[Contribution from the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture]

Reactions of Unsaturated Fatty Alcohols. IV. Oxidative Degradation of Lauryl Isopropyl Ether[1]

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Received February 14, 1958

Lauryl isopropyl ether containing catalytic amounts of cobalt naphthenate was degraded with oxygen at 150°. Degradation products were separated by distillation, solvent extraction, and chromatography.

Isolated oxidation products indicate attack at both carbon atoms adjacent to the ether oxygen. Degradation products isolated were lauric acid, acetone, isopropyl laurate, lower fatty acids from C_2 to C_{11} and their esters, carbon dioxide, isopropyl alcohol, and polymerized acidic products.

Lauric acid and isopropyl laurate were oxidized under the same conditions as lauryl isopropyl ether. Lauric acid gave small amounts of lower acids in the homologous series as degradation products. Isopropyl laurate was oxidized to fatty acids from C_2 to C_{12} in about one third the quantities found from lauryl isopropyl ether.

Previously,[3] we reported the polymerization and film properties of some unsaturated fatty vinyl ethers. During evaluation work it was observed that certain of these films dissolved rapidly in 5% aqueous alkali. This result was unexpected because an ether linkage should be resistant to alkali. Further work demonstrated that the vinyl ether polymer films were being degraded by oxygen during the baking process or while standing in air for several days. Infrared spectroscopic studies on the oxidized films indicated hydroxyl, carbonyl, and ester groups. Chemical data on the alkali-soluble products from the oxidized films that were baked showed that C_{18} acids corresponding to the alkyl group in the vinyl ethers were present.

Since oxidation of stearyl vinyl ether polymer would not be complicated by double bonds in the fatty side chains, this polymer was oxidized under the same conditions as those used for the unsaturated vinyl ethers. Stearic acid was identified as an oxidation product, thus establishing oxidative attack at the alpha carbon atom of the fatty side chain. No oxidation products derived from the vinyl chain of the polymer could be identified. To obtain a clearer picture of the nature of this oxidation, we selected lauryl isopropyl ether because it contained the same carbon skeleton about the ether oxygen as found in the vinyl ether polymers.

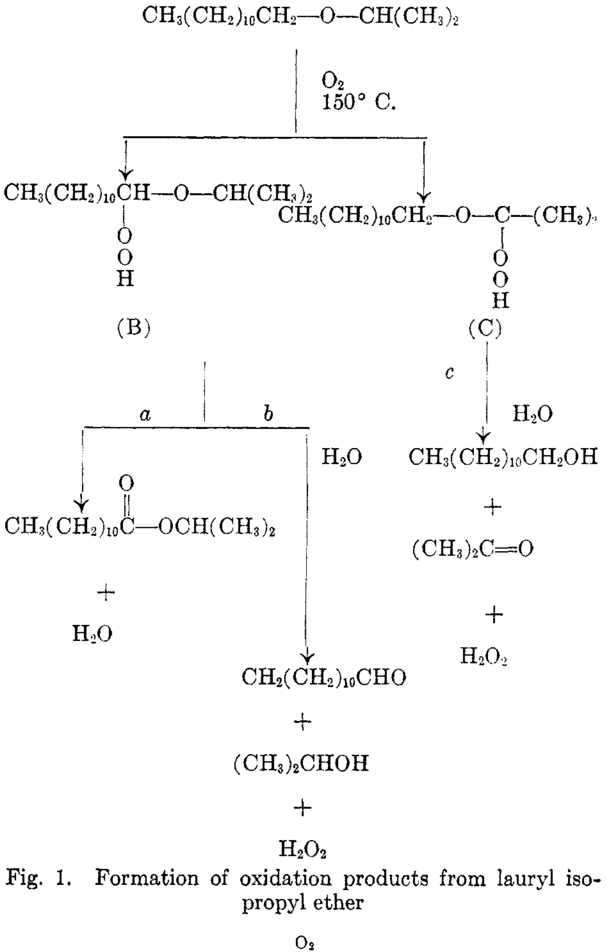
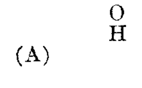


Fig. 1. Formation of oxidation products from lauryl isopropyl ether



$$R{-}CH_2{-}O{-}R \xrightarrow{O_2} R{-}\underset{\substack{|\\ O\\ O\\ H}}{C}H{-}O{-}R$$

(A)

Oxidation of ethers by oxygen to form "peroxides" has been known for many years. More recent work[4,5] has shown that oxygen initially attacks a carbon atom adjacent to the ether oxygen to form a hydroperoxide (A). Metallic ions, such as cobalt, are known to catalyze oxidations of this type as well as to promote subsequent decomposition of the hydroperoxide into other radicals and end products.[6,7] Equations shown in Fig. 1

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(1) Presented at the fall meeting of American Oil Chemists' Society, Cincinnati, Ohio, Sept. 30–Oct. 2, 1957.

