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PREPARING GLYCIDYL ESTERS OF HIGHER FATTY ACIDS

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The present invention relates to a novel method of preparing glycidyl esters of fatty acids containing about ten or more carbon atoms. In general, the method comprises reacting such an acid with epichlorohydrin, using an excess of the latter as the solvent medium. More specifically the reaction is carried out in the presence of an alkali metal salt and a quaternary ammonium halide catalyst.

There is a growing commercial interest in these glycidyl esters of long chain fatty acids and derivatives therefrom. For instance, acetoglycerides prepared from these glycidyl esters by reaction with acetic acid have found utility as components of protective food coatings. However, a method of making the glycidyl esters which is suitable for commercial development has not been available.

In the past, for example, it was found that these glycidyl esters could be prepared by the direct reaction of epichlorohydrin with an alkali metal salt of the fatty acid. However, this reaction must be carried out under strictly anhydrous conditions. It is both tedious and commercially impractical to remove all traces of moisture from the alkali metal salt of a higher fatty acid. Furthermore, if this is not accomplished the yields of the glycidyl esters are greatly lowered and those of the such high-boiling by-products as the diacylglyceryl glycidyl and triacyldiglyceryl glycidyl ethers are proportionately increased.

It is, therefore, a principal object of this invention to provide an improved procedure for the preparation of glycidyl esters of fatty acids containing ten or more carbon atoms. Such a method not only should produce better product yields but in operation should be inexpensive and easily controlled. More specific objects and advantages will be apparent from the accompanying description.

In the instant invention this has been accomplished by an improved method of preparing the glycidyl esters wherein the technically difficult operation of isolating the alkali metal salts of the fatty acids has been eliminated. In general, this unexpectedly successful result is accomplished in a novel direct reaction of the fatty acid with epichlorohydrin in the presence of an alkali metal salt such as a carbonate and a quaternary ammonium halide catalyst.

Normally, it would be expected that the product of the direct reaction of epichlorohydrin and a fatty acid would be a halogenated monoglyceride such as the 3-chloro-1-monoglyceride. Surprisingly, in the process of the present invention this does not occur.

In the process of the present invention, epichlorohydrin also serves as the solvent medium. It is used in substantial excess over the amount required stoichiometrically. From nine to thirteen moles of epichlorohydrin per mole of fatty acid are usually employed, this large excess being necessary as a solvent in the early stages of the reaction.

The present process is not particularly limited as to the fatty acid employed. Any fatty acid of above about 10-12 carbon atoms may be treated. Shorter chain acids are generally too reactive. In general, there is no upper limit on the number of carbon atoms in the chain. How-

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ever, the most useful product range includes those acids which contain from 12 to about 26 carbon atoms. Typical fatty acids employed in the process are lauric, myristic, palmitic, oleic, stearic, 12-hydroxystearic, linoleic, linolenic, arachidic, behenic and cerotic acids. Commercially available fatty acid mixtures also may be treated.

A feature of the invention is the use as a catalyst of about 0.0025 to about 0.01 mole of a quaternary ammonium halide per mole of fatty acid. More can be used but the added cost is not warranted. Equivalent quaternary salts prepared from any amine may be substituted but their added cost is not warranted by better results. Typical quaternary ammonium halides which may be employed for the reaction include tetramethylammonium chloride, tetramethylammonium iodide, tetraethylammonium bromide, tetraethylammonium iodide, tetrapropylammonium chloride, tetraisobutylammonium iodide, benzyltrimethylammonium chloride, benzyltrimethylammonium bromide and benzyltriethylammonium iodide and the like.

Temperature, in the process of the present invention, is important to the extent that the fatty acid being treated should be maintained in the liquid state. However, excessive temperatures should be avoided. In general, the temperature range will be from 80 to about 140° C., with a range of about 100-120° C. constituting good practice.

When combined at reactive temperature, the fatty acid and epichlorohydrin produce an acidic mass. Reaction to produce the desired glycidyl esters results from providing the catalyst. However, if this reaction is allowed to continue several factors cause an increase in hydrogen ion concentration. Unless this is controlled, the desired high yields of glycidyl esters are not obtained. Rather, products such as the above noted halogenated monoglycerides will be favored.

Accordingly, in the process of this invention, a material which will not interfere with the other reactants is required to serve as a neutralizer or acceptor for hydrogen ions. For this purpose an alkali metal carbonate such as Na_2CO_3 or K_2CO_3 and the like, is best suited. Organic amines in general tend to interfere with the reaction. Materials which are appreciably more acidic or more basic than the alkali-metal carbonates are less satisfactory. A sufficient amount of hydrogen ion acceptor must be provided to control the hydrogen ion concentration. An excess does neither harm nor good. Accordingly about one to one and one half moles of alkali-metal carbonate, or its equivalent, is used for each mole of fatty acid treated.

It must be emphasized that the use of both the quaternary ammonium halide and the alkali-metal carbonate, or their above-noted equivalents, is necessary. If both are not present, the physical operation of the process is impaired and the product yield is reduced.

