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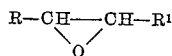
ALDEHYDES AND METHOD OF PREPARATION
Warren D. Niederhauser, Huntsville, Ala., assignor to Rohm & Haas Company, Philadelphia, Pa., a corporation of Delaware
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9 Claims. (Cl. 260-398)

This invention concerns a process for treating 1,2-epoxides to yield aldehydes. This invention also deals with a group of novel and useful β -hydroxyaldehydes and α,β -unsaturated aldehydes.

The process of this invention comprises treating 1,2-epoxides with carbon monoxide and hydrogen gases under pressure and elevated temperatures in the presence of a hydroformylation catalyst. There results useful aldehydes.

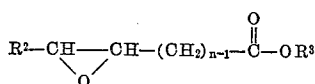
The instant process is applicable to compounds containing one or a plurality of 1,2-epoxide groups. When there are employed as starting materials, polyepoxides, such as alkyl esters of epoxidized water-insoluble fatty acids or epoxidized glyceryl esters, there may be obtained products which are mixtures of poly- β -hydroxyaldehydes and of poly- α,β -unsaturated aldehydes. At the present time, however, it is preferred to use somewhat simpler starting materials which may be classified within the following three groups:

Group A which may be represented by Formula I



where R and R¹ are hydrogen atoms or alkyl groups containing from one to preferably twelve carbon atoms, R and R¹ being alike or different;

Group B which may be represented by Formula II

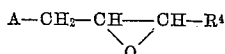


where R² represents an alkyl group containing from one to eleven carbon atoms,

R³ represents an alkyl group containing one to eighteen, preferably one to eight carbon atoms, and

n is an integer from eight to eleven, the total number of carbon atoms of compounds of group B preferably ranging from twenty to thirty, and

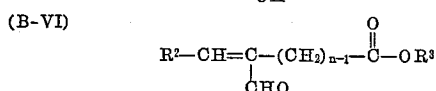
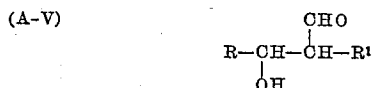
Group C which may be represented by Formula III



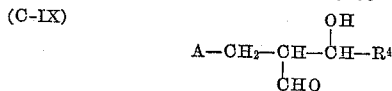
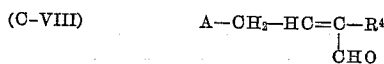
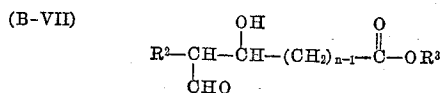
where A is an aryl group, preferably containing from six to eight carbon atoms, such as phenyl, tolyl, and xylyl, and

R⁴ is an alkyl group containing from one to six, preferably one, carbon atoms.

The process of this invention yields valuable compounds, a number of which are new. The products resulting from said groups A, B, and C, respectively, may be represented by the following formulas, in which the alphabetical designation corresponds to that given to the starting epoxides and the even numbers designate the α,β -unsaturated aldehydes, whereas the uneven numbers specify the β -hydroxyaldehyde products,



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in which R, R¹, R², R³, R⁴, A, and n have the definition assigned above. In each case illustrated above, the α,β -unsaturated aldehyde products include the isomers in which the formyl group and the vicinal vinylenic hydrogen atom are on either carbon of the vinylenic unsaturation. Likewise, in the β -hydroxyaldehyde products there are included the isomers in which the hydroxyl and formyl groups are interchangeably bonded onto either of the vicinal carbon atoms onto which originally the epoxy oxygen was bonded. In the appended claims, the term "isomer" is intended to define the position interchangeability of the formyl, hydroxyl, and vinylenic hydrogen on the carbon atom originally supporting the epoxide oxygen.

In accordance with the process of this invention, 1,2-epoxides of the groups A, B, and C are subjected to hydrogen and carbon monoxide gases under pressure and elevated temperature in the presence of a hydroformylation catalyst. The total carbon monoxide and hydrogen gas pressure under which the reaction is carried out should preferably range from 900 to 10,000 p.s.i.; advantageously, it is maintained in the range of 1500 to 3000 p.s.i. The reactive temperatures range from 100° to 200° C., preferably from 120° to 150° C.

