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3,362,971
**OZONOLYSIS OF OLEFINS IN AN ALKOXY-
 ALKANOL SOLVENT**

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ABSTRACT OF THE DISCLOSURE

A process is described for preparing carboxylic acids (and ketones) from olefins by (1) ozonizing said olefins in an alkoxyalkanol and then (2) oxidizing said ozonized olefin with an oxygen-containing gas in the same alkoxyalkanol solvent. The addition of an aqueous acid organic or mineral in step (2) improves the yield of product obtained.

Non-cyclic olefins having from 6 to about 30 carbon atoms are suitable reactants. A preferred alkoxyalkanol is 2-methoxy ethanol; sulfuric acid is a preferred mineral acid.

The process can be carried out as both a batch and continuous process.

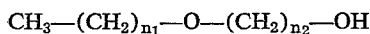
This invention relates to a novel process for the preparation of carboxylic acids. More specifically it relates to a preparation of carboxylic acids from olefins using ozone as an oxidant.

An object of this invention is to provide a method for the preparation of carboxylic acids. Another object is to provide a means for oxidizing olefins to carboxylic acids. Additional objects will be apparent from the following detailed description and appended claims.

The objects of this invention are accomplished by providing a process for the preparation of a carboxylic acid, said process comprising:

- (a) reacting ozone with a non-vinylidene olefin having from 6 to about 30 carbon atoms, said olefin being free of aromatic and cycloalkenyl radicals, and
- (b) reacting the product thereby produced with an oxidizing gas containing elemental oxygen at a temperature within the range of from about 50 to about 180° C.;

said process being carried out in the presence of an alkoxyalkanol having the formula:



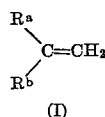
wherein n_1 is an integer having a value of 0-3 and n_2 is an integer having a value of from 2-6.

In a highly preferred embodiment, the lower alkoxyalkanol employed is methoxyethanol. In another preferred embodiment the product produced in the ozonization step is reacted with an oxygen-containing gas in the presence of water and a mineral acid. In another preferred embodiment the ozonization step is carried out at a temperature of from about -80° to about 35° C.

The process of this invention comprises two chemical reactions; first a reaction of an olefin with ozone, and second, a reaction of the products thereby produced with an oxygen-containing gas. It has been found that the yield of carboxylic acid product is increased if the first reaction is carried out in one solvent and the second in another. Hence, a preferred embodiment of the process of this invention also comprises a solvent-addition step.

Olefins having at least two hydrogens bonded to the carbon atoms in the ethylenic linkage other than vinylidene olefins yield carboxylic acids when reacted according to this process. Vinylidene olefins have the formula:

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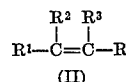


wherein R^a and R^b are hydrocarbon or substituted hydrocarbon radicals. Vinylidene olefins yield ketones when subjected to the process of this invention. A preferred embodiment of this invention is a process which entails the oxidation of a mixture of olefins comprising one or more vinylidene olefins. The ketone-carboxylic acid mixtures afforded by this preferred embodiment have desirable properties.

Certain types of non-vinylidene olefins are preferred reactants. Preferred olefins are free of aromatic and cycloalkenyl groups. More preferably, the olefins are free of other organic groups which undergo extraneous side reactions. In other words, the preferred olefinic starting materials are free of cyclic structures which contain carbon-carbon unsaturation and more preferably, contain organic radicals (bonded to the ethylenic bond) which are stable under the reaction conditions employed. Thus, the more preferred olefins have at least one free ethylenic linkage and do not contain organic radicals which undergo extraneous side reactions under the reaction conditions employed. A free ethylenic linkage is an ethylenic bond which is not in juxtaposition with substituent groups which prevent the process from being carried out by steric hindrance or by such a gross perturbation of the electronic characteristics of the ethylenic linkage that it is incapable of reacting as an ordinary double bond.

