Title: PROCESS FOR THE PREPARATION OF A DICHLORO PROPANOL PRODUCT

Abstract: The present invention relates to a process for the preparation of a dichloropropanol product, wherein the dichloropropanol product comprises a mixture of 1,2-dichloroprop-3-ol and 1,3-dichloropropan-2-ol. Said process comprises the steps of: (a) contacting glycerol with hydrochloric acid in a molar ratio of glycerol to hydrochloric acid of about less than 1 to about 100 to form a first product mixture comprising 1-chloropropane-2,3-diol as a major constituent; and (b) contacting said first product mixture comprising 1-chloropropane-2,3-diol with hydrochloric acid in a molar ratio of 1-chloropropane-2,3-diol to hydrochloric acid of about less than 1 to about 100 to form the dichloropropanol product.
Process for the preparation of a dichloropropanol product

Field of the invention

The present invention relates to a method of selectively producing dichloropropanols from glycerine and hydrochloric acid and to their use in a method of producing halohydroxyoalkyl-N,N,N-trialkylammonium salts and epichlorohydrin.

Background of the invention

Glycerol (or glycerine) is the main by-product of biodiesel production, with the generation of approximately 100 kg of glycerine for every 1000 kg of biodiesel. Several chemical industries have developed processes for the conversion of glycerol into chemical products having added value, in particular dichloropropanols and epichlorohydrin.

Epichlorohydrin is used as a building block in the manufacture of plastics, epoxy resins, phenoxy resins and other polymers, as a solvent for cellulose, resins and paints, for the reinforcement of paper (used for instance in the food industry to manufacture tea bags) It has furthermore found use as in water purification and as an insect fumigant. The demand for epichlorohydrin is soaring and is set to exceed the world-wide production capacities by 2010.

Conventionally, epichlorohydrin is manufactured from oil-derived propylene through the intermediacy of allyl chloride to form dichlorohydrins. Ring closure of the dichlorohydrin mixture with caustic affords epichlorohydrin which is distilled to high purity. Disadvantages of using allyl chloride are that the free radical chlorination of propylene to allyl chloride is not very selective, resulting in the formation of substantial fractions of 1,2-dichloropropane, as well as that propylene is a hydrocarbon feedstock and long-term, global forecast of propylene prices keep rising.
Hence, an economically viable process for the production of epichlorohydrin from abundantly available glycerol is much desired.


The preparation of dichloropropanols from glycerol is well known in the art. German Patent Specification 197.308 to CF. Boehringer & Sonne, incorporated by reference herein, discloses a process for the conversion of glycerol into monochloropropane diols and dichloropropanols in the presence of an organic acid as catalyst, for example acetic acid, propionic acid, formic acid, tartaric acid, 1,9-nonanedioc acid (azelaic acid), cinnamic acid and phenylacetic acid.

US 2.144.612 to the Dow Chemical Company, incorporated by reference herein, discloses a process wherein glycerol is converted with hydrochloric acid into dichloropropanols wherein an aliphatic carboxylic acid, preferably acetic acid, is used as catalyst. US 2.198.600, also to the Dow Chemical Company, incorporated by reference herein, discloses a process for the extraction of dichloropropanol from aqueous solutions by using di-n-butyl ether as an extracting solvent. Both processes teach the vaporization or azeotropes with water to provide high conversion and a process need for sub-atmospheric or atmospheric pressure conditions to accomplish water removal.

German Patent Specification 1.075.103 to Veb Leuna Werke, incorporated by reference herein, discloses a process wherein glycerol is converted into 1,3-dichloropropan-2-ol which is subsequently converted into epichlorohydrin.

A more recent process is disclosed in WO 2005/021476 to Spolek Pro Chemickou A Hutni Vyrobu, Akciova Spolecnost, incorporated by reference herein, in which a series of hydrochlorination reactions is disclosed in which the water of reaction is removed in an atmospheric or sub-atmospheric process by reactive distillation. A similar process is disclosed in WO 2005/054167 to Solvay S.A., incorporated by reference herein, wherein it is additionally disclosed that when the reaction is carried out under higher total pressures (HCl partial pressure not specified), the rate of reaction is improved.

WO 2005/097722, WO 2005/1 15954, WO 2005/1 16004 and WO 2006/020234, all to the Dow Chemical Company, all incorporated by reference herein, disclose similar processes wherein superatmospheric partial pressures of hydrochloric acid are employed in the presence of a catalyst.