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(3) W. J. Schneider, L. E. Gast, E. H. Melvin, C. A. Glass, and H. M. Teeter, *J. Am. Oil Chemists' Soc.*, **34**, 244 (1957).

(4) A. M. Clover, *J. Am. Chem. Soc.*, **44**, 1107 (1922).

(5) A. Rieche and R. Meister, *Angew. Chem.*, **49**, 101 (1936).

(6) A. Robertson and W. A. Waters, *Trans. Faraday Soc.*, **42**, 201 (1946).

(7) A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1574 (1948).

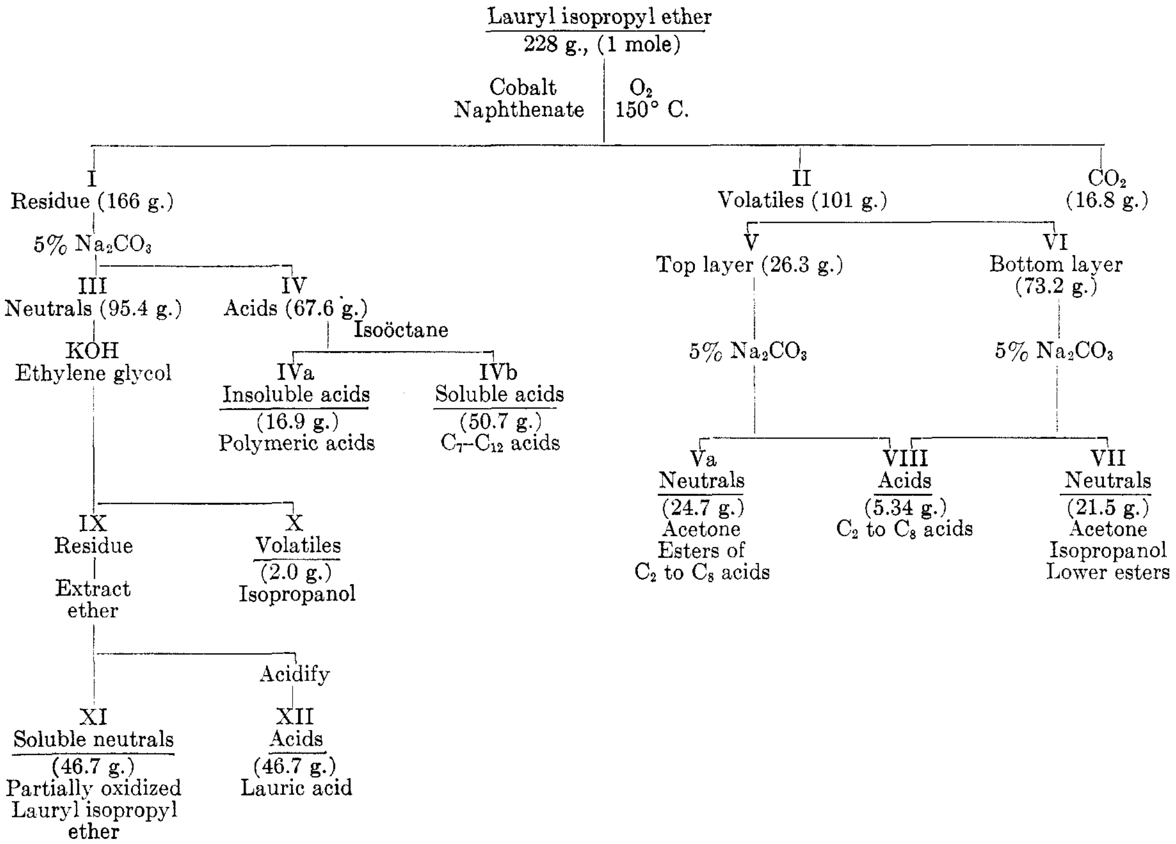


Fig. 2. Fractionation of oxidized lauryl isopropyl ether

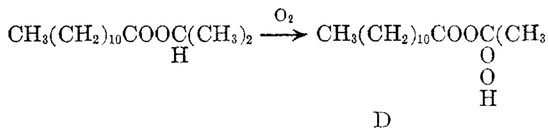
present a simplified route to formation of the more important oxidation products from lauryl isopropyl ether. Carbonyl compounds, alcohols, acids, and esters are products known to be formed from hydroperoxide decompositions.[5,7] According to the scheme shown in Fig. 1, either carbon adjacent to the oxygen could be oxidized, but the tertiary carbon in the isopropyl group is probably most susceptible to attack.[8] Decomposition of hydroperoxide (B) by route *a* would produce isopropyl laurate and water, whereas route *b* would yield lauryl aldehyde and isopropyl alcohol. The water necessary for reaction *b* is supplied from reaction *a*.

