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PREPARATION OF ALIPHATIC HYDROPEROXIDES AND ALIPHATIC CARBOXYLIC ACIDS

Ernest J. Kahler and Glenn W. Kinzer, Columbus, Ohio, assignors, by mesne assignments, to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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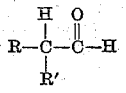
10 Claims. (Cl. 260—530)

This invention relates to a novel method of preparing aliphatic hydroperoxides. More specifically, it is concerned with the preparation of alkyl hydroperoxides, particularly secondary alkyl hydroperoxides, by the oxidation of alkyl aldehydes in the presence of certain unsaturated hydrocarbons.

The preparation of aliphatic hydroperoxides, e. g. propyl and isopropyl hydroperoxides, by treating a dialkyl sulfate with hydrogen peroxide has been described by Medvedev et al. (Ber. 65B, 133–7, 1932). U. S. 2,176,407 describes the preparation of secondary alkyl hydroperoxides by the action of hydrogen peroxide on alcohols such as sec.-butanol and isopropanol in the presence of a salt such as Na_2SO_4 or $CaSO_4$. Other methods of preparing hydroperoxides, particularly the secondary alkyl hydroperoxides are described in U. S. 2,421,392 and in the work of Hoch et al. in Ber. 72B, 1562–8, 1939. These prior art techniques, however, do not offer the simplicity of operation inherent in the method of the present invention nor are they adapted to commercial scale production. Furthermore, none of the prior art techniques provide a commercial method of preparing such peroxides from aldehydes. The advent of the commercial Oxo process has made substantial quantities of aldehydes available and created a demand for as many useful derivatives of these compounds as possible.

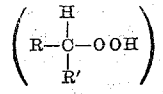
It is an object of the present invention to provide a novel technique for the preparation of valuable aliphatic hydroperoxides. An additional object is to provide a method of producing such valuable products from aliphatic aldehydes. It is a further object to provide a method whereby substantial yields of both hydroperoxides and carboxylic acids may be obtained by the oxidation of aliphatic aldehydes. These and additional objects will be apparent from the following detailed description of the present invention.

We have made the surprising discovery that aliphatic aldehydes, represented by the empirical structure



wherein R represents an alkyl or an alkylene radical containing from 1 to about 24 carbon atoms and R′ represents a hydrogen atom, an alkyl or an alkylene radical containing from about 1 to about 24 carbon atoms and the total number of carbon atoms in R and R′ does not

exceed about 24, may be oxidized in the liquid phase to produce substantial yields of aliphatic hydroperoxides



containing one carbon atom less than the original aldehyde, if there is present during the oxidation an unsaturated hydrocarbon selected from a hereinafter defined class. The oxidation is conducted in accordance herewith by contacting the aldehyde with an oxygen-containing gas.

Whereas the oxidation of an aldehyde under conditions hereinafter described, would ordinarily result in a substantial yield of the corresponding carboxylic acid and essentially no hydroperoxide, by virtue of the addition of an unsaturated hydrocarbon of the hereinafter defined class production of carboxylic acids is inhibited to a substantial extent and good yields of hydroperoxides are obtainable. Unsaturated hydrocarbons useful, in accordance herewith, are those containing a tertiary carbon atom which is either alpha or beta to the double bond. Such compounds may be acyclic, alicyclic, bicyclic, monoolefinic or polyolefinic; and the polyolefinic compounds may be either conjugated or unconjugated. Examples of such compounds will hereinafter be set forth.

Whereas, the art has indicated the possibility that peroxides may comprise intermediate reaction products through oxidation of aldehydes to acids, Haber et al., Ber. 64, 2844 (1931), and it has even been reccomended that a catalyst capable of decomposing peroxides be employed during such an oxidation (U. S. 2,010,358 and 2,212,900), no one has, until now, been able to oxidize aldehydes to produce and recover substantial quantities of valuable hydroperoxides or to inhibit the production of carboxylic acids as hereinafter described.