To achieve substantially complete reaction, the carbon monoxide and hydrogen gases are employed in a minimum of 1 mole of each gas per epoxide equivalent in the starting material; an excess such as to 1.5 moles per epoxide equivalent of either one or of both gases may be employed if desired. Once this minimum requirement of gas is satisfied, the hydrogen to carbon monoxide ratio is not critical, a one to one ratio being quite suitable. Ratios of hydrogen to carbon monoxide in the range of 3 to 1 and 1 to 3, respectively, may also be employed when desired. The gasses may be fed to the reaction environment singly or mixed. To promote the reaction, the reacting vessel may be agitated. The progress and extent of the conversion of the epoxides to the aldehydes may be followed by the consumption of the carbon monoxide and hydrogen gases, the conversion being substantially complete when no more consumption of the gases is registered. Also, bromine determinations, analysis for oxirane oxygen and hydroxyl number may be used as an aid in determining the extent of formation of β -hydroxyaldehydes and α,β -unsaturated aldehydes.

If desired, the reaction is carried out in the presence of one or more inert organic volatile solvents. Suitable for this purpose are hydrocarbons, such as benzene, ethylbenzene, diethylbenzene, toluene, xylene, cumene, n-hexane, propane, cyclohexane, and the like. Such an optional inert solvent generally facilitates handling of the starting materials and of the products, particularly of the lower molecular weight materials.

In accordance with this invention, the conversion of 1,2-epoxides to aldehydes is carried out in the presence of a hydroformylation catalyst which is a compound of the metals of group VIII of the periodic table having an atomic number from 26 to 28, inclusive, and preferably capable of forming a metal carbonyl under the conditions of the reaction. Such metals include iron, cobalt, and nickel. Cobalt compounds have been found to be espe-

cially suited for the present purpose, particularly oil soluble cobalt salts such as cobalt salts of fatty acids containing two to eighteen, and especially four to eight carbon atoms. Typical are cobalt butyrate, cobalt octanoate, cobalt oleates, and the like. Other useful cobalt compounds include cobalt formate, cobalt acetate, cobalt carbonyl, cobalt anhydride, cobalt carbonate, Raney cobalt, cobalt naphthenate, and the like. Finely divided reduced metallic cobalt may also be suitable in special cases. The catalysts may be employed as such or deposited on granular carriers or in intimate mixtures with metallic, mineral, or ceramic materials like kieselghur, clay, glass powder, and the like. The hydroformylation catalyst is used in an amount in the range of 0.1 to 20 and preferably 0.5 to 2 weight percent, calculated as nickel, cobalt or iron metal based on the starting material.

In accordance with a preferred aspect of this invention, 1 mole of a suitable epoxide and cobalt, as cobalt carbonyl in benzene, in an amount of 1% of carbonyl on the weight of epoxide are charged to a stainless steel autoclave. The autoclave is fed with a mixture of carbon monoxide and hydrogen in a 1 to 1 molar ratio till the pressure reaches 2000 p.s.i.; heating is applied to reach 130° to 140° C. while the autoclave is rocked. When the pressure stops decreasing, the conversion to aldehydes is substantially completed. Pressures and temperatures are allowed to drop and the products are isolated. This may be effectuated by suitable procedures as by fractional distillation under reduced pressure.

The aldehyde products formed are generally mixtures of β -hydroxyaldehydes, α,β -unsaturated hydroxyaldehydes and their respective isomers. By suitable methods the separation of saturated aldehydes from the unsaturated ones may be effectively carried out. If desired, in an optional refinement of the present method, the formation of α,β -unsaturated aldehydes may be further promoted by continuing heating the product resulting for the conversion of the starting epoxides, at atmospheric pressure or higher, preferably in the presence of water and an acidic catalyst, such as formic acid, acetic acid, boric acid, or mineral acid, such as sulfuric acid. On the other hand, if it is desired to favor the yields of saturated β -hydroxyaldehydes, it is preferable in the isolation step, to remove residual catalyst from the products of the conversion of the epoxides. This may be effectuated by converting the cobalt to a water-soluble salt by acid-wash thermal treatment or other suitable means.

Typical of the new β -hydroxyaldehydes prepared in accordance with the present method there may be named:

2-methyl-3-hydroxy-4-phenylbutanal,
2-benzyl-3-hydroxybutanal,
2-ethyl-3-hydroxy-4-phenylbutanal,
2-butyl-3-hydroxy-4-phenylbutanal,
2-hexyl-3-hydroxy-4-phenylbutanal,
2-methyl-3-hydroxy-4-xylylbutanal,
2-(2,4'-dimethylbenzyl)-3-hydroxybutanal,
2-methyl-3-hydroxy-4-tolylbutanal,
2-methyl-4-xylyl-2-butenal,
Methyl 9,(10)-hydroxy-10,(9)-formylstearate,
Ethyl 9,(10)-hydroxy-10,(9)-formylstearate,
Hexyl 9,(10)-hydroxy-10,(9)-formylstearate,
Octyl 9,(10)-hydroxy-10,(9)-formylstearate,
Methyl 13,(14)-hydroxy-14,(13)-formyldocosanoate,
Ethyl 9,(10)-hydroxy-10,(9)-formylhexadecanoate,
Butyl 9,(10)-hydroxy-10,(9)-formyldodecanoate, the respective isomers, and the like.

