

hydrate could be recovered quantitatively with no evidence of polymer formation.

Catalytic hydrogenation. Methyl oleate (15.0 g., 0.05 g. mole) having an iodine value of 84.8 and n_D 1.4481 (30.2°) was dissolved in 210 ml. of methyl acetate and 40 ml. of methanol. The ozonization was carried out as before. The amount of ozone consumed was 118% of the theoretical, and 2.9% of theory was found to have been absorbed by the potassium iodide solution. At the end of the ozonization the solution was purged with nitrogen, then hydrogen. The catalyst (0.1 g. of 10% palladium on charcoal) was dispersed in a small amount of methyl acetate and added to the solution through a dropping funnel. The solution was allowed to warm to 22° gradually as hydrogen was passed through the solution, and at the end of 1.5 hr. a negative test for peroxide (carried out with potassium iodide in glacial acetic acid) was obtained. Analysis of this solution by the hydroxylamine hydrochloride method gave misleading results because of hydrolysis of the ester to acetic acid. Distillation of this solution gave a product of indefinite composition.

In a similar experiment the product was converted to the dimethyl acetal. To the product solution was added 25 ml. of 2,2-dimethoxypropane and 0.1 g. of ammonium chloride. The mixture was distilled at atmospheric pressure to a pot temperature of 95° to remove the methyl acetate. An additional 50 ml. of methanol and 15 ml. of 2,2-dimethoxypropane were added and the distillation continued to a pot temperature of 105°, at which point the vapor temperature was 64.5°. The total heating period was about 6 hr. The residue was cooled, filtered, transferred to a similar distillation flask equipped with a nitrogen capillary ebullator, and distilled under reduced pressure through a 1 in. \times 6 in. glass helices packed column. There was recovered from 15.0 g. of methyl oleate, 7.69 g. (82%) of a fraction boiling 56.5–70° (0.35 mm.) $n_D^{30.2}$ 1.4166, and a fraction (10.13 g., 87%) boiling 95–103° (0.35 mm.) $n_D^{30.2}$ 1.4302. Since the

latter value did not agree with that recorded in the literature⁷ ($n_D^{30.2}$ 1.4312) for the dimethyl acetal of methyl azelaaldehyde, elemental analyses were carried out on a redistilled fraction having a boiling point of 88° (0.25 mm.), $n_D^{30.2}$ 1.4301.

Anal. Calcd. for $C_{12}H_{24}O_4$: C, 62.04; H, 10.41; sapon. equiv. 232.3. Found: C, 61.89; H, 10.29; sapon. equiv. 231.

A more convenient procedure involved ozonization in the ethyl acetate–acetic acid solvent mixture followed by catalytic hydrogenation. Direct distillation of the product solution resulted in the isolation of methyl azelaaldehyde, $n_D^{30.2}$ 1.4347, in 83% yield. Analysis by the hydroxylamine hydrochloride method indicated a purity of 87%. Apparently, a relatively low proportion polymeric peroxides, which are reported to be found as well as the acetoxy peroxides,¹⁴ were present.

The other solvents which were tried (Table I) resulted in low yields of impure products.

Isolation of the methoxy hydroperoxides. Methyl oleate (6.0 g., 0.020 g. mole) was ozonized in 150 ml. of methanol in the manner described. The amount of ozone consumed was 107% of theory and the amount absorbed in the potassium iodide trap was 6.0% theory. The solution was filtered, and methanol was removed in a rotary evaporator at a temperature of 21° first under vacuum from a water aspirator and then finally at a pressure of 0.2 mm. for a total time of about 18 hr. under vacuum. The colorless oil which remained weighed 7.8 g.