The present invention is applicable to diverse aliphatic aldehydes. Thus, suitable for use in accordance herewith are the normal aldehydes: acetaldehyde, propanal, butanal, valeral, hexanal, heptanal, nonanal, dodecanal, octadecanal, etc.; and the secondary aldehydes such as isobutanal, 2-ethylbutanal, 2-ethylhexanal, etc. It is not essential to employ individual aldehydes in accordance herewith and mixtures thereof may be oxidized to produce corresponding mixtures of hydroperoxides. Thus, for example, the aldehyde product resulting from the oxoation of a n-butylene-isobutylene codimer (hereinafter described in detail) comprises a mixture of isomeric aldehydes containing 9 carbon atoms. The term "oxoation" as used herein means the catalytic carbonylation of an olefin by reaction with carbon monoxide in the presence of hydrogen as is illustrated by the well-known Oxo process. The aldehydes may contain unsaturation such as for example in octadecenal, dodecenal, etc.

A typical Oxo-derived nonyl aldehyde fraction of the type referred to above has a boiling range at 5 mm. Hg of 104 to 126° F. Specific gravity, 60/60° F. of 0.838, a refractive index n_D^{20} 1.428 and an average molecular weight of 142.

The following illustrates a typical primary nonyl aldehyde composition that is derivable from n-butylene-iso-

butylene codimer in accordance with the so-called Oxo process:

	Percent by weight
2,3,3,4-tetramethyl-1-pentanal	3
2,3,4,4-tetramethyl-1-pentanal	24
3-ethyl-4,4-dimethyl-1-pentanal	6
3-isopropyl-4-methyl-1-pentanal	9
3,4,4-trimethyl-1-hexanal	9
3,4,5-trimethyl-1-hexanal	18
3,5,5-trimethyl-1-hexanal	12
4,4,5-trimethyl-1-hexanal	4
4,5,5-trimethyl-1-hexanal	1
Dimethyl-1-heptanals	14

The Oxo nonyl aldehydes referred to above may be prepared from an n-butylene-isobutylene codimer by treating the same with carbon monoxide and hydrogen under Oxo process conditions, for example, as described in U. S. 2,327,066. The carbonylation reaction is ordinarily carried out at an elevated temperature and pressure in the presence of an iron or cobalt catalyst.

Olefins which may be employed in accordance herewith are those selected from the group consisting of unsaturated hydrocarbons wherein there is a tertiary carbon atom in either the alpha (α) or beta (β) position with respect to a double bond therein. Examples of such olefins are commercial di-isobutylene (comprising 80% of 2,4,4-trimethyl-1-pentene and 20% of 2,4,4-trimethyl-2-pentene), each of the individual di-isobutylene components, 2-methyl-2-butene, 2-methyl-1-butene, 2-ethyl-1-hexene, 3-methyl-2-pentene, 2-methyl-2-pentene, n-butylene-isobutylene codimer, referred to above and hereinafter described in greater detail, as well as 3-methyl-1-butene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, 2-methyl-1-pentene, 3-methyl-1-pentene, 4-methyl-2-pentene, 2,3-dimethyl-1-pentene, 2,4-dimethyl-1-pentene, 3,4-dimethyl-1-pentene, 2,3-dimethyl-2-pentene, 2,4-dimethyl-2-pentene, 3,4-dimethyl-2-pentene, 3,4,4-trimethyl-2-pentene, 2,3,4-trimethyl-1-pentene, 2,3,4-trimethyl-2-pentene, 2-methyl-1-hexene, 3-methyl-1-hexene, 2-methyl-2-hexene, 3-methyl-2-hexene, 4-methyl-2-hexene, 2-methyl-3-hexene, 3-methyl-3-hexene, 2,3-dimethyl-1-hexene, 2,4-dimethyl-1-hexene, 2,3-dimethyl-2-hexene, 2,4-dimethyl-2-hexene, 3,4-dimethyl-2-hexene, etc.

Examples of diolefins which may be employed are of the methyl pentadienes, e. g. 3-methyl-1,3-pentadiene, 2-methyl-1,3-pentadiene, etc., dipentadiene, dicyclopentadiene, 2-methyl-2,4-hexadiene, etc.