Typical α,β -unsaturated aldehydes prepared in accordance with this method include:

2-methyl-4-phenyl-2-butenal, and its isomer
2-benzyl-2-butenal,
2-ethyl-4-phenyl-2-butenal,
2-butyl-4-phenyl-2-butenal,
2-hexyl-4-phenyl-2-butenal,
2-methyl-4-xylyl-2-butenal,

2-methyl-4-tolyl-2-butenal,
Methyl 9,(10)-formyloleate,
Ethyl 9,(10)-formyloleate,
Octyl 9,(10)-formyloleate,
Ethyl 15,(16)-formylrucate,
Butyl 9,(10)-formylpalmitoleate, the respective isomers, and the like.

The new β -hydroxyaldehydes of this invention are useful in the preparation of the corresponding α,β -unsaturated aldehydes. Conversion to α,β -unsaturated aldehydes may be effected by heating the aldols at high temperatures, such as above 150° C., at atmospheric pressures or under superatmospheric pressures. Advantageously, this conversion may be carried out in the presence of a catalyst. The β -hydroxyaldehydes of this invention are valuable in preparing glycols by catalytic reduction such as with platinum, nickel, Raney type catalysts, at temperatures above 100° C. and at superatmospheric pressures. Moreover, the oxidation of selected β -hydroxyaldehydes of this invention yields valuable hydroxydicarboxylic acids. The oxidation may be accomplished with a mild oxidizing agent such as alkaline solutions containing silver or copper salts, or hydrogen peroxide. In this manner, methyl 8-hydroxy-9-formylstearate yields the corresponding acid ester. The new α,β -unsaturated aldehydes of this invention are valuable for preparing unsaturated dibasic acids by oxidation. Oxidation, such as with hydrogen peroxide, under mild conditions yields hydroxy-acids. Another use for the α,β -unsaturated aldehydes is as adjuncts in odoriferous compositions. The more pungent α,β -unsaturated aldehydes may be useful in insect repellent preparations, the other aldehydes which have more pleasant fragrance may be used as bases or additives in cosmetic preparations. A typical insect repellent composition may be prepared from:

(A)

30 parts of dimethyl phthalate
5.0 parts of alkylphenoxypolyethoxyethanol of an ethylene oxide of 12, a non-ionic water soluble surface-active agent

(B)

10 parts of mineral oil
55 parts water
0.1 part of a suitable unsaturated aldehyde of this invention

Portion A is heated to 55° C., portion B to 60° C.; then A and B are mixed with vigorous agitation. The α,β -unsaturated aldehyde is added at 55° C., the mixture is then homogenized. Likewise, suntan lotions may be prepared in which anhydrous lanolin and methyl salicylate may be mixed with part A.

One skilled in the art will appreciate that in accordance with the steps and conditions of the instant process, compounds containing 1,2-epoxide are efficiently converted into valuable compounds having formyl and hydroxyl groups bonded onto vicinal carbon atoms, and into compounds where the formyl group is bonded onto a carbon atom which, with another carbon atom, forms a vinylene unsaturation. Under the conditions of this process, only the carbon atoms to which the epoxide groups are bonded are affected, whereas, irrespective of the location and number of epoxide groups in the starting materials, the remaining portions of the molecule are left intact. The following examples are provided as a further illustration of this invention and not by way of limitation. Unless otherwise indicated, all parts are by weight.

Example 1

To a stainless steel autoclave of 300 cc. capacity, there are charged 29 parts of propylene oxide, 40 parts of xylene, and 5 parts of a solution of cobalt carbonyl in benzene containing 3% cobalt. The vessel is closed and it is filled with a mixture of carbon monoxide and hydrogen in a 1 to 1 volume ratio until a pressure of 2100

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p.s.i. is recorded. The vessel is heated to within a temperature range of 130° to 140° C. with rocking for one hour to insure mixing. The pressure drops smoothly during the reaction. When pressure dropped to 960 p.s.i. and no further drop is recorded, the autoclave is cooled to 20° C. The product is removed; it is distilled rapidly and the distillate is separated from the lower water layer. The product is redistilled through a packed column to give 5.5 parts of methacrolein and 9 parts of crotonaldehyde.