In carrying out the reaction, the mode of adding the reactants is not necessarily critical. In general, at a temperature at which the fatty acid is in liquid condition, the fatty acid, hydrogen ion acceptor and catalyst are usually combined and stirred for sufficient time to insure good mixing, and the epichlorohydrin added thereto. At the conclusion of the reaction, any unreacted neutralizer and/or precipitated products, such as alkali metal halides and bicarbonate are removed, as by filtration. Clarified liquor is washer to remove any remaining water-soluble material and the quaternary ammonium halide catalyst. The excess epichlorohydrin is then removed, as by distillation. The residual crude glycidyl ester is obtained in high yield and may be used as such or improved in grade by any of several known methods.

The invention is further illustrated, but not limited, by the following examples:

Example I

One gram (0.005 mole) of tetramethylammonium chloride and 152 g. (1.10 moles) of potassium carbonate were added to 284 g. (1.00 mole) of stearic acid maintained at 105° C. After stirring for a period of 7-8 minutes, 1162 g. (12.50 moles) of epichlorohydrin which had been preheated to 110° C. were added. The mixture was stirred and held at 108-110° C. for two hours, then cooled to 45-47° C. and filtered. The filtrate was washed three times with water, and the unreacted epichlorohydrin was removed by distillation under reduced pressure. The residue, crude glycidyl stearate, melted at 48-50° C., and had an oxirane oxygen content of 3.66% which is 78% of the theoretical value of 4.70%.

The crude glycidyl stearate was acetylated by reaction with glacial acetic acid at 90° C. for one hour. After removal of the excess acetic acid by distillation under reduced pressure and water-washing to neutrality, the 3-aceto-1-stearin derivative was obtained which melted at 42-43° C. and analyzed as follows: acid number 0.7 (theory 0.0); saponification value 274 (theory 280); and hydroxyl value 138 (theory 140).

Example II

Two grams (0.01 mole) of tetramethylammonium iodide and 116.5 g. (1.10 moles) of sodium carbonate were added to 312.5 g. (1.00 mole) of arachidic acid maintained at 105° C. After stirring for a period of ten minutes, 1162 g. (12.50 moles) of epichlorohydrin which had been preheated to 110° C. were added. The mixture was stirred and held at 110-112° C. for one hour and forty minutes, then cooled to 50° C. and filtered. The filtrate was washed three times with water, and the unreacted epichlorohydrin was removed by distillation under reduced pressure. The residue, crude glycidyl arachidate, melted at 56-57° C., and had an oxirane oxygen content of 3.67% which is 85% of the theoretical value of 4.35%.

The crude glycidyl arachidate was acetylated by reaction with glacial acetic acid at 90° C. for one hour. After removal of the excess acetic acid and water-washing to neutrality, the 3-aceto-1-arachidin derivative was obtained which melted at 48-50° C. and analyzed as follows: acid number 0.3 (theory 0.0); saponification value 251 (theory 262); and hydroxyl value 124 (theory 131).

Example III

A mixture consisting of 289 g. of hydrogenated tall oil fatty acid, 116.5 g. of sodium carbonate and 2 g. of tetramethylammonium iodide was heated to about 110° C. After stirring for a period of about 10 minutes, 930 g. of epichlorohydrin which had been preheated to 112° C. were added. The mixture was stirred and maintained at about 110° C. for 1.5 hours, then cooled to 40° C. and filtered. The filtrate was washed with water, and the excess epichlorohydrin was distilled off under reduced pressure. The crude glycidyl ester was obtained in quantitative yield, M.P. 50-52° C. By analysis 3.94% oxirane oxygen was found which is 85% of the theoretical value of 4.64%. The crude ester was acetylated by reaction with glacial acetic acid at 90° C. for a period of one hour. After removing the excess acetic acid by distillation under reduced pressure and water-washing until neutral, the white waxy product melted at 44-46° C. and analyzed as follows: acid number 0.3 (theory 0.0); saponification value 277 (theory 278); and hydroxyl value 138 (theory 138).

We claim:

1. A method according to claim 4 in which the reaction is carried out at a temperature within the range of from about 80° C. to about 140° C.

2. A method according to claim 4 in which said fatty acid contains from about 12 to about 26 carbon atoms.

3. A method according to claim 4 in which said fatty acid is stearic acid.

4. A method of preparing a glycidyl ester of long chain fatty acids which comprises: forming a mixture comprising a molten fatty acid containing at least ten carbon atoms, an alkali-metal carbonate, and a quaternary ammonium halide catalyst in about the mol ratios of 1.0:1.0-1.5:0.0025-0.01, respectively; adding thereto from about 9 to about 13 moles of epichlorohydrin per mol of fatty acid; maintaining resultant mixture at a temperature above the melting point of the fatty acid until reaction substantially ceases, whereby said ester is formed, and recovering product glycidyl ester of said fatty acid from resultant solution.

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