Title: NOVEL METHODS FOR THE PREPARATION OF GLYCEROL CARBONATE ESTERS

Abstract

Processes for the preparation of glycerol carbonate esters of general formula (I) wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms are disclosed. These esters are prepared by reacting glycerol esters of carboxylic acids with a carbonate source in the presence of a catalyst.
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NOVEL METHODS FOR THE PREPARATION OF GLYCEROL CARBONATE ESTERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to novel methods for the preparation of glycerol carbonate esters having the formula

wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms.

2. Description of the Related Art

Glycerol carbonate esters are known. See for example U.S. Patent 3,225,063. Glycerol carbonate esters have been prepared by several different methods. A common way to prepare the esters is to allow glycerol carbonate to react with an electrophile such as an acyl chloride. Please see Oehlenschläger, J.; Gerchken, G. *Lipids* 1978, 13, 557-562.
Cyclic anhydrides of dicarboxylic acids have also been reacted with glycerol carbonate to afford the corresponding half ester as described by D'Alelio, G.F. U.S. Patent 3,225,063, 1965. The glycerol carbonate ester of methacrylic acid has been prepared by treating the corresponding glycidyl ester with carbon dioxide as disclosed in Brindöpke, G. U.S. Patent 4,835,289, 1989 and also by a transesterification reaction between glycerol carbonate and methyl methacrylate Fang, J.C.; Hill, S. U.S. patent 2,967,173, 1961. All of the above methods are viable routes to the desired esters, but they are not economically attractive because they require expensive starting materials such as glycerol carbonate or a glycidyl ester or they employ harmful reagents such as carboxylic acid chlorides.

To achieve a desirable synthesis, the ester should be produced economically. Economy in the production of the ester is reflected in both the cost of the starting materials and the length of reaction time and number of steps required to produce the compound.

It would therefore be desirable to provide methods of preparing glycerol carbonate ester compounds employing relatively inexpensive starting materials with as few reaction steps as possible, thus lowering the overall cost of the product. Accordingly, it is a primary object of this invention to produce a commercially important glycerol carbonate ester with improved economy.

**BRIEF SUMMARY OF THE INVENTION**

This invention relates to novel methods for the preparation of glycerol carbonate esters and to their use in reducing the viscosity of surfactants. More particularly, this invention is directed to the preparation of glycerol carbonate esters from starting materials such as feedstocks fats. The compounds of the present invention have the general formula
wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms.

R as used hereinafter has the same meaning as defined. As examples of alkyl, there may be mentioned methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, and the like. Examples of alkenyl are propenyl, butenyl, hexadecenyl, octadecenyl and the like.

Methods of preparing glycerol carbonate ester compounds in accordance with embodiments of the present invention comprise reacting glycerol esters of carboxylic acids, for example triglyceride compounds with a carbonate source such as di-lower alkyl carbonate or diphenyl carbonate in the presence of a catalyst, for example, strong bases such as alkali metal alkoxides to form the corresponding glycerol carbonate ester of the general formula I and two moles of methyl esters. The reaction may be represented by the scheme below.

wherein R is as defined above. It will be understood by those of ordinary skill in the art that in some instances,
R will be a single alkyl or alkenyl group having from 1 to about 22 carbon atoms. In other cases, R will be a combination of alkyl or alkenyl groups having from 1 to about 22 carbon atoms. For example, one of the R groups could be $\text{C}_{13}\text{H}_{27}$, another could be $\text{C}_{17}\text{H}_{33}$ while another could be $\text{C}_{11}\text{H}_{23}$. In another glycerol ester, two of the R groups could be $\text{C}_{17}\text{H}_{33}$ while the other could be $\text{C}_{15}\text{H}_{31}$. In cases where the starting glycerol ester is a naturally occurring fat or oil wherein there is usually a distribution of R groups, the glycerol carbonate produced in the process according to the invention will have the same distribution of R groups as the starting glycerol ester. For example, coconut oil is a glycerol triester which typically contains about about 45% lauric acid ($R = \text{C}_{12}\text{H}_{23}$), about 18% myristic acid ($R = \text{C}_{14}\text{H}_{27}$), and about 11% palmitic acid ($R = \text{C}_{16}\text{H}_{31}$). The glycerol carbonate produced in the process according to the invention will contain the same distribution of R groups in the ester product.

