This invention discloses a process for the conversion of glycerol to glycidol

A Process for the synthesis of glycidol from glycerol

Technical field of invention: This invention discloses a process for the conversion of glycerol to glycidol

Background and prior art:

Glycidol is a high value added component in the production of a number of polymers, pharmaceuticals, textile, cosmetics and photochemical industries. Glycidol has been produced industrially by oxidation of allyl alcohol with hydrogen peroxide. This method suffers from a serious drawback that, it has large number of steps necessary for extracting pure glycidol from reaction mixture. Hence other improved methods have been proposed, which start from Glycerol carbonate as the starting material

US2636040 talks about the synthesis starting from glycerol and ethylene carbonate, which is a two step process and yield of the product is ~60-70%.

US6316641 discloses a process of synthesizing an epoxide, particularly glycidol using a zeolite catalyst at high temperature and reduced pressure, which may be operable in continuous mode also. The reaction is carried out under reduced pressure and temperature in a range of 170-210°C to obtain glycidol yield of 66-83%.

US 2856413 discloses a method for conversion of glycerol carbonate to glycidol in the presence of alkali and alkaline earth phosphates, pyrophosphates, chlorides, bromides, acetates, carbonates and bicarbonates as catalysts. The reaction is carried out in a temperature range of 125-175°C to obtain 70-82% yield of glycidol. The prior art processes prepare glycidol by a process starting from Glycerol carbonate, which is not readily available. Glycerol carbonate is generally obtained by transesterification of glycerol using basic catalyst. Thus glycerol is converted to glycerol carbonate in one step using basic catalyst. In another separate step glycerol carbonate is converted to glycidol using basic catalysts. There are no reports on the conversion of glycerol to glycerol carbonate in one pot using dialkyl carbamates as transesterification reagents.

Glycerol is a non-toxic biodegradable compound, which can be obtained from glucose fermentation, sorbitol hydrogenolysis, or in huge amounts during the production of biodiesel from the transesterification of plant oils and animal fats. The effective utilization of the glycerol that is formed during the production of biodiesel is a key factor to promote biodiesel commercialization and future developments. This has led to development in the synthesis of value added chemicals from glycerol and among various products proposed,

glycerol carbonate and glycidol are important products with many applications. A simple process to convert glycerol to glycidol, a value added component with a good demand is a need in the art.

It will be desirable to develop a single pot process for the synthesis of glycidol starting from glycerol, which is formed as by-product in bio-diesel synthesis.

Another need in the art that needs to be addressed is to propose the use of a simple catalytic system that can convert glycerol to value added product, glycidol, which would preferably be recyclable.

A further need in the art to be addressed it to propose a simple process of preparation of glycidol with high conversion rate and selectivity.

Objects of invention:

It is therefore an object of the invention to disclose a simple process of conversion of glycerol to glycidol using a catalyst resulting in high conversion rate of glycerol and possessing a high degree of selectivity towards glycidol.

Detailed description of invention:

Abbreviations used:

Tetramethylammonium hydroxide: (25% aqueous solution of [TMA][OH])

Tetraethylammonium hydroxide: (35% aqueous solution of [TEA][OH])

Tetrabutylammonium hydroxide: (40% aqueous solution of [TBA][OH])

Tetrapropylammonium hydroxide: (20% aquous solution of ([TPA][OH])

Tetramethylammonium bicarbonate: ([TMA][HCO_3])

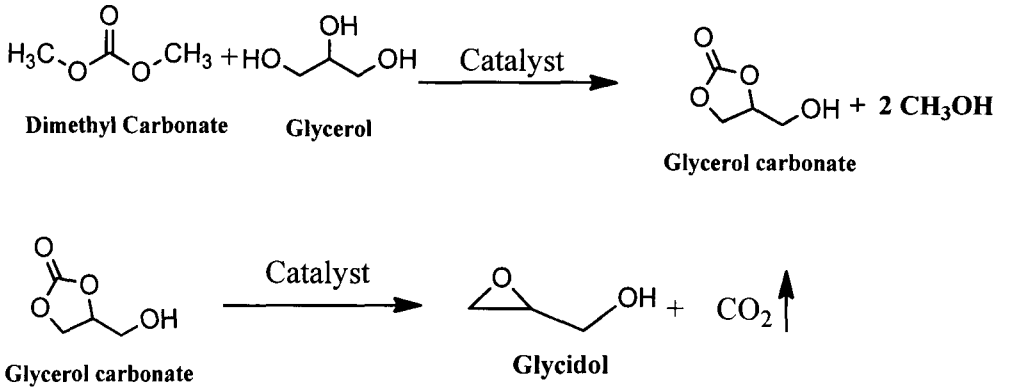
Tetrabutylammonium bicarbonate ([TBA][HCO_3])

[BMIM][OH]: 3-butyl-1methyl-1H-imidazol-3-ium hydroxide

[Me-DABCO][OH]: 1-methyl-4aza-1-1azoniabicyclo[2,2,2] octyl hydroxide

In accordance with the objectives of the invention, the inventors disclose a simple one pot, two step process for synthesizing glycidol from glycerol catalysed by ionic liquids.

The process of the invention is depicted in Scheme 1.