Thus, the more preferred olefinic reactants do not contain an oxygen, nitrogen, or sulfur atom bonded to a carbon atom adjacent to the double bond and the olefinic linkage to be reacted is not part of a conjugated diene system. In other words, the more preferred olefinic reactants contain a double bond which is isolated by at least one methylene group ($-\text{CH}_2-$) from any non-hydrocarbon substituent group or other ethylenic linkage.

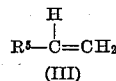
Highly preferred olefinic reactants are hydrocarbon olefins, that is, olefins which are solely composed of carbon and hydrogen. Most preferably the olefinic reactants have the formula:



wherein R^1 , R^2 , R^3 , and R^4 are groups selected from the class consisting of hydrogen and alkyl radicals having from one to about 28 carbon atoms, such that at least two of said groups are selected from hydrogen and said olefin has from six to about 30 carbon atoms and a non-vinylidene configuration.

Although olefins having cycloalkyl groups are applicable in this invention, olefins having alkyl radicals bonded to the ethylenic linkage are preferred because they are more readily available. Although the process of this invention can be employed to oxidize small olefinic compounds, such as ethylene and propylene, better results are usually obtained when an olefin having from six and preferably eight to about thirty carbon atoms is employed as a reactant. Olefins having from six to twenty carbon atoms are more preferred.

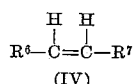
Thus, one type of preferred olefin reactant is selected from the terminal olefins having the formula:



wherein R^5 is an alkyl radical having from 4 to 28 carbon atoms.

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Another type of preferred olefin reactant is selected from the internal olefins having the formula:



wherein R^6 and R^7 are selected from the alkyl radicals having from 1 to about 27 carbon atoms, such that the total number of carbon atoms in R^6 and R^7 is at least 4 and not more than about 28. The most preferred internal olefins are β -olefins, that is, the olefinic linkage is one carbon atom removed from the end of the chain.

The alkyl radicals which are bonded to the olefinic linkages and the olefinic reactants employed in this process can be *n*-heptyl, *n*-octyl, *n*-nonyl, *n*-decyl, *n*-undecyl, *n*-dodecyl, *n*-tridecyl, *n*-tetradecyl, *n*-pentadecyl, *n*-hexadecyl, *n*-heptadecyl, *n*-octadecyl, and the like, and all positional isomers thereof. The most preferred radicals have from 12 to about 18 carbon atoms and the highly preferred radicals have an even number of carbon atoms. In other words, the highly preferred radicals are the dodecyl, tetradecyl, hexadecyl, and octadecyl radicals. Since they are more readily available, olefins containing straight chain alkyl groups are more preferred than the olefins which contain branched alkyl radicals.

The first step of this process comprises reacting one or more olefins of the type described above with ozone. It is preferred that the ozone be in the gaseous state and more preferably admixed in a minor amount with an inert carrier gas. Carrier gases which may be employed are the inert gases such as argon and neon and the like and most preferably, nitrogen, oxygen, air, carbon dioxide, and mixtures thereof. In a preferred embodiment, the carrier gas contains at least 20 percent by weight oxygen and more preferably is substantially pure oxygen. In other words, in this more preferred embodiment the ozone reactant is an ozone-oxygen gaseous stream. The concentration of the ozone in the carrier gas is not critical and may range from about 0.001 to about 30 percent by weight. Most preferably the concentration is within the range of about 0.001 to about 20 percent by weight. In a highly preferred embodiment the ozone concentration is from about 0.01 to about 10 weight percent.

The first step of this process can be carried out by contacting a molar equivalent ratio of olefin and ozone; however, it is not necessary to do so. Thus, good results are obtained if a slight excess of olefin is employed; for example, from about 1.20 moles of olefin per each mole of ozone. However, in many instances, higher yields are obtained when an excess of ozone is used. In general it is preferred that from 1 to about 2 moles of ozone be employed per each mole of olefin. Greater excesses of ozone such as 3 moles per mole of olefin can be employed if desired. However, in many instances, significant advantages are not obtained with these higher mole ratios.