In a certain preferred embodiment of the present invention, glycerol esters of carboxylic acids comprise triglycerides and, preferably, naturally occurring triglycerides such as coconut oil, linseed oil, cottonseed oil, palm oil, soybean oil, high-oleic sunflower oil and the like. Preferred triglycerides also comprise glycerol tricaprylate and trilaurate. However, in principle, any natural oil or fat can be used. These naturally occurring oils provide inexpensive routes to preparing the glycerol carbonate ester of general formula I. Preferably, the oil used should have an acid value of up to about 0.1 mg KOH/g. Additionally, di-lower alkyl carbonate may comprise dimethyl carbonate, diethyl carbonate, dipropyl carbonate and the like. Di-lower alkyl carbonate serves as an inexpensive and relatively non-toxic source of carbonate. Diphenyl carbonate may also be advantageously employed. The molar ratio of alkyl carbonate to triglyceride can be from 1/1 to 3/1. The preferred ratio is from 1/1 to 1.5/1.
Isolation of the desired glycerol carbonate ester from the crude reaction mixture may be accomplished in a number of ways. For example, a solvent such as diethyl ether, may be added to the crude product mixture followed by aqueous washings, then drying, filtering and concentrating the product. The methyl esters may then be removed by a wiped film evaporation method leaving the glycerol carbonate esters. A preferable method of isolating the glycerol carbonate ester comprises performing aqueous washings of the crude product mixture within the reactor vessel and without using diethyl ether solvent. The crude product can then proceed directly to wiped film evaporation of the methyl esters. It is accordingly a principal object of the present invention to provide novel methods of preparing glycerol carbonate ester compounds.

These and other objects, features and advantages of the present invention may be more clearly understood by considering the following description of specific embodiments.

DESCRIPTION OF SPECIFIC EMBODIMENTS

Examples of R in Formula I are alkyl or alkenyl having from 1 to about 22 carbon atoms. Alkyl may be straight chain, branched or cyclic. As examples of alkyl, there may be mentioned methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, and the like. Preferred examples of alkyl are those corresponding to the naturally occurring triglycerides previously mentioned as starting materials.

The glycerol carbonate esters may be synthesized using a novel one step ester interchange reaction. In a certain preferred embodiment, triglycerides comprising natural oils are reacted with dimethyl carbonate in the presence of a catalyst, e.g. an alkali metal alkoxide, such as sodium methoxide, to produce the desired glycerol carbonate ester along with two moles of methyl ester. This reaction may be represented by the following scheme below.
wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms and preferably R corresponds to alkyl and alkenyl groups in triglycerides comprising natural oils.

Natural oils comprise coconut oil, linseed oil, cottonseed oil, palm oil, soybean oil, high-oleic sunflower oil and the like and preferably, the triglyceride compound has an acid value of up to about 0.1 mg KOH/g. For example, the exchange reaction precedes quite well when food-grade coconut oil (acid value <0.1 mg KOH/g) is used, however when crude coconut oil (acid value = 10.8 mg KOH/g) is used, virtually no reaction is observed. This is thought to be due to the presence of carboxylic acids which react with bases present thus inactivating the catalyst. Also, it is presumed that the carboxylic acid salts will react with any cyclic carbonate formed to afford diglycerides.

The catalyst typically is a strong base comprising preferably alkali metal alkoxides, e.g. sodium methoxide, sodium ethoxide, potassium tert-butoxide, and the like, with sodium methoxide being the preferred catalyst. However, other catalysts such as amidines and cyclic amidines, Na₂CO₃, NaHCO₃, K₂CO₃ and zinc hydrotalcite of the formula Zn₆Al₂(OH)₁₆(CO₃)₄H₂O may also be employed. The reaction may proceed at room temperature, however it is preferably carried out in the temperature range from about 100°C to about 150°C with a more preferable temperature of about 110°C to 140°C. Reaction pressure is the autogenous pressure developed by the reaction mixture in a closed
reactor which may range from about 5 psi to about 100 psi above atmospheric temperature with typical values ranging from about 10 psi to about 50 psi. The reaction may be carried out under an atmosphere of nitrogen, with mechanical stirring until a desired quantity of triglyceride is converted to the desired glycerol carbonate ester. Typical reaction times approach about 4 to about 24 hours, depending upon the nature of the reactants. Longer reaction times lead to greater triglyceride conversion, however, they also lead to decreased yield of glycerol carbonate ester.

The desired product can then be isolated by adding diethyl ether to the crude reaction mixture, followed by aqueous washings, then drying, with MgSO₄ filtering and concentrating the product by known techniques such as rotary evaporation. The methyl esters can then be recovered by a wiped film evaporation method. An alternate preferable method of isolating the product comprises performing the aqueous washings within the reactor vessel and without diethyl ether solvent. The crude product can then proceed directly to wiped film evaporation of the methyl esters.