Hydroperoxide (C), formed by attack at the tertiary carbon atom of isopropyl group, could decompose into lauryl alcohol and acetone by route *c*, a process similar to that indicated by route *b*.[5] (C) could not decompose by route *a* because there is no hydrogen left on the α-carbon atom.

The products actually isolated as shown in Fig. 2 strongly support the series of equations postulated in Fig. 1.

Lauryl aldehyde was not isolated as a degradation product since it is relatively nonvolatile and would remain in the reactor to be oxidized to lauric acid and its lower homologs as shown later. Isopropyl alcohol, volatile under conditions of the reaction, was isolated from fractions V and VII, of Fig. 2 as the 3,5-dinitrobenzoate. Some acetone could be derived from this material by oxidation. Isopropyl laurate was identified in fraction III by saponifying the ester component and characterizing the lauric acid and isopropyl alcohol formed. The acetone formed was found in fractions V and VII, whereas the lauryl alcohol remaining in the oxidation mixture would presumably be converted to lauryl aldehyde, lauric acid, and other products formed by their degradation.

Isopropyl laurate, formed by route *a*, is partially oxidized through the hydroperoxide to lauric acid. This oxidation could proceed by attack at the tertiary hydrogen of the isopropyl group to form hydroperoxide (D) which would decompose into acetone and lauric acid as follows:



$$CH_3(CH_2)_{10}COO\underset{H}{C}(CH_3)_2 \xrightarrow{O_2} CH_3(CH_2)_{10}COO\underset{\substack{O\\O\\H}}{C}(CH_3)_2$$

D

$$\xrightarrow{H_2O} CH_3(CH_2)_{10}COOH + (CH_3)_2C{=}O + H_2O_2$$

Decomposition of (B) by route *a* or *b* and of (C) by route *c* leads to products that can eventually be oxidized to lauric acid, lower acids in the homologous series, and carbon dioxide as shown in Table I. A possible mechanism for this oxidation will be discussed later.

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[8] R. C. Larsen, R. E. Thorpe, and F. A. Armfield, *Ind. Eng. Chem.*, **34**, 183 (1942).

TABLE I

ACIDS FROM OXIDATION OF ISOPROPYL LAURYL ETHER

Fatty Acid	Threshold Vol. (Ml.)[a] Known	Threshold Vol. (Ml.)[a] Unknown[b]	Percentage of Total Acids Mole	Percentage of Total Acids Weight
C_{12}	19	19[b]	30.7	41.3
C_{11}	22	21	11.3	14.1
C_{10}	25	25	6.8	7.9
C_9	30	29	5.3	5.6
C_8	37	38[b]	5.9	5.7
C_7	47	51	5.8	5.1
C_6	62	64	6.1	4.8
C_5	81	86	6.5	4.5
C_4	107	112	8.6	5.1
C_3	163	167[b]	8.3	4.1
C_2	300	305	4.7	1.9

[a] These values are reported for a 2 × 8 cm. column bed containing approximately 7.5 g. of silicic acid. [b] Identity verified by production of a single band when rechromatographed with the appropriate known acid.

On a molar basis, lauric acid was formed in 3 to 5 times the amount of any other acids. Acids from C_5 to C_{10} were formed in roughly equal amounts. These data indicate that lauric acid was formed more rapidly than it was destroyed and accumulated in the degradation mixture.

Data in Table I suggest that C_3 and C_4 acids are more resistant to oxidation than the other acids; however, the higher yields of C_3 and C_4 acids may merely reflect the conditions under which oxidation was carried out. These acids were partially distilled from the reaction mixture into the trap because their boiling points are near or below the temperature of oxidation (150°). Thus, being protected from further oxidation, they tend to accumulate more than the less volatile acids. This phenomenon also accounts for the smaller quantity of acetic acid found among the products. Formic acid would not be an expected oxidation product because it contains an aldehyde, as well as an acid group, and it is easily oxidized to unstable carbonic acid.

Oxidation of lauryl isopropyl ether is difficult to interpret on a quantitative basis because all oxidation routes lead to intermediates that can be converted, at least in part, to identical products. According to the reactions proposed in Fig. 1, the moles of isopropyl laurate, acetone, isopropyl alcohol, and unreacted lauryl isopropyl ether present in the oxidation mixture should total one mole. The amount of each product isolated along with the unreacted lauryl isopropyl ether is shown in Table II. Approximately 86% of the starting ether is accounted for.