The amount of ozone admitted to the reaction zone can be determined by any method known in the art. For example, when an ozone-oxygen stream is employed, the concentration of the ozone can be determined by the difference in thermal conductivity of the ozone-oxygen mixture as compared with the thermal conductivity of pure oxygen. Multiplication of the concentration of ozone by the total volume of gas admitted yields the amount of ozone admitted to the reaction zone.

In order to insure a complete utilization of the ozone and thereby keep the cost at a minimum, it is frequently desirable to regulate the flow of ozone through the liquid reaction mass so that the ozone added is completely reacted with the olefin. In some instances higher yields of product are obtained if the ozone-containing stream is pushed through the reaction mixture at a rate which affords the presence of ozone in the effluent gaseous stream. A convenient method for determining if the ozone is completely utilized in the reaction zone is the passage of the effluent gas through an aqueous potassium iodide tower.

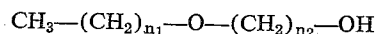
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Any ozone which is not utilized by the reaction mixture oxidizes the iodide to free iodine. The presence of free iodine can be quantitatively determined by titration with sodium thiosulfate according to the method in Scott's Standard Methods of Chemical Analysis, volume 1, page 279.

The first step of this process can be conducted at atmospheric, superatmospheric, or subatmospheric pressures. The exact atmosphere employed is not critical, and in most cases the reaction is effectively carried out at substantially atmospheric pressure.

The reaction of ozone with an olefin in this process is carried out at a temperature within the range of from about -100° to about 50° C. More preferably, the reaction temperature is within the range of from about -80° to about 35° C. The most preferred reaction temperatures are within the range of from about -10° to about 35° C. In most instances, heat is evolved during the reaction of ozone with the olefin; hence, efficient cooling means are usually desired.

In this process, the reaction of ozone with an olefin is conducted in the presence of a lower alkoxyalkanol as a reaction medium. Preferred alkoxyalkanols have the formula:



wherein n_1 is an integer having a value of 0-3 and n_2 is an integer having a value of from 2-6. Illustrative but non-limiting examples of alkoxyalkanols of this type include 1,3-propylene glycol monopropyl ether, ethylene glycol monobutyl ether, 1,3-propylene glycol monomethyl ether, 1,5-pentylene glycol monoethyl ether, 1,6-hexylene glycol monobutyl ether, and the like. The process can be extended to employ bidentate ether alkanols such as diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, and the like. In many instances the bidentate ether alkanols are not readily removed by distillation from the desired carboxylic acid products. Therefore, in general, they are not preferred.

A small amount of water in the lower alkoxyalkanol can be tolerated. In general, the amount of water should be less than about 5 percent, most preferably less than 3 percent by weight. Sufficient lower alkanol should be employed to produce a readily fluid reaction mixture. Generally, a weight of alkanol amounting to at least the weight of olefin reactant is required, and in most cases, at least twice this amount is desirable. Up to 20 or more times the weight of the olefin reactant can be employed if desired.

This process is carried out by contacting the olefin and ozone in the reaction medium of the type specified above at the desired temperature and pressure. The method of contacting the reactants is not critical and any method known in the art can be employed. Frequently, it is desirable to admix the olefin and the lower alkanol in a reaction vessel and subsequently pass ozone or an ozone-containing gas through the resultant liquid. Agitation of the liquid medium containing the olefinic reactant is not critical. However, in many instances agitation by either stirring or rocking enhances the rate of reaction and provides a more even reaction rate. In many instances the agitation caused by the bubbling of the ozone-containing gas through the liquid reaction mixture is sufficient.

The time of reaction between ozone and an olefin is not a truly independent variable but depends at least to some extent on the other reaction conditions employed, such as the concentration of ozone. For example, higher temperatures and efficient agitation of the reaction mixture usually result in a lessening of reaction time. On the other hand, inefficient contacting of the reactants usually lengthens the reaction time. In most instances, the reaction is complete after a reaction time within the range of from about 15 minutes to 35 hours.