Anal. Calcd. for $C_{20}H_{40}O_6$: (an equimolar mixture of I and II) C, 63.80; H, 10.71; methoxyl, 16.48. Found: C, 63.3; H, 10.8; methoxyl, 19.5.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND BACTERIOLOGY, STATE UNIVERSITY OF IOWA]

Preparation of Long Chain Alkyl Hydroperoxides¹

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Dodecyl, tetradecyl, hexadecyl, and octadecyl hydroperoxides have been prepared for testing as intermediates in the biological oxidation of saturated hydrocarbons. The hydroperoxides were prepared in a state of purity varying from 92–100 per cent by the alkylation of hydrogen peroxide in basic medium with the corresponding alkyl methanesulfonate.

In the study of the oxidation of saturated hydrocarbons by certain microorganisms, recent data indicate that biological oxidation of paraffins occurred at one terminal carbon and did not involve the formation of an olefin, epoxide, or 1,2-glycol.⁴

In this work a series of hydroperoxides containing twelve, fourteen, sixteen, and eighteen carbon atoms

have been synthesized for testing as possible intermediates in this oxidation.

Of the methods available the reaction of a Grignard reagent with oxygen⁵ and the alkylation of hydrogen peroxide with alkyl methanesulfonates⁶ were studied as possible sources of these compounds.

Treatment of dodecylmagnesium bromide with oxygen at –75° gave a peroxidic product which could not be separated by distillation under reduced pressure from the tetracosane formed. In contrast to the stability reported for decyl hydroperoxide towards distillation,⁶ dodecyl hydroper-

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(2) Abstracted in part from the Ph.D. Thesis of P. D. Klimstra, June 1959.

(3) American Chemical Society–Petroleum Research Fund Predoctoral Fellow.

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TABLE I
 ALKYL METHANESULFONATES

Methane- sulfonate	Reaction Temp.	Yield, %	M.P.	Formula	Analyses			
					Carbon, %		Hydrogen, %	
					Calcd.	Found	Calcd.	Found
Dodecyl	5-10°	70.2	33°	C ₁₃ H ₂₈ SO ₃	59.10	59.36	10.67	10.30
Tetradecyl	45-50°	72.5	44-45°	C ₁₅ H ₃₂ SO ₃	61.60	61.27	10.92	10.38
Hexadecyl	55-60°	72.6	54.5-56°	C ₁₇ H ₃₆ SO ₃	63.71	63.79	11.32	11.43
Octadecyl	50-60°	69.7	61-62°	C ₁₉ H ₄₀ SO ₃	65.51	65.44	11.50	11.22

oxide undergoes decomposition since fractions containing dodecanal-1 and dodecanol-1 were obtained. Separation of the acidic hydroperoxide from the neutral materials by means of alkali, which was used successfully in the methanesulfonate method, was not investigated.

The method of Williams and Mosher⁶ with suitable modifications gave the desired hydroperoxides in a state of purity varying from 92-100 per cent. Due to the insolubility of the sulfonates, the alkylation of the hydrogen peroxide had to be carried out in a large volume of methanol. The only water introduced into the reaction mixture was that present in the 30 per cent hydrogen peroxide used. The yields and physical properties of the hydroperoxides are given in Table II. The low yield of octadecyl hydroperoxide obtained is caused by the poor solubility of octadecyl methanesulfonate in methanol.

By-products obtained in the preparation of dodecyl, tetradecyl, and hexadecyl hydroperoxides were the corresponding alkyl peroxides. Only tetradecyl and hexadecyl peroxides were isolated in a pure condition.

The only indication of a hydroperoxide group by infrared analysis was a shift in the hydroxyl peak for the corresponding alcohol from 2.94 to 2.84 μ . Williams and Mosher⁷ have reported a similar shift in the peak of the hydroxyl group for the lower members of the alkyl hydroperoxide series. In addition they found a band at about 11.8 μ for the oxygen-oxygen group which became smaller as the alkyl group became larger. This band was not observed for the hydroperoxides prepared in this work. Bands for carbonyl and water impurities were also reported by Williams and Mosher and were likewise found in this study. The carbonyl peak found for dodecyl hydroperoxide could be duplicated in optical density by using an amount of dodecanal-1 calculated equivalent to the amount of impurity present in the dodecyl hydroperoxide. The aldehydes and water probably result from the attack of the base on the hydroperoxide according to the scheme proposed by Kornblum,⁸ and were difficult to remove from the lower members.

