisfactory[6] and the methyl and ethyl hydroperoxides were dangerously unstable. Recently Lindstrom[7] has added the *n*-butyl hydroperoxide to the list of pure saturated normal hydroperoxides which have been made by the method of Baeyer and Villiger. By the use of methanol solvent the yield was greatly improved. A recent communication by Walling and Buckler[8] reports the preparation of hydroperoxides by the action of oxygen on Grignard reagents.[9] This shows promise of being a useful and general method.

The use of alkyl methanesulfonates as alkylating agents for hydrogen peroxide has not been previously reported. Rieche[4] was actively engaged in a search for new alkylating agents for hydrogen peroxide but failed to mention alkyl methanesulfonates in any of his publications. Medwedew and Alexjewa[6d] stated that they were unsuccessful in attempts at making alkyl hydroperoxides by alkylation of hydrogen peroxide with alkyl toluenesulfonates or by the alkylation of sodium or barium peroxide with alkyl halides. Harris and Egerton[6c] concluded after extensive studies that the strongly alkaline reaction mixture required to bring about the alkylation of hydrogen peroxide rapidly decomposed the alkyl hydroperoxide as formed and consequently appreciable yields by this general method were unlikely.

We have now found that acceptable yields of *n*-alkyl hydroperoxides result from the alkylation of 30% hydrogen peroxide by alkyl methanesulfonates in aqueous methanol solvent in the presence of potassium hydroxide at room temperature. We chose to study the reaction of alkyl methanesulfo-

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(1) Shell Development Co., Agricultural Division, Denver, Colorado.

(2) N. A. Milas, U. S. Patent 2,223,807 (Dec. 3, 1940).

(3) W. A. Waters, Oxidation Processes, in Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 1120.

(4) (a) A. Rieche, "Alkyl Peroxyde und Ozonide," Verlag von T. Steinkopff, Dresden und Leipzig, 1931; (b) W. Eggersglüss, "Organische Peroxyde," Verlag Chemie, Weinheim, 1951; (c) R. Criegee, "Peroxyde, in Houben-Weyl, Methoden der Organischen Chemie," Vol. VIII, Georg Thieme Verlag, Stuttgart, 1952, Chapt. 1.

(5) A. Baeyer and V. Villiger, *Ber.*, **23**, 3387 (1900); **34**, 738 (1901).

(6) (a) Methyl hydroperoxide, 12% yield, ref. 5; (b) ethyl hydroperoxide, 21% yield, A. Rieche and Hitz, *Ber.*, **62**, 2458 (1929); (c) *n*-propyl hydroperoxide, 1.3% yield, E. J. Harris and A. C. Egerton, *Proc. Roy. Soc.* (*London*), **A173**, 126 (1939); (d) S. S. Medwedew and E. N. Alexejewa, *Ber.*, **85B**, 133 (1952), report the preparation of the *n*-propyl hydroperoxide in 27% solution (determined by titration) but they were unable to isolate any of the pure substance.

(7) E. G. Lindstrom, THIS JOURNAL, **75**, 5123 (1953).

(8) C. Walling and S. A. Buckler, *ibid.*, **75**, 4372 (1953).

(9) J. Schmidlin, *Ber.*, **39**, 631, 4184 (1906), reported a 54% yield of triphenylmethyl hydroperoxide by the action of oxygen on triphenylmethylmagnesium chloride.

nates in preference to alkyl toluenesulfonates because of their lower molecular weight and higher alcohol solubility. The *n*-alkyl methanesulfonates were all readily prepared in good yield by the action of methanesulfonyl chloride on the corresponding alcohol in the presence of pyridine.[10]

$$CH_3SO_2Cl + HOR + C_5H_5N \longrightarrow CH_3SO_3R + C_5H_5N{\cdot}HCl$$

These alkyl methane-*sulfonates* are therefore readily available and inexpensive intermediates. This is in contrast to the difficulties in preparing the higher alkyl *sulfates*. The synthesis and properties of those compounds which have not been previously reported are summarized in Tables I and II.