After the ozonization of the olefin is completed, the resultant product is then reacted with oxygen to prepare

the desired carboxylic acids. This second step can be carried out in the presence of the alkoxyalkanol described above. In a preferred embodiment a second step is also carried out in the presence of water and an acid. Thus, it is preferred that before the ozonization product is contacted with oxygen that an aqueous acid mixture be added to the reaction mixture.

From the above it is understood that the oxidation step is preferably carried out in the presence of a second reaction medium consisting essentially of alkoxyalkanol employed in the first step, water and a catalytic quantity of an acid. The acid may be either a mineral acid or an organic acid. Preferred organic acids are carboxylic acids having a boiling point below about 80° C. Most preferably they are lower fatty acids having from 1 to about 5 carbon atoms. Thus, the most preferred acids are formic, acetic, propionic, n-butyric, n-valeric acid, and the like. Other acids which may be employed if desired include trimethylacetic acid, caproic acid, caprylic acid, fluoroacetic acid, chloroacetic acid, bromoacetic acid, dichloroacetic acid, trichloroacetic acid, trifluoroacetic acid, β -chloropropionic acid, α -dichloropropionic acid, and the like. In addition, other acids such as glycolic acid and lactic acid can be employed if desired.

In general, one or more of the above acids is admixed with water so that the concentration of acid is from about 5 to about 98 percent by weight. A preferred concentration range is from about 30 to about 75 weight percent, and a most preferred range is from about 40 to about 60 percent by weight. The organic acid-water mixture can be admixed with a catalytic quantity of a mineral acid. Typical mineral acid catalysts which can be employed include hydrochloric acid, sulfuric acid, metaphosphoric acid, triphosphoric acid, pyrophosphoric acid, orthophosphoric acid, and the like. Mineral acids of this type can also be used without the presence of an organic acid.

In general, an amount of mineral acid between about 0.0001 and 15 moles per each mole of starting olefin is employed. A preferred acid concentration is from 0.001 to 1.0 mole and a most preferred range from 0.001 to 0.3 mole per mole of olefin.

If desired, the second reaction mixture can contain minor amounts of other materials. Adjuvants which may be added to the mixture include metal salts; most preferably, the salts of the metals within Group VIII of the Periodic Table. Of these salts, those of iron, cobalt, nickel, palladium, and platinum are preferred. Most preferably, cobalt, palladium and platinum salts are employed. Typical metal salts are iron chloride, cobaltous acetate, and the like. Metal oxides are also suitable adjuvants. Typical metal oxides which may be employed are silver oxide, cupric oxide, ferric oxide, and the like. Usually the above adjuvants are employed in minor amounts. Thus, their concentration within the second reaction medium is usually within the range of from about 0.0001 to about 1.0 weight percent.

The second chemical reaction in the process of this invention comprises the oxidation of the products of the ozonization reaction (preferably admixed with the acidic reaction mixture described above) with an oxygen-containing gas. The oxygen-containing gas may be pure oxygen or air or oxygen admixed with an inert carrier gas. Carrier gases which may be employed are the inert gases such as argon, neon, and the like; nitrogen, carbon dioxide, steam, and mixtures thereof. In a preferred embodiment, the carrier gas contains at least 20 percent by weight oxygen. Highly preferred oxygen-containing gases are pure oxygen and air.

It is preferred that the amount of oxygen employed be sufficient to oxidize all of the ozonization residue to the corresponding carboxylic acid(s). In general, at least a stoichiometric equivalent of oxygen is employed. A slight excess of oxygen frequently increases the yield. Thus, in many instances it is desirable to employ from about 1.0

to about 4 moles of oxygen per each mole of starting olefin. Most preferably, the amount of oxygen employed is within the range of from about 1.0 to about 2.5 moles. In many instances it is desirable to contact the reaction mixture with more oxygen, say 50 or 100 or more moles per mole of starting olefin, to insure that the reaction is substantially complete.