A major disadvantage of these known processes directed to the preparation of dichloropropanol from glycerol is its low selectivity, i.e. products are formed that comprise significant amounts of both 1,2-dichloropropan-3-ol and 1,3-dichloropropan-2-ol. This is particularly disadvantageous if these dichloropropanols are to be used in the synthesis of epichlorohydrin. That is, when such a mixture is used in the above-mentioned dehydrochlorination processes using caustic, the saponification conditions cannot be optimized since the saponification reaction rate constant of the 1,3-dichloro isomer with hydroxide is larger by about 30 times than the 2,3-dichloro isomer. Hence, when the reaction conditions are adapted to the 1,3-dichloro isomer, the desired dehydrochlorination of the 2,3-dichloro will not complete, resulting in the presence of unreacted 2,3-dichloro isomer in the waste liquid. On the other hand, when the dehydrochlorination reaction conditions are adapted for the 2,3-dichloro isomer, the saponification conditions may become too harsh for the 1,3-dichloro isomer, due to increased reaction times and temperatures, resulting in unwanted side reactions such as the hydrolysis of the desired epichlorohydrin product. Thus, the yield of the desired epichlorohydrin is limited.
In an attempt to overcome the problem of side products, WO 2006/11810 to Aser S.R.L., incorporated by reference herein, discloses a one-step process for the preparation of 1,3-dichloropropan-2-ol from glycerol and gaseous anhydrous hydrochloric acid, at atmospheric to superatmospheric pressure, in the presence of low volatility organic acids as catalysts, e.g. citric acid, malonic acid and tartaric acid, comprising the continuous elimination of water and of 1,3-dichloropropan-2-ol by stripping with gaseous hydrochloric acid. The use of large excess amounts of hydrochloric acid is, however, economically problematic and the inherent pollution of water with the unreacted hydrochloric acid results in an aqueous hydrochloric acid stream that is difficult to recycle.

It is an object of the present invention to provide a process which enables the selective preparation of either 1,2-dichloropropan-3-ol [2,3-dichlorohydrin; CAS No. 616-23-9] or 1,3-dichloropropan-2-ol [1,3-dichlorohydrin; CAS No. 96-23-1]. It is a further object of this invention to provide a process for the selective preparation of organic acid esters of 1,2-dichloropropan-3-ol and 1,3-dichloropropan-2-ol, respectively, and unsaturated organic acids en diacids.

It is a further object of the invention to provide a process for preparing a dichloropropanol product that consumes less hydrochloric acid.

In another aspect the invention relates to the application of the dichloropropanol product according to invention in the preparation of chemical compounds having added value. Examples of such chemical compounds are 3-chloro-2-hydroxypropyl-N,N,N-trialkylammonium salts and 2-chloro-3-hydroxypropyl-N,N,N-trialkylammonium salts.

Quaternary ammonium compounds in general find use in a wide variety of applications, including as fabric softeners, anti-static agents and wetting agents. Halohydroxy-N,N,N-trialkylammonium salts, such as 3-chloro-2-hydroxypropyl trimethylammonium chloride (CHMAC; CAS no. 3327-22-8) are reactive chemical intermediates used for the modification of both natural and synthetic polymers, particularly in the production of cationic polysaccharides such as starch and cellulose. They are generally prepared by reaction of trialkylamines or their salts with epihalohydrins, for instance by methods disclosed in US. 2,876,217, US 3,135,788; US 4,450,295, US 4,594,452 and US 5,463,127, all incorporated by reference herein.
US 4,594,452 discloses the synthesis of 3-chloro-2-hydroxypropyl trialkyl ammonium salts by reaction of epichlorohydrin with trialkylamine hydrochloride in chloroform, which is a non-solvent for the reaction product. US 4,982,000 discloses a process for preparing quaternary ammonium compounds comprising the reaction of a tertiary amine, an hydroxylated or thiolated alkylation agent and an epoxy compound. US 5,463,127 discloses the preparation of halohydroxypropyl trialkylammoniumhalides by reacting an epihalohydrin with trialkylamine hydrochloride and up to ten percent free trialkylamine.

Austrian Patent Specification 414.237 B to DSM Fine Chemicals NFG GmbH & Co. KG, incorporated by reference, discloses a process for the preparation of halogen alkyl ammonium salts, wherein a slight excess of dihalogen-C3-C24-alkane is reacted with trimethyl amine in ethyl acetate as solvent at a temperature of -15°C to 100°C and a pressure of 1 to 10 bar. After the reaction is completed, the reaction mixture is cooled and the solid product is isolated by filtration and is finally dried. The dihalogen-C3-C24-alkane may be 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane and is preferably 1,6-dibromohexane. A process for preparing halohydroxyalkyl ammonium salts is, however, not disclosed.