Example 2

A hydrogenation bomb is charged with a mixture of 22 parts of ethylene oxide, 40 parts of xylene, and 3.5 parts of a benzene solution of cobalt carbonyl containing 3% cobalt. Pressure is applied to 1500 p.s.i. while heating is maintained within a range of 150° to 180° C. with rocking. When no further drop in pressure is recorded, the bomb is cooled to 25° C. The product is removed and filtered to remove catalyst. Distillation under reduced pressure yields acrolein.

Example 3

A stainless steel autoclave of 300 cc. capacity is charged with 60 parts of 1,2-epoxyoctane, 35 parts of xylene, and 8 parts of cobalt carbonyl in xylene containing 5% cobalt. The closed vessel is filled with a mixture of carbon monoxide and hydrogen gas to a pressure of 2700 p.s.i. The vessel is heated, with rocking, to and at a temperature of 135° C. for one hour. As the pressure stops decreasing, heating is discontinued and the vessel is allowed to cool to room temperature. Residual catalyst is removed from the product. Distillation through a packed column, under reduced pressure, gives α -n-hexylacrolein and β -n-hexylacrolein. The hydroxyl number is nil. The two aldehydes are further separated by fractional distillation under reduced pressure. Following the same procedure, 1,2-epoxyhexane is reacted with carbon monoxide hydrogen in the presence of cobalt carbonyl to yield α -n-butylacrolein and β -n-butylacrolein.

Likewise, the treatment of 1,2-epoxydecane and the treatment of 1,2-epoxydodecane proceeds in a similar manner with comparable results.

Example 4

To a hydrogenation bomb of 300 cc. capacity, there are charged 87 parts of methyl 9,10-epoxystearate, 50 parts of benzene, and 8 parts of cobalt carbonyl in benzene having a 3% cobalt content. Carbon monoxide and hydrogen are fed into the bomb to a pressure of 2600 p.s.i. and heat is applied to and maintained at 120° to 150° C. for one hour, with rocking. Upon a drop of pressure to 1420 p.s.i., and when no further uptake of gas is recorded, the bomb is cooled to room temperature. Catalyst is separated and solvent is distilled from the product. There is obtained 91 parts of an oil, which is a mixture of the isomers of methyl 9,(10)-hydroxy-10,(9)-formylstearate and of methyl 9,(10)-formyloleate. These products are separated by fractional distillation under reduced pressure.

Example 5

The bomb is charged with 87 parts of ethyl 9,10-epoxystearate, 55 parts of benzene and 8 parts of cobalt butyrate in benzene having a 3% cobalt content. The reaction proceeds in the manner described above. The products are ethyl 9,(10)-hydroxy-10,(9)-formylstearate and ethyl 9,(10)-formyloleate.

Example 6

The procedure of Example 4 is again followed and the resulting oily product which is formed is fractionally distilled in the presence of 1 gram of phosphoric acid under reduced pressure. The product obtained is an increased proportion of methyl 9,(10)-formyloleate. Separation is effectuated by fractional distillation under reduced pressure.

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Example 7

Following the procedure of Example 4, octyl-9,10-epoxystearate is treated in the presence of cobalt carbonyl with a mixture of carbon monoxide and hydrogen under pressure to yield octyl-9,(10)-hydroxy-(9)-formylstearate and octyl-9,(10)-formyloleate. The products are separated by fractional distillation under reduced pressure.

Methyl 13,(14)-epoxybehenate is treated in a similar manner to yield methyl 13,(14)-hydroxy-14,(13)-formyldocosanoate and methyl 15,(16)-formylterucate. The products are separated by fractional distillation under a reduced pressure of 1 mm. of mercury.

Example 8

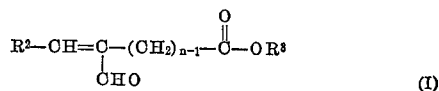
A mixture of 71 parts of 1-phenyl-2,3-epoxybutane, 40 parts of benzene, and 5 parts of a solution of cobalt carbonyl in benzene containing 3% cobalt are placed in a rocking autoclave. The autoclave is filled with hydrogen and carbon monoxide in a 1 to 1 volume ratio to a pressure of 3000 p.s.i. and heated for 1½ hours at 140° to 150° C. When the pressure stops decreasing, heating is discontinued and the bomb is allowed to cool to room temperature. Catalyst is filtered off and the product is distilled over a vacuum steam bath to give 77 parts of a mixture of 2-methyl-3-hydroxyl-4-phenylbutenal, 2-methyl-3-phenyl-2-butenal, and their respective isomers. The products are separated by fractional distillation at pressure reduced to 1 mm. of mercury.