The oxidation of the ozonization residues is carried out at a temperature which affords a reasonable rate of reaction and a minimum of by-product formation. In general, suitable reaction temperatures are within the range of from about 30 to about 180° C. More preferably, the reaction temperature is within the range of from about 40 to about 175° C., and most preferably between about 50 to about 150° C.

The oxidation step is conveniently carried out by bubbling oxygen through the liquid reaction mixture. In many instances, the bubbling action causes sufficient agitation to insure sufficient contact of the reactants. If desired, other agitation means such as stirring and rocking can be employed. The time of reaction is not a truly independent variable but is dependent at least in part on the other reaction conditions employed. In most instances the reaction is substantially complete in from about one-half to about 60 hours.

The process of this invention can be carried out as a batch process or as a continuous operation. In many instances, higher yields of product are obtained when the ozonization step is carried out in an apparatus similar to an Oldershaw distilling column. In other words, it is preferred that the reaction be carried out in an apparatus having a multiplicity of reaction zones. Such an apparatus provides a continuous process, a minimum residence time and thereby obviates to a great extent any possible side reactions. A typical internally fed counter-current apparatus for laboratory-scale operations is illustrated in FIGURE 5 on page 7 of Basic Manual of Applications and Laboratory Ozonization Techniques; the Welsbach Corporation, Ozone Processes Division, Westmoreland and Stokley Streets, Philadelphia, Pa. Similarly, the second reaction step is conveniently carried out in a multi-stage reactor having a contact time of about one hour at each stage. In a highly preferred embodiment, the ozonization product admixed with the second reaction medium is fed continuously into one stage of a multi-stage reaction provided with means for bubbling an oxygen-containing gas through a portion of the fed reaction mixture and overflow means which, by siphoning action, carries the oxygen-treated reaction mixture from one stage to another. The second stage is also provided with means for bubbling oxygen through the fed reaction mixture and siphoning means to carry the treated mixture to another stage. The number of stages which are employed is not critical; however, from 4 to about 12 are preferred. Each stage except the last one also has means for bubbling oxygen through the mixture to be treated and overflow means to convey the treated mixture to the next stage. The last stage has means for bubbling oxygen through the reaction mixture and means to forward the treated material to a product collection device. The latter means may, as above, be a siphoning apparatus. In a highly preferred embodiment, the reaction mixture at each successive stage is heated to a higher temperature. Thus, for example, the temperature of the fed reaction mixture at the first stage can be about 50° C., the second 60° C., the third 70° C., and so on.

In a very highly preferred embodiment, the process of this invention is carried out on a mixture of olefins having from 12 to about 26 carbon atoms. Preferably the mixture contains at least about 60 percent of C₁₂-C₁₆ olefins which do not have a vinylidene structure. Preferably the olefin, when reacted according to the process of this invention, will yield a mixture of fatty acids which is predominantly composed of C₁₁-C₁₅ acids. Thus, for example, the process is most preferably carried out on olefinic mixtures which contain a high percentage of terminal olefins with-

in the C_{12} - C_{16} range and high percentages of β -olefins within the C_{13} - C_{17} range. Preferably the olefin mixture should yield a fatty acid mixture which is predominantly C_{11} or C_{12} acid or mixtures thereof. Thus, the preferred olefin feeds yield a product of the following description.

Acid:	Percent by weight
C_9 - C_{10} -----	1-3
C_{11} - C_{12} -----	60-70
C_{13} - C_{14} -----	20-30
C_{15} - C_{16} -----	7-10

The following examples serve to illustrate the process of this invention but do not limit it. All parts are parts by weight unless otherwise noted.

Example I

Into a reaction vessel equipped with efficient cooling means is charged 13.46 parts of 1-dodecene and 65 parts of methoxyethanol. An ozone-oxygen stream, 0.935 millimole ozone per liter, is bubbled into the resultant mixture until a 25 percent excess of ozone is admitted. During the bubbling the temperature of the reaction vessel is maintained within the range of from -20° to -30° C. After the ozone contacting has been completed the resultant mixture is warmed to room temperature.