Initial experiments on the alkylation of hydrogen peroxide were on an analytical scale without isolation of products; the yield of hydroperoxide was determined by extraction and titration.[11] The first experiments, using ethyl alcohol as solvent and sodium hydroxide as base, were unsuccessful but it was found that satisfactory amounts of hydroperoxide were formed when the *n*-alkyl methanesulfonate and hydrogen peroxide were treated in homogeneous solution in methanol solvent with potassium hydroxide.

$$CH_3SO_3R + HOOH \xrightarrow[CH_3OH]{KOH} CH_3SO_3H + R\text{-}OOH$$

The yields of distilled hydroperoxides for the standardized set of conditions described in the Experimental section and shown in Table III were 38 to 45%. These are certainly not optimum since the yield for *n*-heptyl hydroperoxide was raised from 38 to 56% by slight modifications of the standard procedure. The yield of 38% for the purified *n*-propyl hydroperoxide compares to the previously reported yield of 1.5%[6c] according to the method of Baeyer and Villiger. The boiling points, refractive indices and densities were determined on each compound and are reported in Table IV. Infrared spectra have been taken and will be reported separately.

A qualitative indication of the stabilities of these *n*-alkyl hydroperoxides (and several secondary alkyl hydroperoxides to be reported in a subsequent paper) was obtained by heating small samples of the undiluted hydroperoxides in 1.5-mm. Pyrex capillary tubes at a rate of 2° per minute. All the samples began to decompose smoothly with the evolution of a gas at approximately 90–100°. The decomposition of tertiary butyl hydroperoxide was completely comparable. Direct heating with a flame failed to cause a detonation. Samples ground between glass plates or hit with a hammer failed to explode. Nothing unusual was observed in the combustion analysis of these compounds. A weak detonation occurred during the distillation at 2 mm. pressure of a crude three-gram sample of *n*-octyl hydroperoxide at a bath temperature of 68°. Since a subsequent sample distilled without decomposition, it was assumed that in this case impurities, probably acid, were present.

The prevalent idea[12] that the order of stability of the hydroperoxides is tertiary > secondary > primary requires reevaluation based on further experimental evidence.

**Acknowledgment.**—We wish to acknowledge the assistance of the California Research Corporation for both bringing to our attention the lack of information concerning these higher *n*-alkyl hydroperoxides and for a generous grant which made these investigations possible.

## Experimental[13]

**The Preparation of *n*-Alkyl Methanesulfonates.**—The procedure employed in the preparation of *n*-alkyl methanesulfonates followed that reported by Sekera and Marvel[10] for the preparation of *n*-butyl methanesulfonate. A mixture of 22.9 g. (0.20 mole) of methanesulfonyl chloride (Eastman Kodak Co.) and an equivalent amount of the alcohol was stirred in an ice–brine-bath while 31.6 g. (0.40 mole) of dry pyridine was added at a temperature of 0–5° over a period of 3.5 hours. The stirring was continued for one-quarter hour; then the reaction mixture was then poured into 125 ml. of ice-cold 10% hydrochloric acid and the product extracted with 75 ml. of ether. The resulting solution was washed with two 20-ml. portions of water followed by a 30-ml. portion of saturated sodium bicarbonate solution. The solution was dried over anhydrous potassium carbonate, filtered, and heated on a steam-bath to remove the ether. The residue was distilled at reduced pressure to give the methanesulfonate.

TABLE I

THE PREPARATION OF *n*-ALKYL METHANESULFONATES

| Alcohol used | g. | Methane-sulfonate, yield, g. | % | B.p. °C. | Mm. | M.p., °C. |
|---|---|---|---|---|---|---|
| *n*-Propyl | 12.0 | 22.8 | 83 | 110 | 20 | ... |
| *n*-Butyl | 14.8 | 26.2 | 81 | 77–79 | 2 | ... |
| *n*-Amyl | 17.6 | 28.0 | 84 | 81–83 | 2 | ... |
| *n*-Hexyl | 20.6 | 26.6 | 72 | 89–92 | 2 | ... |
| *n*-Heptyl | 23.2 | 31.7 | 82 | 104–106 | 2 | ... |
| *n*-Octyl | 26.0 | 33.5 | 81 | 110–114 | 2 | ... |
| *n*-Nonyl | 28.6 | 28.0 | 67 | 89 | 0.3 | 6–7 |
| *n*-Decyl | 31.6 | 30.5 | 68 | 120–122 | 0.5 | 16–17 |

Each of the products was redistilled to obtain an analytical sample. The preparation and properties of the samples and the results of the analyses are indicated in Table II.

**The Preparation of *n*-Alkyl Hydroperoxides.**—The first experiments were exploratory and were evaluated by two analytical procedures rather than by isolation of the pure hydroperoxide. In the first procedure, aliquots of the reaction mixture were withdrawn at intervals and titrated with standard acid to determine the amount of unreacted potassium hydroxide. This gave an indication of the time required for substantially complete reaction. The major reaction must be the alkylation of the hydrogen peroxide as shown by the much greater rate of disappearance of base in the presence of than in the absence of hydrogen peroxide. However hydrolysis of the alkyl methanesulfonate and possibly other side reactions are involved. Table III lists the results of two such representative studies.