It is also possible to prepare quaternary halohydroxyalkyl ammonium salts not from epichlorohydrin, but directly from its precursor dichloropropanol by reaction with trimethylamine. Xiu-ying Han, Yi-xin Yan, Zhi-ming Bai, Gai-mei Bo, Do-xin Li in Shanxi Daxue Zuebao, Ziran Kexueban 25(4), 379 - 380, 2002 (Chem. Abstr. 139, 36295) discloses the treatment of glycerol with HCl in acetic acid to yield 43% of 1,3-dichloropropan-2-ol which was then treated with aqueous trimethylamine to give 73% of 3-chloro-2-hydroxypropyl trimethylammonium chloride. Commercially, the latter product is available as a 65 wt.% solution in water. However, the presence of large amounts of water is economically unattractive in terms of storage and transport costs.

Hence, a need in the art exists for a process of preparing anhydrous halohydroxy-N,N,N-trialkylammonium salts from dichloropropanol.
Summary of the invention

The inventors have now found that 1,2-dichloropropan-3-ol or 1,3-dichloropropan-2-ol can be selectively prepared by a two-step process in which glycerol is first reacted with a sub-stoichiometric quantity of hydrochloric acid to produce a chloropropanediol reaction mixture, which is reacted in a second step to produce dichloropropanol. The invention also relates to a process for separating 1-chloropropan-2,3-diol and 2-chloropropan-1,3-diol and to a process for the preparation of 3-chloro-2-hydroxypropyl-N,N,N-trialkylammonium salts, 2-chloro-3-hydroxypropyl-N,N,N-trialkylammonium salts or mixtures thereof by contacting 1,3-dichloropropan-2-ol, 1,2-dichloropropan-3-ol or a mixture thereof with a trialkylamine. The present invention further relates to methods for the preparation of organic acid esters of 1,2-dichloropropan-3-ol and 1,3-dichloropropan-2-ol, respectively, and unsaturated organic acids en diacids.

Accordingly, the present invention relates to a process for the preparation of a dichloropropanol product, wherein the dichloropropanol product comprises a mixture of 1,2-dichloropropan-3-ol and 1,3-dichloropropan-2-ol, said process comprising the steps of:

(a) contacting glycerol with hydrochloric acid in a molar ratio of glycerol to hydrochloric acid of about less than 1 to about 100 to form a first product mixture comprising 1-chloropropane-2,3-diol as a major constituent; and

(b) contacting said first product mixture comprising 1-chloropropane-2,3-diol as a major constituent with hydrochloric acid in a molar ratio of 1-chloropropane-2,3-diol to hydrochloric acid of about less than 1 to about 100 to form the dichloropropanol product.

Detailed description of the invention

The verb "to comprise" as is used in this description and in the claims and its conjugations are used in its non-limiting sense to mean that items following the word are included, but items not specifically mentioned are not excluded. In addition,
reference to an element by the indefinite article "a" or "an" does not exclude the possibility that more than one of the element are present, unless the context clearly requires that there is one and only one of the elements. The indefinite article "a" or "an" thus usually means "at least one".

The term "chloropropanediol" is intended to mean a mixture of isomers comprising 3-chloropropane-1,2-diol (CAS no. 96-24-2) and 2-chloropropane-1,3-diol (CAS no. 497-04-01) including their stereochemical isomers. The term "dichloropropanol" is intended to mean a mixture of isomers comprising 1,3-dichloropropan-2-ol (CAS no. 96-23-1) and 1,2-dichloropropan-3-ol (CAS no. 616-23-9) including its stereochemical isomers.

Preparation of monochloropropanediol

In an first aspect, the present invention relates to a process for the preparation of a dichloropropanol product, wherein the dichloropropanol product comprises a mixture of 1,2-dichloropropan-3-ol and 1,3-dichloropropan-2-ol, said process comprising in a first step contacting glycerol with hydrochloric acid in a molar ratio of glycerol to hydrochloric acid of about less than 1 to about 100:1 to form a first product comprising l-chloropropane-2,3-diol as a major constituent; and in a second step contacting said first product comprising l-chloropropane-2,3-diol as a major constituent with hydrochloric acid in a molar ratio of l-chloropropane-2,3-diol to hydrochloric acid of about less than 1 to about 100 to form the dichloropropanol product. Accordingly, it is therefore preferred that a sub-stoichiometric amount of hydrochloric acid is used with respect to glycerol and l-chloropropane-2,3-diol.