The reaction product is admixed with 40 parts of water and 1.86 parts of concentrated sulfuric acid. The resultant mixture is then heated to reflux and oxygen bubbled through the heated mixture for 5 and $\frac{1}{4}$ hours. (The oxygen is bubbled through at a rate of 80 cc. per minute.) The resultant mixture is cooled to ambient temperature.

The reaction mixture is extracted three times with petroleum ether. The petroleum ether portions used are successively, 70 parts, 52.5 parts and 35 parts. After extraction, the combined organic layers are washed with water. The water layer is separated and the resultant organic fraction dried over anhydrous sodium sulfate. After drying, the organic material is separated by filtration. The filtrate is distilled at ambient temperature and aspirator pressure to yield a residue of crude undecanoic acid. The crude product is further purified by fractional distillation.

When the above procedure is repeated except that the reaction mixture obtained from the ozonization step is not admixed with sulfuric acid and water prior to carrying out the reaction with oxygen, the yield of product is slightly reduced.

Similar results are obtained when the ozone stream contains 5.0 or 20.0 millimoles of ozone per liter.

High yields of undecanoic acid are obtained when the procedure of the above example is followed except that the ozone is admixed with carbon dioxide, nitrogen or air.

Example II

The process of Example I is repeated except that ethoxyethanol (ethylene glycol monoethyl ether) is employed instead of methoxyethanol. Similar results are obtained. Similar results are also obtained when ethylene glycol monopropyl ether is employed.

Example III

The procedure of Example I is followed except that 3.72 parts of concentrated sulfuric acid is added to the ozonization product prior to contacting said product with gaseous oxygen. Similarly, high yields of undecanoic acid are obtained when 0.5 or 5.0 parts of concentrated sulfuric acid is added to the ozonization product prior to the secondary oxidation reaction. Similar results are obtained when the reaction of oxygen with the ozonization product is carried out at a temperature of 150° C.

Example IV

The process of Example I is repeated except that the ozonization reaction is carried out at a temperature of -80° C. and 5.0 parts of orthophosphoric acid is employed in place of the sulfuric acid in the second oxidation step. Similar results are obtained with hydrochloric

acid, metaphosphoric acid, pyrophosphoric acid, and triphosphoric acid are employed.

Similar results are obtained when the above acids are employed in a concentration range of from 0.001 to 5.0 moles per mole of starting olefin.

Example V

The procedure of Example IV is followed except that the ozonization step is carried out at a temperature of 10° C. Similar results are obtained if a stoichiometric amount of ozone is employed in the reaction.

Example VI

The procedure of Example II is followed except that trichloroacetic acid is added prior to oxidizing the ozonization product. Similar results are obtained when n-butyric acid, isobutyric acid, n-valeric acid, and isovaleric acid are employed. Similarly, mixtures of acetic and sulfuric or orthophosphoric acid yield good results.

Example VII

The procedure of Example VI is followed except that the second step, the reaction of the ozonization product with oxygen, is carried out at a temperature of 50° C. Similar results are obtained when the reaction is carried out at a temperature of 180° C.

Example VIII

Decene-1 is reacted according to the procedure of Example I except that the second reaction mixture comprises, in addition to the methoxymethanol, a mixture of 10 parts of water, 70 parts of glacial acetic acid and 1.68 parts of sulfuric acid. Pelargonic acid is obtained. The reaction is repeated except that the second reaction medium contains 5 parts of water, 80 parts of glacial acetic acid and 3 parts of sulfuric acid. Similar results are obtained when 90 parts of water, 10 parts of glacial acetic acid and 6 parts of sulfuric acid are present in the second reaction medium. Similar results are obtained when octadecene-1 is employed to yield heptadecanoic acid.