The selected esters of the present invention are useful to lower the viscosity of concentrated aqueous solutions of certain surfactants, such as sulfated ethoxylated fatty alcohols of the general formula C₁₂₋₁₄H₂₅₋₂₉O(CH₂CH₂O)₁₋₃OSO₃⁻Na⁺. In a commercial embodiment, the composition comprises an effective viscosity reducing amount of the selected esters and the surfactants. The presence of the selected esters reduces the viscosity of concentrated aqueous solutions of the surfactant and permits greater ease of handling.

The following examples set forth certain specific embodiments of the invention and are provided to enable those of skill in the art to practice the invention and, further, to illustrate the utility of the invention in certain applications. These examples should not be
construed to limit the scope of the invention, which is limited only by the lawful scope of the appended claims.

EXAMPLE I

300.6 g (0.638 mol) of tricaprylin (Sigma, dried over 3A sieves), 86.39 g (0.960 mol) of dimethyl carbonate (Aldrich) and 3.89 g (1 wt %) of sodium methoxide (Aldrich) were added to a two liter autoclave. After sealing the autoclave, the contents were mechanically stirred at about 750 rpm and heated to about 130°C with a heating mantle. While at about 130°C, the reaction pressure was approximately 35 psi. After 11 h at about 130°C (tricaprylin conversion > 95%), the reaction mixture was allowed to cool to room temperature. The crude reaction mixture was diluted with 500 ml of ether and subsequently washed with 100 ml of water. The aqueous washing was then extracted with 500 ml of ether. The two ether layers were combined and washed with water (2 x 200 ml) and brine (200 ml). The resulting ether solution was dried over magnesium sulfate, filtered and concentrated by rotary evaporation to give 346.0 g of crude product. The methyl caprylate was then removed by vacuum distillation (head temp.: 27-34°C, vacuum: 122-175 millitorr, pot temp.: 40-50°C) to yield 206.2 g (0.845 mol) of methyl caprylate (99% yield). The residue was then subjected to Kugelrohr distillation (vacuum: 40-50 millitorr, pot temp 110-115°C) to afford 102 g of distillate which contained ca. 91 g of the glycerol carbonate ester of caprylic acid (58% yield). The pot residue (15.5 g) primarily consisted of tricaprylin about 50%, diglycerides about 14% and the glycerol carbonate ester of caprylic acid about 25%.

EXAMPLE II

Experimental-Coconut Oil - 10-Gallon Reactor

To a dry 10 gallon stainless steel reactor the following chemicals were added: 22.5 kg (32.4 mol) of ARGA partially hydrogenated coconut oil, 4.38 kg (48.6 mol, 1.5 equivalents) dimethyl carbonate (DMC), and 0.270 kg (5 moles, 1 wt%) sodium methoxide (NaOMe). The reactor was
then pressure tested to 50 psi with nitrogen. The pressure was reduced to atmospheric pressure and the reactor was sealed.

The sealed reactor was heated to 130°C, and mechanically stirred at a rate of 250 rpm. The reaction mixture was heated at 130°C for 24 hours, developing an internal pressure of 17 psi. The reactor was cooled to 50°C and a 2 ml NMR sample was then removed. Proton NMR analysis showed these mol % values: 22 mol% fatty esters of glycerol carbonate, 60 mol % fatty methyl esters, 4 mol % glycerol carbonate, 3 mol % coconut oil, and 11 mol % DMC.

The excess DMC was removed under vacuum (1-2 torr) at 50°C overnight, 0.546 kg of DMC was removed. NMR of the crude product showed that 6.6 mol % DMC remained in the product. Additional DMC was removed from the crude product overnight for ca 16 hours under 1.5 torr vacuum and at a 72°C reactor temperature. 0.887 kg DMC was further removed. NMR showed virtually no DMC in the crude product. Total mass of DMC recovered: 1.43 kg (15.9 mol) (0.5 equivalents).

EXAMPLE III
Aqueous Work-Up of the Crude Product

The crude product at 50°C was slowly quenched with ca. four liters of ~50°C water, while mechanically stirring at a rate of 100 rpm. The aqueous phase and the organic phase were mixed at a stir rate of 100 rpm for 30 minutes. The mixture was then allowed to separate for 80 minutes. The lower aqueous phase was then removed through a foot valve.