TABLE II

MOLE OF DEGRADATION PRODUCTS ISOLATED FROM ONE MOLE OF LAURYL ISOPROPYL ETHER

Compound	Mole
Isopropyl laurate	0.23
Acetone	0.22
Isopropanol	0.20
Unreacted lauryl isopropyl ether	0.21
	0.86

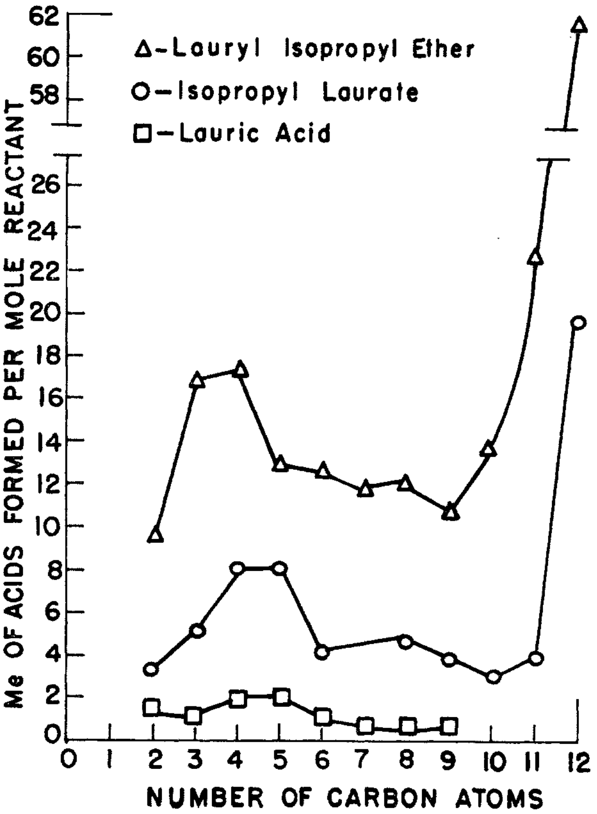

Fig. 3. Acids from the oxidation of lauryl isopropyl ether, isopropyl laurate, and lauric acid

Fig. 3 shows that under identical conditions of oxidation, isopropyl lauryl ether produces more lauric acid and lower acid homologs than isopropyl laurate and is more readily oxidized than lauric acid. Apparently the 12-carbon chain in isopropyl lauryl ether is more easily oxidized to lower acid homologs than the 12-carbon chain in lauric acid. This behavior may be due to differences in the oxidation processes of these substances. Any proposed reaction sequence for the formation of lower acids from these materials must account for the products isolated. Random attack at all possible positions along the 12-carbon chain appears to be a minor reaction since dibasic acids would be expected as products along with the lower monobasic acids. No dibasic acids were isolated from the reaction mixture. Reaction exclusively at the alpha position in lauric acid is unlikely because this center is considered somewhat deactivated toward radicals that seek points of high electron density, *e.g.*, oxygen and chlorine. In addition an alpha attack mechanism would produce some hydroxy and keto acid intermediates of short chain length that would distill from the reaction mixture into the trap. No products of this type were isolated. A possible reaction sequence for isopropyl lauryl ether that accounts for the acidic products formed and seems reasonable in view of current thinking on oxidation can be illustrated as follows: Hydroperoxides formed from lauryl isopropyl ether decompose into free radicals of various types. For example, hydroperoxides decompose at elevated temperatures:[7]

$$ROOH \rightleftharpoons RO\cdot + \cdot OH$$

Lauryl aldehyde formed from ether cleavage (see Figure 1) is susceptible to attack by hydroxy or alkoxy radicals yielding a carbonyl radical as shown by reaction 1.

$$RCH_2CHO + \cdot OH \longrightarrow RCH_2\dot{C}{=}O + H_2O \qquad (1)$$

$$RCH_2\dot{C}{=}O \longrightarrow RCH_2\cdot + CO \qquad (2)$$

$$RCH_2\dot{C}{=}O + O_2 \longrightarrow RCH_2COOO\cdot \qquad (3)$$

$$RCH_2COOO\cdot + RCH_2CHO \longrightarrow RCH_2COOOH + RCH_2\dot{C}{=}O \qquad (4)$$

Chain decomposition can occur by decarbonylation as shown by reaction 2[9] or oxidation can occur to yield ultimately a peracid shown by reactions 3 and 4.[10] Peracids have been observed to decompose at elevated temperatures to yield an alcohol and carbon dioxide[11] thus producing additional chain degradation. The alcohol produced in reaction 5

$$RCH_2COOOH \xrightarrow{\Delta} [RCH_2COO\cdot + \cdot OH] \longrightarrow RCH_2OH + CO_2 \qquad (5)$$

may be converted to the corresponding aldehyde by a Fenton-type oxidation involving cobalt instead of iron.[12] Although reaction 6 shows the

$$Co^{++} + H_2O_2 \longrightarrow Co^{+++} + \cdot OH + OH^- \qquad (6)$$

$$R'CH_2OH + \cdot OH \longrightarrow R'\dot{C}HOH + H_2O \qquad (7)$$

$$R'\dot{C}HOH + Co^{+++} \longrightarrow R'CHO + H^+ + Co^{++} \qquad (8)$$

decomposition of hydrogen peroxide to a hydroxy radical, an alkyl hydroperoxide would serve as well in this reaction sequence. The aldehyde produced by reaction 8 enters into reactions 1, 2, and 3 to be degraded further.

