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ADDITION OF ORGANIC ACIDS TO THE DOUBLE BOND OF UNSATURATED FATTY COMPOUNDS

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A non-exclusive, irrevocable, royalty-free license in the invention herein described, for all governmental purposes, throughout the world, with the power to grant sub-licenses for such purposes, is hereby granted to the Government of the United States of America.

This application is a continuation-in-part of our co-pending application of the same title, Serial No. 299,322, filed July 16, 1952.

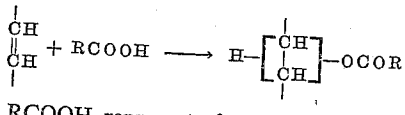
This invention relates to the addition of organic acids to the double bonds of unsaturated fatty compounds, and to the esters thus formed. By fatty compounds we main natural and synthetic glycerides, the fatty acids obtained by the hydrolysis of such glycerides, esters of such fatty acids, and fatty alcohols obtained by the hydrogenation of glycerides.

An object of this invention is to provide processes for reacting aliphatic monocarboxylic acids having no more than two carbon atoms, specifically, formic and acetic acids, with unsaturated fatty compounds to saturate the double bonds of the fatty compounds and form the corresponding acyloxy derivative.

Another object is to provide processes for converting unsaturated fatty compounds into hydroxy fatty compounds.

Another object is to provide novel acyloxy and hydroxy derivatives of fatty compounds. Other objects will appear hereinafter.

In accordance with our invention the double bonds in unsaturated fatty compounds react with formic or acetic acid whereby the acid adds to the double bond thus:



wherein RCOOH represents formic or acetic acid. By use of the ambiguous formula for the product we mean that the mode of addition is unknown; for instance, we are uncertain as to whether addition of formic acid to oleic acid yields 9- or 10-formoxystearic acid. Probably the products are in general a mixture of the possible isomers.

The formoxy and acetoxy fatty derivatives produced by the reaction shown above are useful as plasticizers, lubricants, hydraulic fluids and chemical intermediates. They may be hydrolyzed as shown hereinafter to produce the corresponding hydroxy fatty compounds which are useful for the same general purposes. They appear of special interest as components of alkyd resins, surface-active agents, synthetic lubricants, and greases.

Conventional processes for adding organic acids to olefins, widely used in processing olefinic hydrocarbons, are not practically applicable to unsaturated fatty materials for various reasons: (1) large amounts of the fatty material are often converted to polymeric material of little or no value; (2) the conversion in a single step is usually low and recovery and recycling of non-volatile

fatty material is difficult and expensive; and (3) a variety of products is produced because the polyfunctionality of the fatty compound permits many competing side reactions to take place, especially when drastic conditions and long reaction times are used.

We have discovered that unsaturated fatty compounds react with formic or acetic acid readily at normal pressure and with little or no heating to produce quickly and in high yield the corresponding acyloxy compound. This product is easily separated and purified and the unconverted fatty material is easily recovered and recycled. Thus, overall conversion to the desired product is high while formation of polymers and other undesirable by-products is minimized. While this reaction can be carried out without catalyst, particularly if formic acid is used as a reagent, the presence of strong mineral acid catalyzes the reaction. While any strong mineral acid will produce some catalytic effect, we have discovered that under substantially anhydrous conditions, that is, where the formic or acetic acid used contains not more than about 5% of water, perchloric acid is by far the best catalyst because it enormously accelerates the desired reaction and at the same time minimizes polymerization, migration of the double bonds and other side reactions.

The acyloxy fatty compounds can be saponified to produce the corresponding hydroxy compound. When this is to be done, it is sometimes advantageous to conduct the addition reaction and the saponification reaction consecutively without intermediate isolation of the acyloxy compound.

In our process formic or acetic acid is used both as a reagent and as a solvent for the reactants. The amount used may be varied widely but usually is in the range 0.5 to 2.0 ml. per gram of olefinic compound. The catalyst, if any, is dissolved in the formic or acetic acid. The amount used is usually in the range 0.5 to 2.0% of the weight of olefinic compound to be treated.