In order to study the effect of reaction conditions on the yield of alkyl hydroperoxides, a procedure was devised in which the alkyl hydroperoxide was obtained in benzene solution and then determined iodometrically by the method described by Siggia.[11] The following is a description of a typical run: a reaction mixture which was identical with that used to determine the reaction time of *n*-butyl methanesulfonate with hydrogen peroxide (footnote *a*, Table III) was allowed to stand at room temperature for 14 hours. The mixture was combined with 2.0 g. of 50% potassium hydroxide and extracted with 5 ml. of benzene. The alkaline layer was then neutralized with concentrated hydrochloric acid while being cooled in an ice-bath. The neutralized solution was extracted with four 3-ml. portions of

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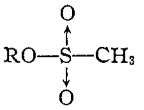
[10] V. C. Sekera and C. S. Marvel, THIS JOURNAL, **55**, 345 (1933).

[11] S. Siggia, "Quantitative Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 100.

[12] See ref. 3, p. 1 and ref. 4c, p. 2.

[13] All melting and boiling points are uncorrected. Analyses were by Microchemical Specialties Company, Berkeley, California.

TABLE II



PROPERTIES[13] OF THE *n*-ALKYL METHANESULFONATES, $RO-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}-CH_3$

| Methane-sulfonate | B.p. °C. | B.p. Mm. | Refractive index $n^{20}D$ | Formula | Analyses,[a] % Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found |
|---|---|---|---|---|---|---|---|---|
| *n*-Propyl | 110 | 20 | 1.4228 | $C_4H_{10}SO_3$ | (Known) | | | |
| *n*-Butyl | 77–79 | 2 | 1.4265 | $C_5H_{12}SO_3$ | (Known) | | | |
| *n*-Amyl | 67 | 1 | 1.4304 | $C_6H_{14}SO_3$ | 43.36 | 43.21 | 8.49 | 8.57 |
| *n*-Hexyl | 78 | 1 | 1.4336 | $C_7H_{16}SO_3$ | 46.65 | 46.59 | 8.95 | 8.75 |
| *n*-Heptyl | 92 | 1.5 | 1.4364 | $C_8H_{18}SO_3$ | 49.47 | 49.14 | 9.34 | 9.31 |
| *n*-Octyl | 98 | 1.5 | 1.4392 | $C_9H_{20}SO_3$ | 51.90 | 51.65 | 9.68 | 9.56 |
| *n*-Nonyl | 89 | 0.3 | 1.4403 | $C_{10}H_{22}SO_3$ | 54.03 | 54.10 | 9.99 | 10.10 |
| *n*-Decyl | 120–122 | 0.5 | 1.4432 | $C_{11}H_{24}SO_3$ | 55.91 | 56.13 | 10.24 | 10.31 |

[a] Each analysis is the average of 2 determinations. The maximum deviation from the average was 0.05 and the average deviation was 0.02.

TABLE III

RATE OF DISAPPEARANCE OF BASE IN THE REACTION OF ALKYL METHANESULFONATES WITH HYDROGEN PEROXIDE IN THE PRESENCE OF BASE

| *n*-Butyl methanesulfonate[a,b] | | | *n*-Heptyl methanesulfonate[c,d] | | |
|---|---|---|---|---|---|
| | % KOH remaining | | | % KOH remaining | |
| Time, hr. | Presence of $H_2O_2$[a] | Absence of $H_2O_2$[b] | Time, hr. | Presence of $H_2O_2$[c] | Absence of $H_2O_2$[d] |
| 0.00 | 100 | 100 | 0.00 | 100 | 100 |
| 1.25 | 55 | 96 | 2.25 | 65 | 98 |
| 3.37 | 33 | 77 | 4.25 | 50 | 94 |
| 5.33 | 24 | 68 | 7.42 | 35 | 85 |
| 19.12 | 6 | 45 | 18.33 | 17 | 52 |

[a] This reaction mixture consisted of 5 ml. of methanol, 1.00 g. (8.9 mmoles) of 50% potassium hydroxide, 4.0 g. (35 mmoles) of "30%" hydrogen peroxide, and 1.22 g. (8.0 mmoles) of *n*-butyl methanesulfonate. The temperature was 25–27°. [b] This hydrolysis mixture was just as in *a* above except 3 g. of water was substituted for the 4 g. of hydrogen peroxide. [c] This reaction mixture consisted of 11 ml. of methanol, 1.3 ml. of water, 3.30 g. (29 mmoles) of hydrogen peroxide, 0.83 g. (7.4 mmoles) of 50% potassium hydroxide, and 1.30 g. (6.7 mmoles) of *n*-heptyl methanesulfonate. The temperature was 24–26°. [d] This mixture was the same as in *c* above except 3.3 g. of water was substituted for the 3.3 g. of hydrogen peroxide.