The process according to the present invention is therefore a two-step process, wherein in the first product the molar amount of 2-chloropropane-1,3-diol (relative to l-chloropropane-2,3-diol) to is less than 10 %, preferably less than 5 %, more preferably less than 4 %.

The first product is preferably further characterised by a molar amount of 1,3-dichloropropan-2-ol (relative to l-chloropropane-2,3-diol) of less than 10 %, preferably
less than 5 %, more preferably less 4 %, even more preferably less than 3 % and in particular less than 2 %.

The first product is preferably also characterised by a molar amount of 1,2-dichloropropan-3-ol (relative to l-chloropropane-2,3-diol) of less than 10 %, preferably less than 5 %, more preferably less 4 %, even more preferably less than 3 % and in particular less than 2 %.

The overall conversion per pass of glycerol to l-chloropropane-2,3-diol in the first step of the present invention is preferably higher than 20%, preferably higher than 25%. Accordingly, it is therefore preferred that the first product comprises at least 25 % by weight of l-chloropropane-2,3-diol, based on the total weight of the first product.

The process according to the present invention can be performed starting from pure glycerol or from unprocessed glycerol obtained as a byproduct of the biodiesel industry. The starting materials need not be free of contaminants such as water, salts or organic impurities. However, it is preferred that a feed is employed comprising at least 92 % by weight of glycerol, more preferably at least 96 % by weight of glycerol.

The first step of the process according to the present invention is carried out at a temperature between 25° and 300°C, preferably between 50° and 250°C, more preferably between 75° and 200°C, yet even more preferably between 75° and 150°, in particular between 80° and 130°C. The second step of the process according to the present invention is carried out at a temperature between 25° and 300°C, preferably between 50° and 250°C, more preferably between 75° and 200°C, yet even more preferably between 75° and 150°, in particular between 80° and 130°C. As will be apparent to the person skilled in the art, the temperatures at which the first and second steps of the process according to the present invention are carried out may be different.

It is preferred that the hydrochloric acid employed in the first and second steps of the process according to the present invention is gaseous hydrochloric acid, since this avoids the preliminary introduction of water in the reaction system, which may have negative effects on the reaction balance.

The gaseous hydrochloric acid is used in a subatmospheric, atmospheric or superatmospheric partial pressure. It is preferred according to one embodiment of the invention that the reaction is carried out under a total pressure of about 10⁵ Pa to about
10^6 Pa, preferably about 10^5 Pa to about 5 \times 10^5 Pa, in particular about 10^5 Pa to about 2.5 \times 10^5 Pa. A total pressure of above 10^5 Pa allows to maintain a sufficiently high concentration of hydrochloric acid in the reactor and thus a sufficiently high reaction rate.

It is further preferred that after completion of the first and/or second step a slight vacuum is applied to remove water from the reaction medium.

According to the invention, it is preferred that the first and/or the second steps are conducted in the presence of a catalyst, more preferably an acid, even more preferably an organic acid, most preferably an C_1 - C_{12} organic acid. The organic acids used as catalysts according to the invention are preferably selected from the group consisting of monocarboxylic acids, dicarboxylic acids, tricarboxylic acids and mixtures thereof. The organic acid may comprise one or two hydroxy groups. Suitable catalysts include acetic acid, oxalic acid and citric acid. To prevent loss of the catalyst due to high reaction temperatures, catalysts are preferred that have higher boiling points and are less volatile than the other reactants. It is preferred that the catalyst is non-volatile under the reaction conditions used. A particularly preferred catalyst is citric acid.

The first step of the process according to the invention is optionally conducted in the presence of a solvent, wherein the weight ratio of the feed to the solvent is preferably about 1 : 1. Suitable solvents include esters, ketones and alcohols. However, the use of solvent is not always economical since it requires separation of the solvent from the products and a recycle of a solvent stream into the process.

**Separation of monochloropropanediols**

The first product of the process according to the invention may be purified into a first stream enriched in 1-chloropropane-2,3-diol and a second stream depleted in 1-chloropropane-2,3-diol, wherein said first stream enriched in 1-chloropropane-2,3-diol is subjected to the second step of the process according to the present invention or is used in a separate process for the manufacture of other chemical compounds. This first stream enriched in 1-chloropropane-2,3-diol preferably comprises at least 25 % by weight of 1-chloropropane-2,3-diol, based on the total weight of said first stream, more
preferably a least 35 % by weight, even more preferably at least 45 % by weight, yet even more preferably more than 50 % by weight and in particular more than 75 % by weight. The purification of the first product may be conducted with techniques known in the art, in particular extraction or (low temperature) crystallisation, wherein the extraction is preferably performed with a solvent or an ionic liquid. An example of a suitable extraction technique is liquid/liquid extraction which may be continuous or batch-wise, preferably continuous. The second stream depleted in 1-chloropropane-2,3-diol preferably comprises less than 25 % by weight of 1-chloropropane-2,3-diol and more than 5 % by weight of 2-chloropropane-1,3-diol, based on the total weight of said second stream, and is optionally recycled as a recycle stream to the first step of the process according to the invention, wherein it is preferred that the blending ratio of the feed and the recycle stream is greater than 1 (i.e. more than 50 % by weight of feed is combined with less than 50 % y weight of recycle stream as total feed for the first step), preferably greater than 2.