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EXPERIMENTAL⁹

Reaction of dodecylmagnesium bromide with oxygen. Dodecylmagnesium bromide was prepared in a flask fitted with a stopcock in the bottom by the addition of dodecyl bromide (25 g.) over a period of 2 hr. to magnesium (2.4 g.) in 125 ml. of dry ether. Dry nitrogen was passed through the system before and during the reaction and a crystal of iodine was necessary to initiate the reaction. All the magnesium disappeared after 2.5 hr.

The resulting Grignard solution was added to an ether solution (100 ml.) saturated with oxygen at -75° in the course of 4 hr. After the addition was completed, oxygen was bubbled through the reaction mixture for an additional 3 hr. The reaction mixture was decomposed with 6*N* hydrochloric acid and extracted with ether. Removal of the ether gave a residue which distilled under reduced pressure (0.02-0.45 mm.) with decomposition. Fractions obtained were further purified by crystallization. The first fraction boiling at 78° (0.045 mm.) was recrystallized from methanol and melted at 26-27°. A positive peroxide test and elemental analysis indicated that this compound was probably dodecyl peroxide.

Anal. Calcd. for C₂₄H₅₀O₂: C, 77.76; H, 13.56. Found: C, 77.30; H, 12.47.

Fraction two distilled at 96-98° (0.3 mm.) and had the odor of dodecanal-1. Elemental analysis, infrared spectra, and a refractive index of 1.4500 at 20° indicated that this fraction was mainly lauryl alcohol.

Fraction three boiling at 150-170° (0.025-0.030 mm.) was recrystallized from methylene chloride and melted at 46-47°. Infrared analysis and carbon-hydrogen values pointed to an impure sample of tetracosane.

Alkyl methanesulfonates. A mixture of methanesulfonyl chloride (0.02 mole) and alcohol (0.20 mole) was stirred at the temperature indicated in Table I while dry pyridine (0.40 mole) was added over a period of 3 hr. The reaction mixture was stirred for an additional 30 min. and poured into 130 ml. of 10 per cent hydrochloric acid. The solution was extracted with two 85-ml. portions of ether and the ether layer was washed with water and a sodium bicarbonate solution. Removal of the ether gave an oily residue which was recrystallized from petroleum ether (b.p. 30-60°). The yields, melting points, and analyses are given in Table I.

Alkyl hydroperoxides. The alkyl methanesulfonate (0.008 mole) dissolved in methanol (for the amount see Table II) was treated at room temperature with 30 per cent hydrogen peroxide (100 g.) and powdered potassium hydroxide (20.0 g.) and the mixture was stirred: dodecyl, 600 ml. methanol, 59 hrs.; tetradecyl, 800 ml. methanol, 65 hr.; hexadecyl, 1.2 l. methanol, 72 hr.; octadecyl, 1.8 l. methanol, 99 hrs. The resulting mixture was cooled in ice and treated with 20 g. of powdered potassium hydroxide in 100 ml. of absolute methanol. The resulting precipitate was filtered, redissolved in methanol, acidified with concentrated hydrochloric acid and extracted with hexane. Evaporation of the hexane after washing with water gave tetradecyl peroxide (3.5 g.),

(9) Boiling points and melting points are not corrected.

TABLE II
YIELDS AND PROPERTIES OF ALKYL HYDROPEROXIDES

Alkyl Group	Yield, %	M.P. °	(OOH) ^{10,11} Analysis, %	Formula	Carbon		Hydrogen	
					Calcd.	Found	Calcd.	Found
<i>n</i> -Dodecyl	55.8	12-13	95	C ₁₂ H ₂₆ O ₂	71.28	71.26	12.87	12.42
<i>n</i> -Tetradecyl	42.4	29-30.5	92	C ₁₄ H ₃₀ O ₂	73.05	73.58	13.05	12.56
<i>n</i> -Hexadecyl	31	42-44	98.8	C ₁₆ H ₃₄ O ₂	74.42	74.24	13.18	13.17
<i>n</i> -Octadecyl	8.9	49-50	100	C ₁₈ H ₃₈ O ₂	75.39	74.81	13.25	13.00

hexadecyl peroxide (2.5 g.), and octadecyl methanesulfonate (17 g.), respectively.