TABLE IV

REACTION OF *n*-ALKYL METHANESULFONATES WITH HYDROGEN PEROXIDE

| Methanesulfonate | g. | Methanol, ml. | Water, ml. | Time, hr. |
|---|---|---|---|---|
| *n*-Propyl | 5.52 | 20 | 0.0 | 20 |
| *n*-Butyl | 6.10 | 25 | 0.0 | 18 |
| *n*-Amyl | 6.65 | 40 | 3.5 | 20 |
| *n*-Hexyl | 7.25 | 45 | 5.0 | 21 |
| *n*-Heptyl | 7.80 | 65 | 8.0 | 24 |
| *n*-Octyl | 8.35 | 90 | 7.0 | 40 |
| *n*-Nonyl | 8.90 | 100 | 8.0 | 40 |
| *n*-Decyl | 9.45 | 125 | 10.0 | 44 |

benzene and the benzene extracts extracted in turn with 5 g. of a 20% potassium hydroxide solution. This basic solution was cooled in ice and brought to the neutral point with concentrated hydrochloric acid. The regenerated *n*-butyl hydroperoxide was extracted from the solution with four 2.5-ml. portions of benzene. It was shown by a control experiment that no appreciable amount of hydrogen peroxide was retained by this double extraction procedure. One-tenth of this solution was then mixed with 25 ml. of absolute ethanol containing 1 ml. of a saturated potassium iodide solution and 1 ml. of glacial acetic acid. This solution was heated to incipient reflux for four minutes and then titrated immediately with 0.111 *N* sodium thiosulfate solution; 8.11 ml. was required to discharge the iodine color. The apparent yield of *n*-butyl hydroperoxide was 56%. A control experiment on an analytically pure sample of *n*-hexyl hydroperoxide gave a value which was 97.7% of the calculated. This indicates that the method described by Siggia[4] is quantitative enough for these determinations.

On the basis of the best conditions determined by the exploratory analytical experiments, the following procedure was used in the synthetic runs where the alkyl hydroperoxide was isolated.

Reaction mixtures were prepared by dissolving the alkyl methanesulfonates (0.040 mole) in methanol and water in the amounts indicated in Table IV. The mixtures were cooled in an ice-bath and combined with 20.0 g. (0.16 mole) of J. T. Baker "C.P. 30%" hydrogen peroxide (27.7% by analysis) and 5.00 g. (0.045 mole) and 50% aqueous potassium hydroxide, in that order. Then the mixtures were placed in a 23–25° (room temperature) water-bath for the periods indicated in Table IV.

The procedure for isolating the product was the same in each case. The mixture was cooled in ice and slowly combined with 15.0 g. of 50% potassium hydroxide. The alkaline mixture was extracted with 25 ml. of benzene to remove unreacted alkyl methanesulfonate, alcohol or dialkyl peroxide. The aqueous layer was cooled in ice, neutralized (*p*H 7) with concentrated hydrochloric acid, and extracted with four 15-ml. portions of benzene. These benzene extracts still contained a small amount of hydrogen peroxide. The combined benzene extracts were extracted with 20 g. of cold 25% potassium hydroxide. The alkaline solution was cooled in ice, neutralized with concentrated hydrochloric acid, and then the neutralized mixture extracted with four 10-ml. portions of benzene (hexane in the case of *n*-octyl hydroperoxide). The hydroperoxide solution was dried over sodium sulfate and then stripped of solvent at aspirator pressure. The residue was distilled to give products in yields of 38 to 44%.

In the synthesis of *n*-propyl hydroperoxide, the water solubility was such that no hydroperoxide separated on neutralization. In this case the neutral solution was extracted with peroxide-free ether, the ether layer was dried over sodium sulfate, and this ether solution was distilled directly without further washing.