Alternatively, the separation of the first product according to the present invention into a first stream enriched in 1-chloropropane-2,3-diol and a second stream depleted in 1-chloropropane-2,3-diol may be effectuated by complexation, i.e. the formation of a temporary complex of 1-chloropropane-2,3-diol and a complexing agent followed by separating off.

Low-temperature crystallisation/extraction/complex formation

Ionic liquids

Ionic liquids (ILs) are salts in which the ions are poorly coordinated, which results in these solvents being liquid below 100°C, or even at room temperature. At least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice. ILs display no vapour pressure up until temperatures of 250°C and are chemically and thermally very stable. These properties render ILs very suitable for use with low losses in separations in a variety of chemical processes. One of the many advantages of ILs is that by choosing the appropriate
anions and cations the ILs can be tuned for specific applications. Recently, it has also been suggested to use (supercritical) CO₂ as an anti-or co-solvent in IL extraction methods.

Dichloropropanol product

Advantageously, the second step of the process according to the present invention produces a dichloropropanol product mixture which comprises at least 50 % by weight of 1,3-dichloropropan-2-ol, based on the total weight of the dichloropropanol product mixture. The dichloropropanol product mixture may further comprise some 1,2-dichloropropan-3-ol as a minor constituent.

Under the preferred conditions of this invention, 1-chloropropane-2,3-diol upon reaction with the sub-stoichiometric amount of hydrochloric acid is converted to 1,3-dichloropropan-2-ol with a selectivity if at least 95 %, preferably at least 96 %, more preferably at least 97 %, yet even more preferably at least 98 % and in particular at least 99 %.

Alternatively, the dichloropropanol product mixture according to the invention, or alternatively any dichloropropanol mixture comprising 1,3-dichloropropan-2-ol and a 1,2-dichloropropan-3-ol may be separated by means of solvent or ionic liquid extraction. Such a mixture can also result from any reaction known in the art comprising the reaction of glycerol and excess hydrochloric acid, whether or not in the presence of an acid catalyst. Such solvent or ionic liquid extractions are in principle known in the art.

Esters of 1,3-dichloropropan-2-ol

In another embodiment of the invention, esters of 1,3-dichloropropan-2-ol and/or 1,2-dichloropropan-3-ol are prepared. Such esters comprise esters of 1,3-dichloropropan-2-ol and 1,2-dichloropropan-3-ol, respectively, and unsaturated organic acids and diacids. These esters are prepared by reacting the 1,3-dichloropropan-2-ol, the 1,2-dichloropropan-3-ol or the dichloropropanol mixture according to the invention with a suitable acid, optionally in the presence of a catalyst.
The reaction is preferably carried out in a solvent such as esters, alcohols or ketones at a temperature between about 25°C and about 150°C.

Suitable acids are selected from the group consisting of acrylic acid and methacrylic acid.

The esters of 1,3-dichloropropan-2-ol and/or 1,2-dichloropropan-3-ol obtained with the above procedure can be separated from the reaction mixture by means of extraction and crystallization methods known in the art.

**Epichlorohydrin**

The invention also relates to the use of a dichloropropanol product or product mixture as obtained by the process as described above in the preparation of epichlorohydrin. Both 1,3-dichloropropan-2-ol and 1,2-dichloropropan-3-ol can readily be converted to epichlorohydrin by dehydrochlorination, commonly through reaction with strong base, as is well-known in the art. Since 1,3-dichloropropan-2-ol possesses a reactivity in the dehydrochlorination reaction that is 30 greater than for its 1,2-dichloropropan-3-ol isomer, this epichlorohydrin process particularly benefits from the present invention in which 1,3-dichloropropan-2-ol is obtained with high selectivity and in high purity.

**Halohydroxyoalkyl-N,N,N-trialkylammonium salts**

In another embodiment of the invention, the dichloropropanol product or product mixture as obtained by the process according to the invention is used in a process for the preparation of halohydroxyoalkyl-N,N,N-trialkylammonium, in particular 3-chloro-2-hydroxypropyl-N,N,N-trialkylammonium salts, the alkyl group being linear or branched and comprising 1 to 6 carbon atoms.