Formic acid is so reactive in our process that the reaction can be carried out without any catalyst. Thus, the reaction of formic acid with oleic acid to produce formoxystearic acid can be carried out by refluxing the reagents without catalyst for 24 hours, or by refluxing 8 hours with sulfuric acid as catalyst, or by refluxing for 5 to 30 minutes with perchloric acid as the catalyst. These data also show the advantage of perchloric acid over sulfuric acid or no catalyst.

The practice of our invention is more specifically illustrated by the following examples.

Example I

One hundred grams of oleic acid (iodine number, 88), 200 ml. of substantially anhydrous formic acid and 1 ml. or 70% perchloric acid were refluxed for 5 minutes. The mixture was then poured into cold water and the upper, oily layer was separated by ether extraction. After evaporation of the ether, 112 g. of material remained which consisted of 80% formoxystearic acid and 20% of unsaturated acid. Saponification with aqueous sodium hydroxide followed by acidification with mineral acid yielded 106 g. of crude hydroxystearic acid having M. P., 72.8–74.0° C.; iodine No. 15.5; acid No., 186.3 and hydroxy oxygen 4.2%.

Crystallization of the crude product from petroleum naphtha achieved substantially complete purification, the unconverted olefinic acid remaining dissolved in the mother liquor. The thus purified hydroxystearic acid and M.P., 73–74°, iodine No. 2; acid No. 187 and hydroxy oxygen 5.2%. Theoretical values are iodine No. 0; acid No. 187; and hydroxyl oxygen 5.3%. The yield of monohydroxystearic acid, based on oleic acid consumed, was about 90%.

Example II

When acetic acid was used instead of the formic acid in Example I and the mixture was refluxed for 15 minutes instead of 5 minutes, the conversion of olefinic acid to hydroxy acid was 40%.

Example III

When elaidic acid was used instead of the oleic acid in Example I, the product was substantially identical in chemical composition and amount with that obtained in Example I.

Example IV

When the perchloric acid catalyst used in Example I was replaced with 5 ml. of 86% sulfuric acid and the mixture was refluxed 8 hours instead of 5 minutes, the conversion of oleic acid to hydroxystearic acid was 65%, as compared to 80% obtained in Example I.

Example V

When the amount of perchloric acid used was reduced from 1 ml. as in Example I, to 0.5 ml. and 30 minutes refluxing was employed, substantially identical results as those obtained in Example I were obtained.

Example VI

When no catalyst was used in an experiment otherwise similar to Example I and the mixture was refluxed for 24 hours, substantially identical results as those obtained in Example I were obtained.

Example VII

When the amount of formic acid used in Example I was cut in half, the conversion remained substantially constant at 80%.

Example VIII

When the amount of perchloric acid used in Example I was doubled there was no significant change in the results obtained.

Example IX

When methyl oleate was used instead of the oleic acid in Example I, a substantially equal degree of addition of formic acid to the double bond was obtained.

The crude methyl formoxystearate produced had saponification No. 294; iodine No. 12.7. It was a clera, oily liquid useful as a plasticizer.

Example X

When oleyl alcohol was used instead of the oleic acid in Example I and the mixture was refluxed one hour instead of 5 minutes, the formic acid not only added to the double bond but also esterified the hydroxyl group, thus yielding formoxyoctadecyl formate.

The crude product (iodine No. 23; saponification No. 287) was saponified by boiling with an excess of 0.2 N alcoholic potassium hydroxide. Evaporation of the alcohol followed by addition of hot water yielded a yellow oil which solidified on cooling to room temperature.

After recrystallization from petroleum ether the product, hydroxystearyl alcohol, melted at 62.5–63.5° C. and contained 10.6% hydroxy oxygen. Unconverted oleyl alcohol was recovered from the filtrate. The yield of the glycol, hydroxystearyl alcohol, on the basis of oleyl alcohol consumed, was 90%.

A reaction time as long as one hour was found desirable in this reaction because of the relatively low solubility of oleyl alcohol in formic acid.

Example XI

One hundred grams of linoleic acid (iodine No. 160; composition, 95% linoleic and 5% oleic acid), 200 ml. of substantially anhydrous formic acid and 1 ml. of 70% perchloric acid were mixed and refluxed for 15 minutes. The mixture was then poured into a large volume of cold water and the upper, oily layer was taken up in ether.

From the washed, ether solution 118 g. of an amber oil, iodine No. 64, and saponification No. 326, was obtained. A similar experiment in which the reaction time was one hour yielded a substantially identical product.