The so-called n-butylene-isobutylene codimer is prepared by effecting the copolymerization of n-butylenes and isobutylene at elevated temperature and pressure in the presence of an acidic catalyst such as sulfuric acid, phosphoric acid, or hydrogen fluoride; or a potentially acidic catalyst such as copper pyrophosphate or boron fluoride; or a solid catalyst such as silica-alumina or acid-treated bentonite. For example, at 140–194° F. sulfuric acid absorbs both n-butylenes and isobutylenes and converts them primarily into the codimer. The codimerization may be carried out in an especially convenient manner by passing a gasiform mixture comprising n-butylenes and isobutylene over a solid granular catalyst, comprising phosphoric acid absorbed on clay or other inert supporting material, at 350–500° F. and around 40 atmospheres. When a charge stream containing 30 percent of n-butylenes and 15 percent of isobutylene is processed under these conditions, approximately 67 percent of the olefins are converted into a product consisting of approximately 85 percent dimer and 15 percent trimer. Fractional distillation of the crude product yields a dimer fraction having properties as in the following illustrative example:

PROPERTIES OF n-BUTYLENE-ISOBUTYLENE CODIMER

Mean molecular weight	110–115.
Specific gravity, 60/60° F	0.73–0.74.
Refractive index, n_D^{20}	1.418–1.425.
True boiling range	200–250° F.
Freezing point	Below —76° F.
Flash point (Tag)	32° F. or lower.
Color (Saybolt)	25–35.
Olefin content	Over 98% by wt.
Total isooctene content	Over 86% by wt.

The following table illustrates the composition of a typical codimer resulting from the above method of preparation, and designates the usual range of proportions of the various components:

COMPOSITION OF n-BUTYLENE-ISOBUTYLENE CODIMERS

	Specimen, percent by wt.	Range, percent by wt.
3,4,4-Trimethyl-2-pentene	12	10–17
3,4,4-Trimethyl-1-pentene	2	1–3
3,3-Dimethyl-2-ethyl-1-butene	3	2–5
2,4,4-Trimethyl-2-pentene	2	1–3
2,4,4-Trimethyl-1-pentene	8	6–10
2,3,3-Trimethyl-1-pentene	5	4–7
3,3,4-Trimethyl-1-pentene	4	3–6
2,3,4-Trimethyl-1-pentene	10	8–14
2,3,4-Trimethyl-2-pentene	35	25–40
3-Methyl-2-isopropyl-1-butene	5	4–7
2,2-Dimethylhexenes	4	2–6
2,3-Dimethylhexenes	5	2–6
2,4-Dimethylhexenes	2	1–3
2,5-Dimethylhexenes	2	1–3

It should be understood that the suggestion of various specific aldehydes and unsaturated materials hereinabove is not intended to function expressly or impliedly for the exclusion of others coming within the broad definitions.

The oxidation of the aldehyde is brought about under liquid phase oxidation conditions by contacting with an oxygen-containing gas such as air. The source of oxygen may be pure oxygen or an oxygen-containing gas such as air and it may be introduced to the reaction mixture at atmospheric or at super-atmospheric pressure. It is often desirable to maintain a pressure on the reaction zone with the oxygen-containing gas in order to permit more rapid reaction at somewhat lower temperatures.

The oxidation of the aldehyde in accordance herewith is carried out at temperatures between about 45° and 125° C., preferably from about 60° to 90° C. To assure satisfactory yields of peroxides, the time of reaction should be at least about one hour and preferably at least about three hours but may be considerably longer as indicated in the examples noted in Table 1.

The volume ratio of aldehyde to unsaturated hydrocarbon in the reaction zone may vary from about 1:1 to about 1:5 and preferably from about 1:2 to about 1:4. It has been found that with ratios of aldehyde to unsaturate on the order of 1:1, the inhibiting effect of unsaturate is insufficient to prevent the formation of carboxylic acids and the preparation of such compounds predominates. At ratios of about 1:5 the amount of peroxide relative to carboxylic acid produced is still substantially greater, but with ratios in excess of about 1:4, the amount of peroxide produced begins to fall off and the production of carboxylic acid increases. Thus, in certain examples employing 2-ethyl-hexaldehyde with codimer in ratios of 1:1, 1:3, and 1:5 the production of peroxide varied from 26% to 59% and then back down to 48% by weight, based on aldehyde converted, respectively. At the same time, the production of carboxylic acid went from 67% to about 20% and then up to 32% respectively. The reason for this apparent peak in reaction ratios is not understood completely but it seems probable that the presence of too little unsaturate permits the carboxylic acid to predominate whereas an excess thereof results in dilution of the reaction mixture to such an extent that longer reaction times are required and a consequent decomposition of the hydroperoxide may occur.