In a similar manner, 1-xylyl-2,3-epoxyhexane is treated yielding 2-methyl-3-hydroxy-4-xylylbutanal, 2-(2,4'-dimethylbenzyl)-3-hydroxybutanal, 2-methyl-4-xylyl-2-butenal, and 2-(2,4'-dimethylbenzyl)-2-butenal.

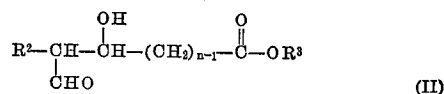
By substituting cobalt carbonyl by an equivalent amount of cobalt butyrate or by cobalt acetate, comparable results are obtained.

I claim:

1. A compound selected from the group consisting of a first compound of the formula

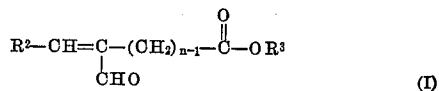


a second compound of the formula



and the isomers of (I) and (II) respectively, in which R^2 represents an alkyl group containing from one to eight carbon atoms, R^3 represents an alkyl group containing from one to eight carbon atoms, and n represents an integer from eight to eleven, the total number of carbon atoms in Compounds I and II ranging from twenty to thirty.

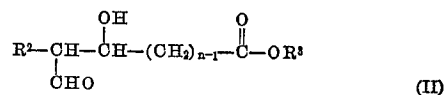
2. A compound having the formula



and its isomer, in which R^2 represents an alkyl group containing from one to eight carbon atoms, R^3 represents an alkyl group containing from one to eight carbon atoms, and n represents an integer from 8 to 11, the total number of carbon atoms of the compound ranging from twenty to thirty.

3. Methyl 9,(10)-formyloleate.

4. A compound having the formula



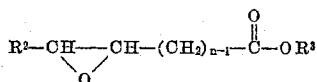
and its isomer, in which R^2 represents an alkyl group containing from one to eight carbon atoms, R^3 represents an

alkyl group containing from one to eight carbon atoms, and n represents an integer from 8 to 11, the total number of carbon atoms of the compound ranging from twenty to thirty.

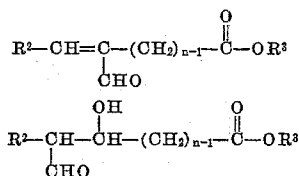
5. Methyl 9,(10)-hydroxy-10(9)-formylstearate.

6. A process which comprises reacting 1,2-epoxides with a mixture of carbon monoxide and hydrogen gases, under superatmospheric pressure in the range of 900 to 10,000 p.s.i., at a temperature ranging from 100° to 200° C. and in the presence of a cobalt hydroformylation catalyst until substantial conversion of said 1,2-epoxides to ester aldehydes, said carbon monoxide and hydrogen gases being employed in a minimum amount of 1 mole of each gas per epoxide equivalent in the starting 1,2-epoxide.

7. A process which comprises reacting a 1,2-epoxide of the formula



with a mixture of carbon monoxide and hydrogen gases in a minimum amount of 1 mole of each gas, under a superatmospheric pressure ranging from 900 to 10,000 p.s.i., at a temperature ranging from 100° to 200° C. and in the presence of cobalt carbonyl, until substantial conversion of said 1,2-epoxide to aldehydes of the formulas



and their respective isomers, in which the above formulas R^2 represents an alkyl group containing from one to eight carbon atoms, R^3 represents an alkyl group containing from one to eight carbon atoms, and n represents an integer from 8 to 11, the total number of carbon atoms in said compounds ranging from twenty to thirty.

8. A process for preparing methyl 9,(10)-hydroxy-10(9)-formylstearate which comprises reacting methyl 9,(10)-epoxystearate with a mixture of at least one mole of carbon monoxide gas and at least one mole of hydrogen gas under superatmospheric pressure, within a temperature range from 100° to 200° C., and in the presence of cobalt carbonyl, and isolating methyl 9,(10)-hydroxy-10(9)-formylstearate.

9. A process for preparing methyl 9,(10)-formyloleate which comprises reacting methyl 9,(10)-epoxystearate with a mixture of at least one mole of carbon monoxide gas and at least one mole of hydrogen gas under superatmospheric pressure, within a temperature range from 100° to 200° C., and in the presence of cobalt carbonyl, and isolating methyl 9,(10)-formyloleate.

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