The organic phase comprising the crude product was then washed with about four liters of 50°C water at a stir rate of 150 rpm. The aqueous and organic phase were mixed for 30 minutes and then allowed to separate for 40 minutes. Approximately 3 liters of the lower aqueous phase was removed.

The organic phase was then washed with about eight liters of 50°C water at a stir rate of 150 rpm. The aqueous and organic phases were mixed for 30 minutes. The
aqueous and organic phases were allowed to separate for 30 minutes. The lower aqueous phase was then removed through the foot valve.

The organic phase was then washed with about eight liters of 50°C brine at a stir rate of 200 rpm. The aqueous and organic phases were mixed for 30 minutes. The aqueous and organic phases were allowed to separate overnight about 15 hours, and then the aqueous phase was removed through the foot valve. This yielded 23.58 kg of crude product, mass balance: 93%.

EXAMPLE IV

Wiped Film Evaporation (WFE) of the Crude Product

The above product was distilled on a 4 inch wiped-film evaporator. The following conditions were used:

First pass: 23.36 kg of crude product was distilled with a jacket temperature of 115°C, a vacuum of 400-500 millitorr and an average feed rate of 0.5 kg/hr. The yield was 11.97 kg residue and 11.16 kg distillate comprising mostly fatty acid methyl esters.

Second pass: 11.94 kg of the first pass residue was distilled with a jacket temperature of 125-130°C, a vacuum of 100-135 millitorr and an average feed rate of 0.42 kg/hr. This yielded 8.37 kg of residue and 3.60 kg of distillate.

Third pass: 8.37 kg of the second pass residue was distilled with a jacket temperature of 135°C, a vacuum of 60-110 millitorr and an average feed rate of 0.33 kg/hr. This yielded 7.00 kg of glycerol carbonate ester residue and 1.27 kg distillate. The yield of fatty acid ester of glycerol carbonate was 64.3% while the yield of fatty acid methyl ester was 95.2%.

Pure samples of the glycerol carbonate esters were obtained by further distillation of the third pass residue. The conditions were a jacket temperature of 150°C, a vacuum of 40-100 millitorr and an average feed rate of 0.25 kg/h. The distilled product had purities of 95-97 % as determined by 400 MHz NMR.
EXAMPLE V

Experimental 3 Gallon Reactor

To a dry three-gallon glass reactor the following chemicals were added: 4.94 kg (7.2 mol) of ARGA partially hydrogenated coconut oil. 0.964 kg (10.7 mol, 1.5 equivalents) of DMC, and 0.0590 kg (1.1 mol, 1 wt%) NaOMe.

The above mixture was heated to 130°C for ca 16 hours while mechanically stirring at a rate of 240-260 rpm. A maximum pressure of 15 psi was reached within the glass reactor. The reaction was then cooled to 56°C, and the pressure dropped to 4 psi. A 2 ml NMR sample was removed from the reactor. Mol % analysis by NMR gave the following results: 2 mol% coconut oil, 66 mol% methyl ester, 19 mol% carbonate ester, 11 mol% DMC, and 2 mol% glycerol carbonate. The reaction mixture was heated for an additional 4 hours at 130°C developing an internal pressure of 15 psi. The reactor was cooled and another 2 ml NMR sample was withdrawn. NMR analysis gave the following results: 1 mol% coconut oil, 65 mol% methyl ester, 20 mol% carbonate ester, 10 mol% DMC, 2 mol% glycerol carbonate and 2 mol% unknown carbonate. This NMR showed virtually no change in the composition of the crude product mixture so the reaction was judged complete.

The crude product mixture was then placed under a vacuum of 1-2 torr for three hours. The mass of DMC collected in the traps was 217 g. NMR analysis of the crude product mixture at this point showed 2 mol% DMC remained. The mixture was placed back under vacuum (1-2 torr) at 50°C and left overnight. The following morning NMR analysis of the crude product mixture showed 1.2 mol% DMC still remained. Mass of DMC collected in the traps was 20.1 g. Total DMC removed was 237.1 g.

EXAMPLE VI

Aqueous Work-Up of the Crude Product

The crude product mixture at 50°C was washed with 0.9 L of 50°C water with a stir rate of 50-80 rpm for 15 minutes. The aqueous organic layer was allowed to separate
for 35 minutes. The aqueous layer was then removed through
the foot valve. An aqueous/organic emulsion interface
containing a dark solid material was also removed.