In Table 1 there are set forth, for purposes of illus-

tration, the results of testing various aldehydes and olefins in accordance with the present invention. The ratio of olefin to aldehyde was substantially 3:1 in each reaction.

Table 1

Aldehyde	Olefin	Time (Hrs.)	Temp., ° C.	Product Composition [2]	
				Hydroperoxide (percent)	Acid (percent)
2-ethylbutanal	codimer [1]	4.5	60–78	53	15
n-hexanal	diisobutylene.	69.5	45–53	26	16
n-butyral	codimer	62	40–45	41	7
nonanal (oxo)	(none)	6	29–40	<1	87
Do	1-octene	7	55	7	50
Do	codimer	16	60–70	64	29
2-ethylhexanal	do	17	50–60	40	12
Do	do	10	60	59	17–23

[1] n-Butylene-isobutylene codimer prepared as described hereinabove and having essentially the properties defined.
[2] Based upon aldehyde charge.

A most significant feature of the above data is that relating to the oxidation of Oxo aldehydes (nonanal) in the absence of olefin and in the presence of 1-octene and codimer respectively. The advantage of having codimer in the preparation of hydroperoxides is particularly well borne out by such data. Hydroperoxides prepared from ethylbutanal and ethylhexanal were isolated and reduced to 3-pentanol and 3-heptanol respectively having boiling points and indexes of refraction of 113–115.2° C., n_D^{20} 1.4083 and 151°–153° C./745 mm., n_D^{20} 1.4204 respectively. These compare with values for authentic 3-pentanol and 3-heptanol of 113.5–115° C., n_D^{20} 1.4090 and 152.7°–154° C./745 mm., n_D^{20} 1.4201 respectively.

Additional olefins were tested for utility in accordance with the present invention. Since such tests were carried out in what is best described as a screening technique, no effort was made to improve yields, contacting, etc. but, standard conditions and the same aldehyde were employed throughout to determine in an essentially qualitative manner the usefulness of certain olefins. The data set forth in Table 2 were obtained (with the exception noted in the table) by withdrawing one-milliliter samples from reaction mixtures of 2-ethylhexanal and any one of various olefins listed and analyzing simply for relative production of peroxide and acid. The results in milliequivalents/milliliter multiplied by a factor of ten (10) are set forth in Table 2 to show the relative amounts of peroxide and acid produced, and to show the suitability of the olefins tested. In each instance a reaction mixture of 20 ml. of 2-ethylhexanal and 60 ml. of the particular olefin was employed. The temperature of the mixture of reactants was raised to 60° C. before establishment of an oxygen feed rate of about one bubble per second. Agitation was vigorous, and the reaction temperature was allowed to rise no higher than 90° C. Such a temperature rise usually took place when hydroperoxide was formed satisfactorily.

Table 2

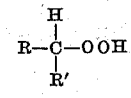
Aldehyde	Olefin	Product Composition	
		Hydroperoxide	Acid
Octadecenal*	codimer	8.6	1.8
2-ethylhexanal	diisobutylene	9.8	13.3
Do	2,4,4-trimethyl-2-pentene	7.8	7.3
Do	2,4,4-trimethyl-1-pentene	9.5	6.9
Do	methylpentadiene	9.4	1.8
Do	dipentene	9.6	3.2
Do	dicyclopentadiene	8.9	5.0
Do	cyclohexene	0.8	1.7

* Reacted at temperature of 50–78° for 3.5 hours.

The peroxides produced in accordance herewith have various uses, for example, as catalytic agents in polymerization processes and in various free radical reactions; as oxidation agents, initiators, or accelerators in various oxidation reactions; and as intermediates in the preparation of alcohols, aldehydes, acids having one carbon atom less than that of the original aldehyde.