The alkyl radical produced in reaction 2 would combine with more oxygen by a series of reactions discussed by Vaughan *et al.*[13] to produce a mole of aldehyde and alcohol by reactions 9, 10, and 11.

$$RCH_2\cdot + O_2 \longrightarrow RCH_2OO\cdot \qquad (9)$$

$$2RCH_2OO\cdot \longrightarrow 2RCH_2O\cdot + O_2 \qquad (10)$$

$$2RCH_2O\cdot \longrightarrow RCHO + RCH_2OH \qquad (11)$$

The aldehyde from reaction 11 can enter into a series of reactions shown by reactions 1, 2, and 3 to produce more chain degradation. The alcohol can be oxidized back to an aldehyde by reactions 7 and 8.

Lower acids isolated in this work could be produced by the decomposition of peracids.[11]

$$RCOOOH \xrightarrow{\Delta} RCOOH + 1/2\ O_2 \qquad (12)$$

This reaction would compete with reaction 5.

With the oxidation of isopropyl laurate, hydrogen peroxide formed along with lauric acid from the decomposition of product D can produce some perlauric acid as illustrated in reaction 13.[14]

$$H_2O_2 + RCOOH \rightleftharpoons RCOOOH + H_2O \qquad (13)$$

Degradation of the carbon chain of the peracid may proceed by reaction 5. Thus, reaction 13 appears to be the major reaction leading to the formation of degradation products from isopropyl laurate. Presumably alkyl hydroperoxides could serve as well as hydrogen peroxide in this reaction. The low yield of acidic products from the ester (see Fig. 3) probably results from the lack of an easily oxidized intermediate, *e.g.*, lauryl aldehyde, to initiate oxidative degradation. Fig. 3 also shows that the oxidation of free lauric acid is curtailed probably by a lack of a good radical source. Random oxidative attack along the 12-carbon chain, however, could produce some hydroperoxy, hydroxy, and alkoxy radicals which would lead to ultimate formation of small amounts of hydrogen peroxide and perlauric acid. Degradation could then proceed as illustrated by reactions previously described. Small amounts of volatile acids (approximately 1%) have been observed as oxidation products of synthetic long chain fatty acids.[15]

EXPERIMENTAL

Lauryl iodide. A mixture of 223 g. (1.2 moles) of 95% lauryl alcohol (Dytol L-79, Rohm & Haas Co.[16]), 12.0 g. (0.384 mole) of red phosphorus, and 160.8 g. (1.32 moles) of iodine were placed in a three-necked, round-bottomed flask fitted with a stirrer and condenser. After the initial exothermic reaction, the mixture was heated by an oil bath at 150° for 5 hr. After cooling, the mixture was taken up in ether and the phosphorus removed by filtration. The products were washed with 5% sodium hydroxide, then with water until free of alkali, and dried over calcium chloride. Ether was stripped off and 327 g. (92% yield) of light amber product remained; n_D^{30}, 1.4800. The crude iodide was distilled using a short Vigreux column to yield 270 g. (82.5% yield) of purified product, b.p. 93–95°/0.2 mm.; n_D^{30}, 1.4801.

Anal. Calcd. for $C_{12}H_{25}I$: C, 48.70; H, 8.51; I, 42.85. Found: C, 48.63; H, 8.46; I, 43.20.

Lauryl isopropyl ether. In a three-necked, round-bottomed flask fitted with a stirrer and dropping funnel were placed 25.3 g. (1.1 moles) of sodium and 330 g. (5.5 moles) of puri-

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(9) C. Walling, *Free Radicals in Solution*, John Wiley and Sons, New York, 1957, p. 278.

(10) H. L. J. Bäckström, *Z. Physik. Chem.*, **B25,** 99 (1934).

(11) W. E. Parker, L. P. Witnauer, and D. Swern, *J. Am. Chem. Soc.*, **80,** 323 (1958).

(12) I. M. Kolthoff and A. I. Medalia, *J. Am. Chem. Soc.*, **71,** 3777 (1949).

(13) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. E. Vaughan, *Discussions Faraday Soc.*, **10,** 242 (1951).