The higher *n*-alkyl hydroperoxides such as *n*-nonyl and *n*-decyl form sparingly soluble grease-like salts in the aqueous potassium hydroxide solution. The following modification was found desirable in these cases. On mixing the reactants as indicated in Table IV, two liquid phases resulted but the mixture became homogeneous within a short time. After 40 hours the reaction mixture was cooled to 0°, 15 g. of 50% aqueous potassium hydroxide was added, and the basic solution extracted with three 15-ml. portions of hexane. The aqueous layer was brought to *p*H 7 with hydrochloric acid and the alkyl hydroperoxide extracted with three 10-ml. portions of benzene. The benzene extracts were washed with water, dried over sodium sulfate and distilled.

A slight modification in the method of isolation of *n*-heptyl hydroperoxide raised the yield from the 38% reported in Table V to 56%. It is probable that the yields of the other lower members might be raised similarly by a suitable modification. The mixture resulting from the reaction of *n*-heptyl methanesulfonate (15.6 g., 0.080 mole), 30% hy-

TABLE V

PROPERTIES[13] OF *n*-ALKYL HYDROPEROXIDES, ROOH

| *n*-Alkyl group | g. | Yield % | B.p., °C. | Press., mm. | $n^{20}$D | Density, $d^{20}_4$ | M.p., °C. | Formula | Analyses,[c] % Carbon Calcd. | Carbon Found | Hydrogen Calcd. | Hydrogen Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *n*-Butyl[b] | 1.15 | 42 | 40–42 | 8 | 1.4057 | 0.907 | ............. | $C_4H_{10}O_2$ | 53.31 | 53.30 | 11.19 | 11.42 |
| *n*-Amyl | 1.80 | 43 | 41–42 | 4 | 1.4146 | .897 | ............. | $C_5H_{12}O_2$ | 57.66 | 57.43 | 11.61 | 11.77 |
| *n*-Hexyl | 2.07 | 44 | 42–43 | 2 | 1.4208 | .891 | ............. | $C_6H_{14}O_2$ | 60.98 | 60.90 | 11.94 | 12.02 |
| *n*-Heptyl | 2.05 | 38 | 46–47 | 0.5 | 1.4265 | .884 | −37.5 to −37.0 | $C_7H_{16}O_2$ | 53.59 | 63.43 | 12.20 | 12.21 |
| *n*-Octyl[a] | 2.23 | 38 | 54–55 | .7 | 1.4311 | .881 | −33 to −32 | $C_8H_{18}O_2$ | 65.71 | 65.83 | 12.41 | 12.59 |
| *n*-Nonyl | 2.48 | 39 | 53–55 | .3 | 1.4330 | .878 | −20 to −19 | $C_9H_{20}O_2$ | 67.45 | 66.86 | 12.58 | 12.61 |
| *n*-Decyl | 3.07 | 45 | 61–63 | .3 | 1.4378 | .871 | − 8.5 to −7.5 | $C_{10}H_{22}O_2$ | 68.91 | 68.89 | 12.72 | 12.91 |

[a] In a similar run a 3-g. sample of crude *n*-octyl hydroperoxide detonated mildly when being distilled at 2 mm. pressure and a bath temperature of 68°. The thermometer was blown from the flask but the flask was not shattered. [b] Reference 7 reports $n^{20}$D 1.4032, $d^{20}_4$ 0.9078 for *n*-butyl hydroperoxide. [c] Each analysis is the average of two determinations. The maximum deviation from the average in any case was 0.10 and the average deviation was 0.06.

drogen peroxide (40.0 g., 0.35 mole), 50% aqueous potassium hydroxide (10.0 g., 0.089 mole), 130 ml. of methanol and 15 ml. of water at 23–25° for 24 hours was made strongly basic at 0° with 30 g. of 50% aqueous potassium hydroxide. After extraction with hexane, the aqueous layer was brought to *p*H 7 and extracted with six 20-ml. portions of benzene. The alkyl hydroperoxide was taken up in 40 ml. of 25% potassium hydroxide and transferred to ether by neutralizing the mixture and extracting with three 15-ml. portions of ether. The ether was dried over sodium sulfate and distilled to give *n*-heptyl hydroperoxide, 5.79 g., 56% yield, b.p. 45–47° (0.05 mm.).

The hydroperoxides were redistilled, and the physical constants of the purified samples determined. The properties of these purified samples as well as their analyses are shown in Table V. Small quantities of the purified hydroperoxides were heated at 2°/min. in 1.5-mm. Pyrex capillary tubes. Under these conditions the first bubbles of gas appeared at 89 to 92°, and bubbling became fairly steady at 110–115°. No violent decompositions were observed, although the temperature reached 160°. The lower members of the series had boiled out of the capillary before 160°, so the effect of the higher temperature on these hydroperoxides was not established; however, direct flame heating of a capillary tube containing *n*-propyl and *n*-butyl hydroperoxide caused only sputtering of the contents.