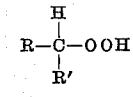
Having thus described our invention, what we claim as novel and desire to protect by Letters Patent is as follows:

1. A method of producing an aliphatic hydroperoxide represented by the structural formula

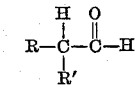


wherein R represents an acyclic hydrocarbon radical containing from 1 to about 24 carbon atoms and R′ represents a constituent selected from the group consisting of hydrogen and acyclic hydrocarbon radicals containing from 1 to about 24 carbon atoms, and wherein the total number of carbon atoms in R and R′ does not exceed about 24, which comprises admixing an aliphatic aldehyde with at least about an equal volume of an unsaturated hydrocarbon selected from the class consisting of those containing a tertiary carbon atom alpha (α) to a double bond and those containing a tertiary carbon atom beta (β) to a double bond, and contacting such admixture of aldehyde and hydrocarbon with an oxygen-containing gas while maintaining said admixture at a temperature between about 45° and about 125° C.

2. The method of producing, simultaneously, aliphatic hydroperoxides represented by the structural formula



wherein R represents an acyclic hydrocarbon radical containing from 1 to about 24 carbon atoms and R′ represents a constituent selected from the group consisting of hydrogen and acyclic hydrocarbon radicals containing from 1 to about 24 carbon atoms, and wherein the total number of carbon atoms in R and R′ does not exceed about 24, and aliphatic carboxylic acids which method comprises admixing an aliphatic aldehyde represented by the structural formula



wherein the substituents R and R′ are as defined above with at least about an equal volume of an unsaturated hydrocarbon selected from the class consisting of those containing a tertiary carbon atom alpha to a double bond and those containing a tertiary carbon atom beta to a double bond, contacting such admixture of aldehyde and hydrocarbon with an oxygen-containing gas while maintaining said admixture at a temperature between about 45° and about 125° C. and recovering aliphatic hydroperoxides and aliphatic carboxylic acids corresponding to the starting aldehyde.

3. The method of claim 2 wherein the aliphatic aldehyde is 2-ethylhexaldehyde.

4. The method of claim 2 wherein the aldehyde is 2-ethylhexaldehyde and the unsaturated hydrocarbon is an n-butylene-isobutylene codimer.

5. The method of claim 2 wherein the aliphatic aldehyde is 2-ethylbutyraldehyde.

6. The method of claim 2 wherein the aldehyde is 2-ethylhexaldehyde and the unsaturated hydrocarbon is di-isobutylene.

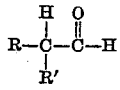
7. The method of claim 2 wherein the aldehyde is 2-ethylbutyraldehyde and the unsaturated hydrocarbon is a n-butylene-isobutylene codimer.

8. The method of claim 2 wherein the aldehyde is

2-ethylbutyraldehyde and the unsaturated hydrocarbon is di-isobutylene.

9. The method of claim 2 wherein the aliphatic aldehyde comprises a mixture of aliphatic aldehydes containing 9 carbon atoms, said mixture of aldehydes being produced by the oxoation of an n-butylene-isobutylene codimer and wherein the unsaturated hydrocarbon is a n-butylene-isobutylene codimer.

10. The method of producing an aliphatic hydroperoxide which comprises admixing an aliphatic aldehyde having the empirical structure



wherein R represents an acyclic hydrocarbon radical containing from 1 to about 24 carbon atoms and R' represents a constituent selected from the group consisting of a hydrogen atom and an acyclic hydrocarbon

radical containing from 1 to about 24 carbon atoms and the total number of carbon atoms in R and R' does not exceed about 24, with an unsaturated hydrocarbon selected from the class consisting of those containing a tertiary carbon atom alpha to a double bond and those containing a tertiary carbon atom beta to a double bond in a volume ratio of from about 1:1 to about 1:5 respectively, contacting such admixture of aldehyde and hydrocarbon with an oxygen-containing gas while maintaining said admixture at a temperature between about 45° and about 125° C. and recovering aliphatic hydroperoxides and aliphatic carboxylic acids corresponding to the starting aldehyde.

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