(14) W. E. Parker, C. Rucinti, C. L. Ogg, and D. Swern, *J. Am. Chem. Soc.*, **77,** 4037 (1955).

(15) A. Davanhov and D. Fedotova, *Organic Chem. Ind.* (U.S.S.R.), **2,** 85 (1936).

(16) Mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

fied isopropyl alcohol. After the rapid initial reaction was completed, the flask was gently heated with stirring until all the sodium had dissolved. To the sodium isopropoxide formed was added dropwise 327 g. (1.1 moles) of lauryl iodide. The mixture was heated at reflux for an additional 2 hr. The solution was filtered to remove sodium iodide, washed with water, and dried over calcium chloride to yield 206.6 g. of product. Distillation of the product gave 78.2 g. of impure dodecene, b.p. 95–96°/10 mm.; n_D^{30}, 1.4240; I.V., 113, and 108.4 g. of lauryl isopropyl ether, b.p. 137–141°/10 mm.; n_D^{30}, 1.4250.

Anal. Calcd. for $C_{15}H_{32}O$: C, 78.80; H, 14.13. Found: C, 78.45; H, 13.93.

Lauric acid. This material was obtained from Distillation Products Industries (White Label grade) and used as received.

Isopropyl laurate. In a round-bottomed flask fitted with a condenser were placed 40 g. (0.2 mole) of lauric acid, 240 g. (4 moles) of isopropyl alcohol, and 1.4 g. of *p*-toluenesulfonic acid. This mixture was heated on a steam bath for 10 hr. After neutralizing the catalyst with sodium carbonate, excess isopropyl alcohol was distilled, and the crude ester was washed until neutral with distilled water and then dried. The product was distilled to yield 41.2 g. (85% yield) of purified ester, b.p. 91°/0.12 mm.; n_D^{30}, 1.4258; acid value, 0.23.

Anal. Calcd. for $C_{15}H_{30}O_2$: C, 74.50; H, 12.51; Sap. equiv., 242.4. Found: C, 74.42; H, 12.44; Sap. equiv., 250.

Oxidative degradation of lauryl isopropyl ether. A mixture of 228 g. (1 mole) of lauryl isopropyl ether and 3.2 g. of a 6% solution of cobalt naphthenate was placed in a flask and heated to 150° for 4 hr. while oxygen was introduced through a fritted-glass tube. The oxidation apparatus was connected to a trap surrounded by a bath of acetone and solid carbon dioxide. The outlet from the trap was connected to an Ascarite tube to absorb any carbon dioxide formed. After 4 hr., 166 g. of material remained in the reactor, 101 g. had collected in the trap as two layers, and 16.8 g. of carbon dioxide (0.38 mole CO_2 per mole ether) were absorbed in the Ascarite tube. A total of 283.8 g. of oxidation products was obtained, representing a pick-up of 55.8 g. of oxygen or 3.49 atoms of oxygen per mole of lauryl isopropyl ether. A flow sheet for the fractionation of the oxidized samples is shown in Fig. 2.

Acidic products. The acids from the oxidative degradation were isolated in fractions IV and VIII (Fig. 2), were separated by partition chromatography on a silicic acid column according to the procedure of Ramsey and Patterson,[17] and were tentatively identified by their threshold volumes. Acid bands containing 2 to 20 mg. of material were easily observed on the column; however, a more reliable method of detecting small amounts of acidic materials was to titrate small portions (1 to 3 ml.) of the eluting solvent with 0.02*N* sodium methoxide. Trace amounts of acids were easily detected by this technique. Threshold volumes were determined from the sharp rise in the titration curves.

Chromatography of fraction VIII showed the presence of lower fatty acids (C_2 to C_6); fraction IV contained the less volatile acids (C_6 to C_{12}). Information obtained on both fractions is combined and summarized in Table I.

Approximately 25% of the acidic material in fraction IV was insoluble in iso-octane and could not be placed on the chromatographic column. The insoluble material was a dark brown viscous oil; neutral equivalent, 372; carbonyl oxygen, 1.76%; sap. equiv., 185. Insolubility in iso-octane suggests a dibasic acid; however, the neutral equivalent was too high. This material appears to be a polymeric acid containing enough polar groups, *e.g.*, carbonyl and carboxyl, to render it insoluble in iso-octane. Infrared spectra on the acidic material show associated hydroxyl, carbonyl, carboxyl, and possibly ester groups in the molecule. The chemical data as shown confirm the presence of these groups.

Volatile neutral products. Neutral compounds were isolated from material in the cold trap. The top layer (fraction V) amounted to 26.3 g. and was extracted with sodium carbonate to remove 1.6 g. (6%) of acidic materials. Fraction VII was obtained as an insoluble oil by saturating fraction VI with sodium carbonate. Qualitative tests on these fractions indicated esters, alcohols, and carbonyl compounds. Fraction VII contained most of the alcohols as evidenced by infrared spectra.