The organic layer was then washed with 1 L of 50°C
water at a stir rate of 50-100 rpm for 35 minutes. The
mixture was allowed to separate for 15 minutes and then the
aqueous layer was removed.

The organic layer was then washed with 1.9 L of 50°C
water at a stir rate of 60-100 rpm for 35 minutes. The
mixture was allowed to separate for 25 minutes and then the
aqueous layer was removed.

The organic layer was then washed with 1.9 L of 50°C
brine and stirred for 45 minutes at a rate of 100-170 rpm.
The mixture was allowed to separate for 75 minutes and then
the aqueous layer was removed.

This yielded 5.31 kg of crude product with a mass
balance of 94%.

It is to be understood that the embodiment of the
invention which has been described is merely illustrative
of applications of the principles of the invention.
Numerous modifications may be made by those skilled in the
art without departing from the true spirit and scope of the
invention.
What is claimed is:

1. A process for the preparation of glycerol carbonate esters of the formula

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O} \\
\text{R} \\
\end{array}
\]

wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms comprising treating glycerol esters of carboxylic acids and a carbonate in the presence of a catalyst to form corresponding glycerol carbonate esters.

2. In the process according to claim 1, wherein said glycerol esters of carboxylic acids comprise triglycerides having the general formula

\[
\begin{array}{c}
\text{O} \equiv \text{C} - \text{R} \\
\text{O} \equiv \text{C} - \text{R} \\
\text{O} \equiv \text{C} - \text{R} \\
\end{array}
\]

wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms.

3. In the process according to claim 2, wherein said triglycerides comprise glycerol tricaprylate and glycerol trilaurate.

4. In the process according to claim 2, wherein said triglycerides comprise natural oils.
5. In the process according to claim 4, wherein said natural oils comprise coconut oil, cottonseed oil, linseed oil, palm oil, soybean oil or high oleic sunflower oil.

6. In the process according to claim 4 wherein said natural oils have an acid value of up to about 0.1 mg KOH/g.

7. In the process according to claim 1 wherein said triglycerides comprise natural oils selected from the group consisting of coconut oil, cottonseed oil, linseed oil, palm oil, soybean oil and high oleic sunflower oil, said triglycerides having an acid value of less than about 0.1 and having the general formula

\[ \text{O} = \text{C-R} \quad \text{O} = \text{C-R} \quad \text{O} = \text{C-R} \\
\text{O} \quad \text{O} \quad \text{O} \]

wherein R is alkyl or alkenyl group having from 1 to about 22 carbon atoms.

8. In the process according to claim 1 wherein said catalyst comprises alkali metal alkoxides.

9. In the process according to claim 1, wherein said catalyst is a member selected from the group consisting of NaOCH₃, amidines and cyclic amidines, Na₂CO₃, NaHCO₃, K₂CO₃ and zinc hydrotalcite.

10. In the process according to claim 1 wherein said carbonate is di-lower alkyl carbonate or diphenyl carbonate.
11. In the process according to claim 10 wherein said di-
lower alkyl carbonate is dimethyl carbonate, diethyl 
carbonate or dipropyl carbonate.

12. A process for the preparation of glycerol carbonate esters of the formula

\[
\begin{align*}
\text{R} & \quad \text{O} \\
\text{O} & \quad \text{R} \\
\text{O} & \quad \text{O}
\end{align*}
\]

wherein R is alkyl or alkenyl corresponding to alkyl or 
alkenyl of naturally occurring triglycerides, comprising 
treating said naturally occurring triglycerides with 
dimethyl carbonate, diethyl carbonate, dipropyl carbonate 
or diphenyl carbonate in the presence of alkali metal 
alkoxides to form corresponding glycerol carbonate esters.

13. A process for the preparation of glycerol carbonate esters of the formula

\[
\begin{align*}
\text{R} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O}
\end{align*}
\]

wherein R is octyl, comprising treating glycerol 
tricaprylate with dimethyl carbonate in the presence of 
sodium methoxide to form corresponding glycerol carbonate esters.
14. A composition comprising a surfactant of the formula 
\( \text{C}_{12-14} \text{H}_{25-29} \text{O(CH}_2\text{CH}_2\text{O})_{1-3} \text{SO}_3^- \text{Na}^+ \) and an amount of glycerol carbonate ester sufficient to lower the viscosity of said surfactant, said glycerol carbonate ester having the formula

![Diagram of the molecular structure]

\( I \)

wherein \( R \) is alkyl or alkenyl group having from 1 to about 22 carbon atoms in a suitable solvent.