The invention also relates to a process for preparing 3-chloro-2-hydroxypropyl-N,N,N-trialkylammonium salts, 2-chloro-3-hydroxypropyl-N,N,N-trialkylammonium salts or mixtures thereof. This process entails reacting 1,3-dichloropropan-2-ol, 1,2-
dichloropropan-3-ol or a mixture thereof with a trialkylamine, the alkyl group being linear or branched and comprising 1 to 6 carbon atoms, under essentially anhydrous conditions. "Essentially anhydrous" is understood to refer to a water content in the reaction mixture of at most 5 percent, based on the total weight of the reaction mixture.

It is preferred that the reaction be carried out in a restricted amount of a solvent, in particular ethyl acetate, preferably in a 20:80 (wt/wt) ratio of DCP to ethyl acetate. The halohydroxy-N,N,N-trialkylammonium salts are poorly soluble in solvents like ethyl acetate and dichloropropanol, whereas dichloropropanol is well soluble in ethyl acetate. During the course of the reaction the concentration of dichloropropanol decreases, causing precipitation of the halohydroxy-N,N,N-trialkylammonium salt and a subsequent shift of the reaction balance, which results in high conversion yields. The reaction is optionally carried out in the presence of a catalyst.

1,2-Dichloropropan-3-ol

Another embodiment of the present invention is the selective conversion of 2-chloropropane-1,3-diol to 1,2-dichloropropan-3-ol upon reacting 2-chloropropane-1,3-diol with a sub-stoichiometric amount of hydrochloric acid. This reaction can be carried out under conditions which are described for the second step of the process for the preparation of the dichloropropanol product. The compound 2-chloropropane-1,3-diol may obviously also be used for the preparation of other compounds of interest.

Examples

Reaction of Glycerine with HCl to 1-chloropropane-2,3-diol using acetic acid as catalyst

In a jacketed glass reactor with reflux condenser, HCl gas (ex cylinder) was added with a pressure-regulating system for the HCl gas, mechanical stirrer and oil bath with thermostat. To 3.29 mole (= 303 grams) glycerol (99.5%), 0.124 mole (= 7.44
grams) acetic acid was added. The temperature was raised to 105 °C and 1.1 mole HCl was added over a period of 5.5 hours, under stirring at 500 rpm, with pressure kept at 1.3 bar. The water formed was removed and collected. Samples were taken at regular intervals (t=0 min, t=64 min, t=177 min, t=295 min, t=323 min). The glycerine mole fraction started to decline after some 60 minutes down to 0.57 mole% (t=64 min: 0.98 mole%; t=177 min: 0.8 mole%; t=295 min: 0.64 mole%; t=323 min: 0.57 mole%).

The l-chloropropane-2,3-diol mole fraction started to increase after some 60 minutes to 0.4 mole% (t=64 min: 0.01 mole%; t=177 min: 0.2 mole%; t=295 min: 0.36 mole%; t=323 min: 0.4 mole%). The relative mole fraction of 2-chloropropane-1,3-diol (relative to l-chloropropane-2,3-diol) formed after 323 minutes was 3.96%, and was 1.5% for 1,3-dichloropropan-2-ol. The analyses were performed with both GC and HPLC.

Reaction of glycerine with HCl to l-chloropropane-2,3-diol using oxalic acid as catalyst.

The reaction was performed as in example 1, but instead of acetic acid as catalyst, 0.25 mole of oxalic acid was used. Glycerine: 2.71 mole (=249 grams), oxalic acid 0.24 mole (=19.2 grams), temperature 105 °C. HCl (1.35 mole) was added over a period of 3.83 hours, with pressure kept at 2 bar. The water formed was removed and collected. Samples were taken at regular intervals (t=0 min; t=52 min; t=125 min; t=230 min). The glycerine mole fraction declined to 0.74 mole% (t=52 min: 0.98 mole%; t=125 min: 0.88 mole%; t=230 min: 0.74 mole%) and the l-chloropropane-2,3-diol mole fraction increased to 0.25 mole% (t=52 min: 0.02 mole%; t=125 min: 0.12 mole%; t=230 min: 0.25 mole%). The relative mole fraction of 2-chloropropane-1,3-diol (relative to l-chloropropane-2,3-diol) formed after 230 minutes was 4.61%, of 1,3-dichloropropan-2-ol was 1.9%, and of 1,2-dichloropropan-3-ol was 0.6%.