Quantitative analyses gave the following results:

	Fraction V	Fraction VII
I.V.	11.1	10.0
Neut. equiv.	870	—
Sap. equiv.	232[a]	529
Carbonyl oxygen	7.1%	6.7%

[a] Corrected for acids.

Small samples (0.15 g. each) of fractions V and VII were combined and treated with an alcoholic solution of 2,4-dinitrophenylhydrazine.[18] After heating 15 min. on a steam bath, the 2,4-dinitrophenylhydrazone was filtered and dried (0.18 g.), m.p. 115–118°. The product was recrystallized from 95% ethanol to yield 0.11 g. of orange-yellow crystals, m.p. 120–121°. A small amount of these crystals was placed on a 2 × 20-cm. chromatographic column packed with Celite-Bentonite.[19] This column was developed with alcohol-chloroform (1:20) to yield a main band followed by three trace bands. The main band was eluted and recovered from the solvent as 2,4-dinitrophenylhydrazone melting at 123°. A mixed melting point obtained with an authentic sample of acetone-2,4-dinitrophenylhydrazone showed no depression. X-ray diffraction patterns were identical for 2,4-dinitrophenylhydrazone and for acetone-2,4-dinitrophenylhydrazone.

Anal. Calcd. for $C_9H_{10}N_4O_4$: C, 45.40; H, 4.25; N, 23.50. Found: C, 45.76; H, 4.16; N, 23.35.

If all of the carbonyl oxygen content of fractions V and VII is due to acetone, 12.8 g. of acetone was obtained from 228 g. of lauryl isopropyl ether or 0.22 mole of acetone per mole of ether.

Since fraction V had a saponification equivalent of 232, considerable ester was indicated. Data on acid components of the ester were obtained by refluxing fraction V with alcoholic potassium hydroxide for 4 hr. A small amount of the recovered acids (74 mg.) was dissolved in iso-octane and chromatographed on a silicic acid column.[12] Results are shown in Table III. The average molecular weight of the acids was 101.5. If isopropyl alcohol is assumed to be the alcoholic component of these esters (isopropyl alcohol was the only alcohol found in the volatile fractions), the mixture would have a saponification equivalent of 143.5. Comparison of this value with an observed saponification equivalent of 232 indicates fraction V was 62% ester. Carbonyl content of fraction V indicated 26% acetone, and extraction of this fraction with sodium carbonate gave 6% acids. It can be assumed that esters accounted for the remaining 68%. This value is in fair agreement with the value of 62% obtained from determining the acid content of the esters. The ester content of fraction V represents 0.113 mole of esters formed per mole of ether oxidized.

Since the infrared spectra of fraction VII showed the presence of considerable alcohol, 0.3 g. of this alcoholic material was treated with 1 g. of 3,5-dinitrobenzoyl chloride,

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[17] L. L. Ramsey and W. I. Patterson, *J. Assoc. Offic. Agr. Chemists*, **31**, 139 (1948).

[18] R. L. Shriner and R. C. Fuson, *Identification of Organic Compounds*, 3rd ed., John Wiley and Sons, New York, 1948, p. 171.

[19] J. A. Elvidge and M. Whalley, *Chem. & Ind.* (*London*), 589 (1955).

TABLE III

ACIDS OBTAINED FROM SAPONIFICATION OF FRACTION V[a]

	Threshold Vol. (Ml.)[b]		Percentage of Total Acids	
Acid	Known	Unknown	Mole	Weight
C_8	37	39	3.97	5.86
C_7	47	46	8.64	11.52
C_6	62	59	14.15	16.84
C_5	81	81	21.25	22.17
C_4	107	108	32.14	29.32
C_3	163	156	14.38	10.91
C_2	300	311	5.45	3.35

[a] Volatile neutral fraction from the oxidation of lauryl isopropyl ether. [b] These values are reported for a 2 × 8 cm. column bed containing approximately 7.5 g. of silicic acid.

and the mixture was heated on a steam bath for 5 to 10 min. The resultant product was washed with water, 2% sodium carbonate solution, and finally with water to yield 0.24 g. of crystals, m.p. 110–115°. The product was recrystallized from 95% ethanol to yield 0.10 g., m.p. 117–118°. A mixed melting point of this material with an authentic sample of isopropyl 3,5-dinitrobenzoate (m.p. 122°) melted at 118–119°.

Anal. Calcd. for $C_{10}H_{10}O_6N_2$: C, 47.3; H, 3.98; N, 11.0. Found: C, 47.1; H, 3.80; N, 10.9.