Tetradecyl peroxide melted at 36.5° and gave an infrared spectra which had only carbon-hydrogen and carbon-oxygen peaks.

Anal. Calcd. for C₂₅H₅₀O₂: C, 78.87; H, 13.61. Found: C, 78.58; H, 13.61.

Hexadecyl peroxide melted at 44-46° and gave a similar spectra to tetradecyl peroxide.

Anal. Calcd. for C₃₂H₆₆O₂: C, 79.67; H, 13.69. Found: C, 79.00; H, 13.43.

The alkaline filtrate from the original precipitate was diluted with water (100 ml.) and extracted twice with 125-ml. portions of hexane. Concentration of the hexane extract gave impure dodecyl peroxide (4 g.) and unreacted tetra-

decyl methanesulfonate (3 g.) and hexadecyl methanesulfonate (4 g.) respectively.

The dodecyl peroxide was difficult to purify. The principal contaminations based on the infrared spectra were the corresponding methanesulfonate and aldehyde.

The basic solution was cooled to 0° and made slightly acid with concentrated hydrochloric acid. Extraction with three 125-ml. portions of hexane followed by removal of the solvent under reduced pressure gave an oil which, in the case of tetradecyl, hexadecyl, and octadecyl hydroperoxides, solidified at room temperature. Further purification was accomplished by dissolving the oil (10 g.) in absolute methanol (100 ml.) containing potassium hydroxide (20 g.), cooling the resulting solution, and then adding water (25 ml.). Extraction with two 30-ml. portions of hexane was followed by acidification of the methanol solution. Three extractions with 30-ml. portions of hexane followed by removal of the solvent gave the hydroperoxide. The properties of these compounds and yields are listed in Table II.

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[CONTRIBUTION FROM THE NAVAL STORES RESEARCH STATION¹]

Preparation of Some Vinyl Alkyl Pinates²

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Some monoalkyl pinates, 2,2-dimethyl-3-(alkoxycarbonyl)cyclobutaneacetic acids and alkyl 2,2-dimethyl-3-(carboxy)cyclobutaneacetates, were vinylated by the vinyl interchange method of Adelman. Vinyloxy carbonyl forms of the ethyl, *n*-butyl, 2-ethylhexyl, and hydronopyl mono esters, and vinyl acetate forms of the ethyl, *n*-butyl, and 2-ethylhexyl mono esters were prepared and characterized. Divinyl pinate and vinyl 2-ethylhexyl phthalate are reported also. The preparation of these esters by vinyl interchange is more satisfactory than by the Reppe procedure.

A study concerned with the internal plasticization of polyvinyl chloride led to the preparation of a number of vinyl alkyl pinates.³

Schildknecht⁴ stated that dibasic acid monovinyl and divinyl esters are generally difficult to prepare. Adelman⁵ reported the preparation of vinyl octyl phthalate and vinyl adipate, presumably mono-

vinyl, by vinyl interchange reaction with vinyl acetate.

Adelman presented evidence to show that esters do not undergo vinyl interchange, *e.g.* only the free carboxyl group of monoethyl phthalate reacted with vinyl acetate.

The synthesis of a number of monoalkyl pinates, the alkyl acetate and the alkyloxy carbonyl forms, is reported in another paper.⁶ Both types of monoethyl, *n*-butyl, 2-ethylhexyl, and -hydronopyl⁷ pinates were prepared. The preparation of the vinyl esters of these half esters are reported in this paper, excepting vinyl 2,2-dimethyl-3-(hydronopyloxy carbonyl)cyclobutane acetate.

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

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(3) In cooperation with Dr. C. S. Marvel, University of Illinois, under contract with the U. S. Department of Agriculture.

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