Reaction of glycerine with HCl to l-chloropropane-2,3-diol using citric acid as catalyst.
Reaction was performed as in example 1, but instead of acetic acid as catalyst, 0.073 mole of citric acid was used. Glycerine: 2.70 mole (= 248 grams), citric acid 0.073 mole (9.928 grams), temperature 115 °C, HCl 1.62 mole added over 3.5 hours, with pressure kept at 2 bar. Samples were taken at regular intervals (t=0 min, t= 75 min ; t= 150 min t= 225 min). The glycerine mole fraction declined to 0.65 mole% (t=75 min 0.91mol% ; t= 150 min 0.8 mole%; t=225 min 0.65 mole%) and the l-chloropropane-2,3-diol mole fraction increased to 0.34 mole% (t=75 min: 0.09 mole%; t=150 min: 0.2 mole %, t=225 min: 0.34 mole%). The relative mole fractions of 2-chloropropane-l,3-diol (relative to l-chloropropane-2,3-diol) after 225 minutes was 4.66 %, for 1,3-dichloropropan-2-ol it was 1.98% and for 1,2-dichloropropan-3-ol it was 3.3%.

Reaction of l-chloropropane-2,3-diol to 1,3-dichloropropan-2-ol using acetic acid as catalyst.

Reaction was performed as in example 1, using l-chloropropane-2,3-diol: 2.68 mole (=279 grams), acetic acid: 0.304 mole (=18.24 grams), temperature 110 °C, HCl 2.50 mole, with pressure kept at 2 bar. Samples were taken at regular intervals (t=0 ; t= 100 min ; t= 225 min ;t= 540 min; t= 1325 min). The l-chloropropane-2,3-diol mole fraction declined to 0.16 mole% (t=100 min 0.91 mole%; t= 225 min 0.82 mole%; t=540 min: 0.55 mole%; t=1325 min 0.16 mole%) and the 1,3-dichloropropan-2-ol mole fraction increased to 0.84% (t=100 min 0.09 mole% ; t= 225 min 0.18 mole%; t= 540 min 0.44 mole%; t= 1325 min 0.84 mole%) The relative mole fraction of 2,3-dichloropropane-1-ol (relative to 1,3-dichloropropan-2-ol) after 540 minutes was 3.52 % and after 1325 minutes 2.55 %. Analysis was performed with HPLC and GC.

Reaction of l-chloropropane-2,3-diol to 1,3-dichloropropan-2-ol using oxalic acid as catalyst.

Reaction was performed as in Example 1, using 2.72 moles (300 g) of l-chloropropane-2,3-diol, 0.3 mole (24 g) of oxalic acid. The temperature was 110 °C.
2.55 moles of HCl were used with pressure kept at 2 bar. Samples were taken at regular intervals (t=0, t=100 min, t=225 min, t=540 min, t=335 min). The 1-chloropropane-2,3-diol fraction decreased to 0.34 mole% (t=100 min: 0.83 mole%; t=225 min: 0.87 mole%; t=540 min: 0.74 mole%; t=1335 min 0.32 mol%). The 1,3-dichloropropan-2-ol mole fraction increased to 0.68 mole% (t=100 min: 0.07 mole%, t=225 min: 0.13 mole%, t=540 min: 0.28 mole%, t=1335 min 0.68 mole%. The relative mole fraction of 2,3-dichloropropan-1-ol (relative to 1,3-dichloropropan-2-ol) after 540 min was 4.16 % and after 1335 min it was 6.75 %.

Preparation of 3-chloro-2-hydroxypropyl-N,N,N-trimethylammonium chloride (CHMAC) from 1,3-dichloropropan-1-ol (U-DCP).

270 gram DCP (2.10 moles) was reacted for 5.5 hours at 40 °C with 100 grams of TMA (1.69 moles) using Ar for controlling the flow (flow 0.45 g/ml) resulting in 0.41 mole TMA/hour. It was estimated that 1.50 moles of TMA had been consumed. The valves have been calibrated with TMA at 20 °C (vapour pressure 91 kPa). The reaction was slightly exothermic and the temperature increase due to the exothermic reaction was estimated to be 5 °C. The reaction was analyzed at t=0, t=40 min, t=102 min, t=157 min, t=327 min and at 5.5 hours, which showed an increase from 0 to 6.38 mole/l CHMAC at t=327 min. The amount of DCP went simultaneously from 7.72 mole at t=0 to 2.51 mole at t=327 min. The reaction mixture was evaporated on a rotary film evaporator at 75 °C at 11 mbar, resulting in crystallization of CHMAC including 6.7% DCP. The colour of the reaction mixture was light brown to very off white. The product was dissolved in 200ml EtOH (99.5% ) and 4.5 gram active coal was used to reduce the colour. This resulted in CHMAC 93% /DCP 7%. The above process was repeated, but now DCP was dissolved in ethyl acetate (50:50). This is a very poor solvent for CHMAC and does not affect the conversion of TMA and DCP to CHMAC, which will precipitate from the reaction mixture.
Claims