Fraction VII and pure isopropyl alcohol were examined in the infrared at 3570 cm.$^{-1}$ Comparison of the hydroxyl bands showed that fraction VII contained approximately 55% isopropyl alcohol by weight, if no other hydroxyl compounds were present. Since fraction VII amounted to 21.5 g., it contains 11.8 g. of isopropyl alcohol or 0.197 mole of isopropyl alcohol formed per mole of lauryl isopropyl ether.

Summarizing these data, fraction VII was found to contain 55% isopropyl alcohol and 24% acetone (by carbonyl analysis). Assuming the remaining material (21%) to be esters and correcting the saponification equivalent of 529 for this amount of ester, a new saponification equivalent of 111 is obtained. Since the esters in fraction VII amounted to 4.52 g. and had an average molecular weight of 111, 0.041 mole of esters was produced per mole of lauryl isopropyl ether oxidized.

Nonvolatile neutrals. Extraction of residue I with sodium carbonate solution gave a neutral fraction III and the previously investigated acidic fraction IV (Figure 2). Functional group analyses on fraction III showed the presence of carbonyl compounds (0.7% carbonyl oxygen) and esters, [sap. equiv., 259 (corrected for acids)]. The infrared spectrum showed bands corresponding to ester and to unreacted lauryl isopropyl ether. A comparison of the spectrum of the unknown with that of an authentic sample of isopropyl laurate gave an estimate of 70-75% ester in fraction III (calculated as isopropyl laurate).

Information on the acidic and alcoholic materials making up the ester in fraction III was obtained as follows: 9.8 g. of sample were treated with 10 g. of ethylene glycol containing 6.6% potassium hydroxide in a test tube fitted with a nitrogen inlet tube and a side arm leading to a receiver cooled by ice. The test tube was heated by an oil bath at 150° for 1.5 hr. as a gentle stream of nitrogen was allowed to flow through the apparatus. Two fractions were obtained as shown in Fig. 2: a residue (IX) and a small amount of volatile material (X). The neutral products were removed from fraction IX by diluting the residue with 2 volumes of distilled water and extracting 5 times with ethyl ether. The ether layers were combined and washed free of alkali with water. The combined ether layer was evaporated to yield 4.1 g. of an odorless yellow oil (XI). *Anal.* Found: C, 75.8; H, 13.55. Empirical formula: $C_{9.3}H_{20}O$. Mol. weight, 240.

The empirical formula shows that XI may be a 9 to 10 carbon atom alcohol or ether. However, the molecular weight corresponds to a partially oxidized isopropyl lauryl ether. The infrared spectra of XI is almost identical with isopropyl lauryl ether except for the hydroxyl adsorption at 3330 cm.$^{-1}$ The alkaline layer from fraction XI was acidified with hydrochloric acid, ether was added, and the layers were separated. The ether layer was washed free of mineral acid, and the ether was evaporated to yield 4.1 g. of acids (XII), neut. equiv., 236.

Fraction X (0.2 g.) was treated with 0.5 g. 3,5-dinitrobenzoyl chloride as described previously to yield 0.15 g. of crystalline ester, m.p. 112–115°. The product was recrystallized from alcohol to yield 0.10 g. a 3,5-dinitrobenzoate, m.p. 118°. A mixed melting point of this material with an authentic sample of isopropyl 3,5-dinitrobenzoate showed no depression.

Purification of fraction XII by partition chromatography on a silicic acid column (2 × 20 cm.) according to the method of Ramsey and Patterson[12] gave only one acid band having the threshold volume of lauric acid. The acid band was recovered and treated with thionyl chloride and ammonia to yield a crystalline amide, m.p. 98°. A mixed melting point determination with authentic lauramide showed no depression; hence, the ester in fraction XII was isopropyl laurate. Since the moles of isopropyl laurate in fraction III would be equivalent to the moles of lauric acid found in fraction XII, 0.23 mole of isopropyl laurate was formed per mole of lauryl isopropyl ether.

Oxidation of lauric acid and isopropyl laurate. Lauric acid and isopropyl laurate were found to be degradation products from lauryl isopropyl ether. Since these compounds are relatively nonvolatile, they were subjected to an oxidative environment during the experiment. In order to obtain data on the type of products formed from their degradation, lauric acid and isopropyl laurate were oxidized for 4 hr. at 150° with oxygen in the presence of cobalt naphthenate. The apparatus was the same as that used to oxidize lauryl isopropyl ether. The acids produced during this treatment were determined by partition chromatography on silicic acid[13] and results are shown in Fig. 3 along with similar data obtained on lauryl isopropyl ether.

Acknowledgment. The authors wish to express their appreciation to Mrs. Clara McGrew for microanalyses, to Mr. C. A. Glass and Miss Jean Mallan for infrared and ultraviolet analyses, and to Dr. J. C. Cowan for his suggestions during the course of this work.

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