Example IX

A mixture of olefins, 26.92 parts, consisting of 65 weight percent dodecene-1, 25 weight percent tetradecene-1 and 10 weight percent hexadecene-1 is oxidized according to the procedure of Example I. The product consists of approximately 65/25/10 weight percent mixture of undecanoic acid, tridecanoic acid and pentadecanoic acid. Similar results are obtained when 1,6-hexylene glycol monomethyl ether is employed in place of the methoxyethanol.

Example X

A 26.92 part portion of an olefinic mixture having the following composition:

- 73.4 mole percent dodecene-2,
- 9.9 mole percent dodecene-3,
- 5.4 mole percent dodecene-4,
- 5.6 mole percent dodecene-1, and
- 5.7 mole percent dodecane

is oxidized according to the procedure of Example IV. The product consists of a mixture of the corresponding carboxylic acids derived by a cleavage of the double bond within the olefinic starting materials. A similar product is obtained when the procedure is carried out using an olefinic mixture having the following composition:

- 6.9 mole percent dodecene-1,
- 75.2 mole percent dodecene-2,
- 4.8 mole percent dodecene-3,
- 6.0 mole percent of a mixture of dodecene-4 and dodecene-5, and
- 7.1 mole percent dodecane.

Similar results are obtained when 1,4-butylene glycol monopropyl ether is employed.

Example XI

A feed stock is prepared containing equal parts by weight of dodecene-1 and ethoxyethanol. This stock is charged to a 17-plate Oldershaw column at a point $\frac{2}{3}$ of the way down the column. Ethoxyethanol containing 2.0 weight percent water is charged to the Oldershaw column at the top. The rate of addition of the dodecene-1 to the column is 45 parts per hour and the rate of addition of the ethoxyethanol-water mixture is 159 parts per hour. The temperature of the column is maintained at 30–35° C. An ozone-oxygen stream is charged to the column at the bottom. The rate of addition of ozone is 11.4–12.2 parts per hour.

The resultant fluid reaction mixture is fed continuously into a reaction column having six stages. Each stage has means for bubbling oxygen through the portion of the fed reaction mixture at each stage and an overflow siphoning means which carries the oxygen-treated reaction mixture from one stage to the succeeding stage. The temperature of the stages are 60°, 70°, 80°, 90°, 100° and 110° C., respectively. Oxygen is bubbled through the column from the bottom at a rate of 4 cubic feet per minute. The residence time at each stage is one hour.

The product obtained from the overflow means at the last stage (temperature 110° C.) contains undecanoic acid. The acid is isolated from the other components by a continuous distillation.

The procedure of the above example is followed except that an olefinic mixture similar to the mixtures employed in Example X is used in place of dodecene-1. The product is a mixture of the corresponding carboxylic acids obtained by cleavage of a double bond within the olefinic feed components. The detergent range acids are separated from the other products by distillation.

Example XII

An olefinic mixture having the following composition:

60 mole percent dodecene-2,
9.9 mole percent dodecene-3,
5.4 mole percent dodecene-4,
5.6 mole percent dodecene-1,
5.7 mole percent dodecane, and
13.4 mole percent 2-pentyl heptene-1

is oxidized according to the procedure of Example V. The product is a mixture comprising the corresponding carboxylic acids derived from the dodecenes and the ketone obtained by the oxidation cleavage of the double bond in the 2-pentyl heptene-1. This product is a superior lubricant. An oil and water emulsion is prepared by adding water to the resultant product mixture. The emulsion has superior lubricant properties.

The long chain carboxylic acids prepared according to the process of this invention are efficaciously employed in the production of soaps. They can be used for the production of potassium or sodium soaps as well as for the production of heavy metal soaps. For this utility a composition of matter comprising C₁₁–C₁₅ acids in which each component is present in a range of 0–100 percent is preferred. Highly preferred mixtures contain the odd carbon numbered acids resulting from direct ozonolysis of even carbon alpha-olefin feed mixtures. Another highly preferred composition is a mixture of the even carbon numbered acids within the above range derived from the oxidation of an even numbered beta-olefin stream.