1. A process for the preparation of a dichloropropanol product, wherein the
dichloropropanol product comprises a mixture of 1,2-dichloropropan-3-ol and
1,3-dichloropropan-2-ol, said process comprising the steps of:

(a) contacting glycerol with hydrochloric acid in a molar ratio of glycerol to
hydrochloric acid of about less than 1 to about 100 to form a first product
mixture comprising 1-chloropropane-2,3-diol as a major constituent; and

(b) contacting said first product mixture comprising 1-chloropropane-2,3-diol
as a major constituent with hydrochloric acid in a molar ratio of 1-
chloropropane-2,3-diol to hydrochloric acid of about less than 1 to about
100 to form the dichloropropanol product.

2. The process according to Claim 1, wherein the hydrochloric acid employed in
step (a) and/or step (b) is gaseous hydrochloric acid.

3. The process according to Claim 2, wherein a subatmospheric, atmospheric or
superatmospheric partial pressure of hydrochloric acid is used.

4. The process according to any one of Claims 1 - 3, wherein the first product
mixture comprises at least 25 % by weight of 1-chloropropane-2,3-diol, based on
the total weight of the first product mixture.

5. The process according to Claim 4, wherein the first product mixture comprises
less than 10 % by weight of 2-chloropropane-1,3-diol, based on the total weight
of the first product mixture.

6. The process according to Claim 5, wherein the first product mixture is separated
in a first stream comprising at least 75 % by weight of 1-chloropropane-2,3-diol
and a second stream comprising 2-chloropropan-1,3-diol.

7. The process according to Claim 5, wherein the first product mixture is separated
by low temperature crystallisation, extraction and/or complexation.

8. The process according to any one of Claims 1 - 7, wherein the dichloropropanol
product comprises 1,3-dichloropropan-2-ol.

9. The process according to any one of Claims 1 - 7, wherein the dichloropropanol
product comprises 1,2-dichloropropan-3-ol.
10. The process according to Claim 9, wherein the dichloropropanol product is separated using extraction, preferably continuous liquid/liquid extraction.

11. The process according to Claim 10, wherein the extraction is performed with a solvent or an ionic liquid.

12. The process according to any one of Claims 1 - 11, wherein step (a) and/or step (b) is conducted in the presence of a catalyst.

13. The process according to Claim 12, wherein the catalyst is an acid.

14. The process according to Claim 13, wherein the catalyst is an C\textsubscript{i} - C\textsubscript{12} organic acid.

15. The process according to Claim 14, wherein the C\textsubscript{i} - C\textsubscript{12} organic acid is selected from the group consisting of monocarboxylic acids, dicarboxylic acids, tricarboxylic acids and mixtures thereof.

16. A process for the preparation of 1,2-dichloropropan-3-ol, wherein 2-chloropropane-1,3-diol is contacted with hydrochloric acid.

17. Use of a dichloropropanol product as obtained by the process according to any one of Claims 1 - 15 in the preparation of epichlorohydrin.

18. Use of a dichloropropanol product as obtained by the process according to any one of Claims 1 - 15 in the preparation of esters of 1,3-dichloropropan-2-ol and saturated and unsaturated C\textsubscript{1} - C\textsubscript{12} organic acids and C\textsubscript{1} - C\textsubscript{12} organic diacids.

19. Use according to claim 18, in which the ester is separated from the reaction mixture by means of extraction or crystallization.

20. Use of a dichloropropanol product as obtained by the process according to any one of Claims 1 - 15 in the preparation of 3-chloro-2-hydroxypropyl-N,N,N-trialkylammonium salts, the alkyl group being linear or branched and comprising 1 to 6 carbon atoms.

21. A process for the preparation of 3-chloro-2-hydroxypropyl-N,N,N-trialkylammonium salts, 2-chloro-3-hydroxypropyl-N,N,N-trialkylammonium salts or mixtures thereof, wherein 1,3-dichloropropan-2-ol, 1,2-dichloropropan-3-ol or a mixture thereof is contacted with a trialkylamine, the alkyl group being linear or branched and comprising 1 to 6 carbon atoms, under essentially anhydrous conditions.