Saponification of the oil with aqueous sodium hydroxide, followed by acidification, yielded 108 g. of mixed hydroxy acids having iodine No. 65; saponification No. 175; acid No. 174; hydroxy oxygen, 5.3%.

The mixed acids were converted to the methyl esters and the latter were fractionally distilled to yield approximately equal amounts of the methyl esters of hydroxy octadecenoic and dihydroxystearic acids. Methyl hydroxydecenoate (an isomer of methyl ricinoleate) was a liquid having iodine No. 63, and hydroxy oxygen, 5.5%. Methyl dihydroxystearate had M. P. 40–43° C.; iodine No. 8.7; and hydroxy oxygen, 9.2%.

Example XII

Thirty-eight grams of the unconverted olefinic acid, isolated in Example I from the petroleum naphtha mother liquor, 76 ml. of substantially anhydrous formic acid and 0.38 ml. of 70% perchloric acid were refluxed for fifteen minutes. The formoxystearic acid obtained (41 grams) had the following characteristics: iodine number 17; acid number 166; saponification number, 279. Saponification and acidification as described in Example I yielded 39 g. of crude monohydroxystearic acid from which the purified product, M. P. 72–3° was obtained by crystallization from petroleum naphtha.

Example XIII

Ten grams of soybean oil (iodine number, 135.4; saponification number, 191) 20 ml. of substantially anhydrous formic acid, 5 ml. of butyl acetate and 0.1 ml. of 70% perchloric acid were refluxed for one hour after the reaction mixture became homogeneous (about two hours were required for homogeneity to be attained). The reaction mixture was diluted with water and the reaction product was dissolved in ether. The ether solution was washed with water to remove residual formic acid, and the ether was evaporated. Approximately 10 grams of formylated soybean oil was obtained; iodine number, 60, and saponification number, 302.

Similar results were obtained when a fifteen minute reaction time was employed after the mixture became homogeneous.

The process of our invention is applicable to other glycerides, as for instance, cottonseed oil, peanut oil, lard oil and olive oil; to other fatty acids, such as linclenic, undecylenic and petroselinic acids; to esters of such acids, as for instance the methyl, ethyl and glyceryl esters; and, in general, to any unsaturated fatty compound.

While it is convenient to carry out our process at reflux temperature, it can also be operated at other temperatures between about 70° C. and the boiling point of the reaction mixture. When lower temperatures are used the reaction time must be correspondingly increased to achieve the same degree of conversion.

The highest conversion that we have been able to achieve consistently in a single treatment of the fatty compound is about 80%. However, as shown in Example XII, we are able to recover and recycle most of the unconverted material and thus achieve an overall conversion approaching 100%.

In general, no solvents other than the organic acid being added to the double bond are required. In the case of glycerides, however, their solubility in formic acid is so low, relatively speaking, that in the interests of efficient and rapid reaction we use a small quantity of a mutual solvent for both formic acid and the glyceride. Solvents which are convenient are butyl acetate, amyl acetate and dioxane. Other solvents will suggest themselves to those skilled in the art; the criteria for a useful solvent are that it have sufficient solubility for both formic acid and the glyceride at reaction temperature, and that it not undergo undesirable reactions which will interfere

with the desired one or impede the isolation of the product.

We claim:

1. The process comprising treating an olefinic fatty compound with a substantially anhydrous aliphatic monocarboxylic acid having not more than two carbon atoms in the presence of a catalytic amount of perchloric acid and at a temperature in the range from about 70° C. to the boiling point of the reaction mixture.

2. The process of claim 1 wherein said monocarboxylic acid is formic acid.

3. The process of claim 1 wherein the said monocarboxylic acid is acetic acid.

4. The process of claim 1 wherein the fatty compound is a fatty acid.

5. The process of claim 1 wherein the fatty compound is oleic acid.

6. The process of claim 1 wherein the fatty compound is linoleic acid.

7. The process of claim 1 wherein the fatty compound is a glyceride.

8. The process of claim 1 wherein the fatty compound is soybean oil.

9. The process of claim 1 wherein the fatty compound is a fatty alcohol.

10. The process of claim 1 wherein the fatty compound is oleyl alcohol.

11. The process of claim 1 wherein the fatty compound is methyl oleate.

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