Many of the acids prepared by the process of this invention are known in the art and they have the many utilities known for these compounds. For example, the soaps prepared therefrom can be used as driers. The acids can be employed as chemical intermediates. For example, they may be esterified or reacted with an active halogen source to prepare the corresponding acyl halide.

Having fully described the novel process of this invention and the utility of the products produced thereby, it

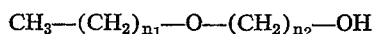
is desired that this invention be limited only within the lawful scope of the appended claims.

I claim:

1. A process for the preparation of a carboxylic acid, said process comprising:

- (a) reacting ozone with a non-vinylidene hydrocarbon olefin having from 6 to about 30 carbon atoms, said olefin being free of aromatic and cycloalkenyl radicals, and
- (b) reacting the product thereby produced with an oxidizing gas containing elemental oxygen at a temperature within the range of from about 50 to about 180° C.;

said process being carried out in the presence of an alkoxy-alkanol having the formula:



wherein n_1 is an integer having a value of 0–3 and n_2 is an integer having a value of from 2–6.

2. The process of claim 1 wherein said ozone is in the gaseous state and is admixed, in a minor amount, with a carrier gas.

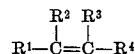
3. The process of claim 2 wherein the concentration of ozone in said carrier gas is from about 0.01 to about 10 percent by weight.

4. The process of claim 3 wherein said carrier gas is selected from the class consisting of nitrogen, oxygen, air, carbon dioxide, and mixtures thereof.

5. The process of claim 4 wherein said carrier gas contains at least 20 percent by weight of oxygen.

6. The process of claim 2 wherein said carrier gas is substantially pure oxygen.

7. The process of claim 1 wherein said olefin has the formula:



wherein R¹, R², R³, and R⁴ are groups selected from the class consisting of hydrogen and alkyl radicals having from one to about 28 carbon atoms, such that at least two of said groups are hydrogen and said olefin has from six to about 30 carbon atoms and a non-vinylidene configuration.

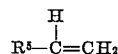
8. The process of claim 7 wherein R², R³, and R⁴ are hydrogen.

9. The process of claim 7 wherein R² and R³ are hydrogen and R¹ and R⁴ are selected from said alkyl radicals.

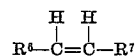
10. The process of claim 9 wherein R⁴ is a methyl group.

11. A process for the preparation of a mixture of carboxylic acids having from 11 to about 25 carbon atoms, said process comprising:

- (1) reacting ozone with an olefin mixture consisting of an olefin having the formula:



and an olefin having the formula:

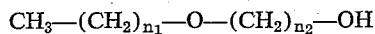


wherein R⁵ is an alkyl radical having from 4 to about 28 carbon atoms and R⁶ and R⁷ are selected from alkyl radicals having from one to about 27 carbon atoms, such that the total number of carbon atoms in R⁶ and R⁷ is at least four and not more than about 28; in the presence of a lower alkanol having from one to three carbon atoms, and at a temperature within the range of from about –80° to about 35° C.;

- (2) reacting the product thereby produced with an oxidizing gas containing elemental oxygen at a temperature within the range of from about 50 to about 180° C. and in the presence of water and a mineral acid;

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said process being carried out in the presence of an alkoxyalkanol having the formula:



wherein n_1 is an integer having a value of 0-3 and n_2 is an integer having a value of from 2-6.

12. Process of claim 11 wherein said mineral acid is sulfuric acid.

13. Process of claim 12 wherein said alkoxy alkanol is methoxyethanol.

14. A process for preparing undecanoic acid which comprises (a) reacting dodecene-1 with ozone in methoxyethanol solvent at a temperature of from -20° to about

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-30° C., (b) adding about 35 percent by weight of 40 parts water:2 parts sulfuric acid solution and (c) heating said mixture to reflux and passing an oxygen-containing gas through said mixture.

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