All of the hydroperoxides had in common a characteristic sharp odor. The butyl and amyl hydroperoxides caused reddening of the skin and resulted in a severe chemical burn when allowed to stay in contact with the skin. The higher hydroperoxides caused irritation of the skin, but the effects were less severe than those of the *n*-butyl and *n*-amyl homologs.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, STANFORD UNIVERSITY]

# Organic Peroxides. II. Secondary Alkyl Hydroperoxides

BY HOMER R. WILLIAMS AND HARRY S. MOSHER

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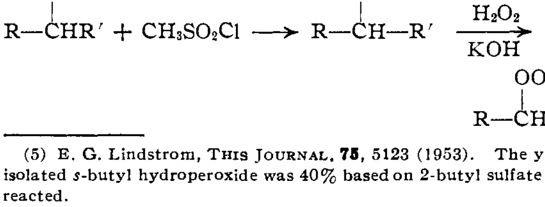
A series of saturated secondary alkyl hydroperoxides has been prepared by the reaction of secondary alkyl methanesulfonates with alkaline hydrogen peroxide in aqueous methanol. Compared with other methods the yields are satisfactory (20–25%) and the application of this method makes potentially available a wide variety of alkyl hydroperoxides previously inaccessible.

Criegee[1] has recently reviewed the methods for synthesis of hydroperoxides. Two of these, the air-oxidation of hydrocarbons and the action of dialkyl sulfates on hydrogen peroxide in the presence of base (the method of Baeyer and Villiger) have been applied successfully to the preparation of saturated secondary alkyl hydroperoxides. For example 2-heptyl hydroperoxide has been reported to result by the air-oxidation of *n*-heptane[2] and cyclohexyl hydroperoxide has been isolated from the air-oxidation of cyclohexane.[3]

The method of Baeyer and Villiger has been used for the preparation of isopropyl hydroperoxide[4] and for *s*-butyl hydroperoxide.[5] In addition to these methods reviewed in Criegee,[1] Walling and Buckler[6] have recently reported the preparation in good yield of several hydroperoxides by low temperature air-oxidation of Grignard reagents. This method is applicable to primary, secondary and tertiary alkyl hydroperoxides.

The recently reported method for the preparation of *n*-alkyl hydroperoxides from alkyl methanesulfonates and hydrogen peroxide[7] has now been extended to include saturated secondary alkyl hydroperoxides.



$$R{-}\overset{OH}{\overset{|}{C}}HR' + CH_3SO_2Cl \longrightarrow R{-}\overset{OSO_2CH_3}{\overset{|}{C}}H{-}R' \xrightarrow[KOH]{H_2O_2} R{-}\overset{OOH}{\overset{|}{C}}H{-}R'$$

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[1] R. Criegee, "Methoden der Organischen Chemie, Vierte Auflage," Vol. VIII, Georg Thieme Verlag, Stuttgart, 1952, pp. 9–61.

[2] K. I. Ivanov, V. K. Sovinova and V. P. Zhakhovskaya, *Doklady Akad. Nauk. S. S. S. R.*, **72**, 903 (1950); *C. A.*, **44**, 8316 (1950). The yield was 0.5–0.6% by titration; the isolated yield was not given.

[3] S. A. Farkas and A. Passaglia, THIS JOURNAL, **72**, 3333 (1950). The yield by titration was 1.9% of the cyclohexane taken and of this 38.3% was isolated in purified form.

[4] (a) S. S. Medvedev and E. N. Alexejeva, *Ber.*, **65B**, 133 (1932). A 50% yield was reported in solution by titration but the amount of isolated material was not reported. (b) W. Eggersglüss, "Organische Peroxyde," Verlag Chemie, G.m.b.h., Weinheim, 1950, p. 79, reports an 11% yield of pure isopropyl hydroperoxide by this method.

[5] E. G. Lindstrom, THIS JOURNAL, **75**, 5123 (1953). The yield of isolated *s*-butyl hydroperoxide was 40% based on 2-butyl sulfate which reacted.

[6] C. Walling and S. A. Buckler, *ibid.*, **75**, 4373 (1953). See also J. Schmidlin, *Ber.*, **39**, 631, 4184 (1909).

[7] H. R. Williams and H. S. Mosher, *ibid.*, **76**, 2984 (1954).