Scheme 1: Synthesis of glycerol carbonate from glycerol and glycidol from glycerol carbonate

The one pot process of the invention comprises:

a. using tetra alkyl compound, preferably hydroxide form as catalyst or reacting tetraalkylammonium hydroxide with carbon dioxide to obtain the corresponding bicarbonate form of said tetra alkyl compound which also can be used as catalyst for the following steps;

b. reacting dialkyl carbonate with glycerol in the presence of catalyst at 75-100 °C and atmospheric pressure for 60-180 minutes to obtain glycerol carbonate and

c. converting glycerol carbonate obtained in step (b) using catalyst of step (b) to obtain glycidol.

The tetra alkylammonium compound of the invention is selected from, but not restricted to [BMIM][OH], [TPA][OH], [TMA][OH]), [TEA][OH]), [TBA][OH], [Me-DABCO][OH, [TMA][HCO_3], [TPA][HCO_3], [TBA][HCO_3], [TEA][HCO_3], [Me-DABCO][OH] and such like.

In an embodiment of the invention, the dialkyl carbonate is replaced by a cyclic carbonate.

The selectivity of the process of invention towards glycidol is at least 40% and the conversion of glycerol is at least 50%.

The tetra alkylammonium salt used as a catalyst for the instant process is homogeneous as exemplified herein and is stable and reusable.

In another embodiment of the invention, the catalyst is optionally heterogenized to inorganic matrix to prepare heterogenized homogeneous catalyst.

In yet another embodiment of the invention, the catalyst of the process of the invention is reusable.

Table 1: Screening of ionic liquids for transesterification of glycerol

Sr. No.	Catalyst	GL Conversion (%)	Selectivity (%)	
			GD	GC
1	[BMIM][OH][a]	59	5	95
2	[TPA][OH]	77	58	42
3	[Me-DABCO][OH][a]	80	11	89
4	[TMA][HCO_3]	83	67	33
5	[TBA][HCO_3]	86	58	42
6	[TEA][OH]	89	43	56
7	[TBA][OH]	90	53	47
8	[TMA][OH]	95	51	47

GL: Glycerol; GD: Glycidol; DMC: Dimethyl carbonate; Reaction conditions: GL: 21.73 mmol, DMC: 65.21 mmol; catalyst: 0.217 mmol; Temperature = 80 °C, time = 90 min, a = 180 min.

Table 2: Effect of GL:DMC ratio on activity and selectivity

Run	GL: DMC	GL Conversion (%)	Selectivity (%)	
			GD	GC
1	1:1[a]	45	51	39
2	1:2[a]	74	55	40
3	1:3[a]	97	52	46
4	2:1[b]	66	43	30
5	3:1[b]	55	45	51

[TMA][OH] = 0.217 mmol; Temperature = 80 °C, time = 90 min, a = conversion with respect to GL, b = conversion with respect to DMC; GL: Glycerol; GD: Glycidol; DMC: Dimethyl carbonate.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that the present invention may be embodied in other specific forms without departing from the essential attributes thereof, and it is therefore desired that the present embodiments and examples be considered in all respects as illustrative and not restrictive.

Examples:

Example 1: Preparation of catalyst, bicarbonate ionic liquid:

Aqueous Tetramethylammonium hydroxide (25% [TMA][OH]) (10 ml) was taken in a 25 ml round bottom flask. CO_2 was bubbled through the solution for 2 h under constant stirring to obtain aq. solution of [TMA][HCO_3]. [TBA][HCO_3] was prepared by following the similar procedure. ^{13}C NMR of the solutions for both the ionic liquids showed the appearance of a peak at δ value of 160, which is characteristic of carbonyl carbon of the bicarbonate group. This indicated the formation of bicarbonate liquids.

Example 2:

0.217 mmol of [BMIM][OH] catalyst with respect to GL was charged to the 50 ml round bottom flask containing GL 2 g, (21.73 mmol) and dimethyl carbonate (DMC) 5.87g, (65.21 mmol). The reaction was

carried out at 80^0C for 180 min. The reaction mixture was cooled, a sample was taken out for analysis and it was diluted with N, N-dimethylformamide. The products were analyzed by gas chromatography on an Agilent 6890 gas chromatograph with HP-Innowax capillary column (30.0mX0.53mmX1.00μm film thickness). Identification of products was done using gas chromatography-mass spectrometry (GC-MS) on an Agilent 6890 N gas chromatograph coupled to an Agilent 5973 MSD mass spectrometer using HP-5 MS capillary column of 30m X 0.32mm X0.25μm dimension. 59% conversion of glycerol was converted, with 5% selectivity to glycidol.

Example 3:

0.217 mmol of [TPA][OH] catalyst with respect to GL was charged to the 50 ml round bottom flask containing GL 2 g, (21.73 mmol) and dimethyl carbonate (DMC) 5.87g, (65.21 mmol). The reaction was carried out at 80^0C for 90 min. The reaction mixture was cooled, a sample was taken out for analysis and it was diluted with N, N-dimethylformamide. The products were analyzed by gas chromatography on an Agilent 6890 gas chromatograph with HP-Innowax capillary column (30.0mX0.53mmX1.00μm film thickness). Identification of products was done using gas chromatography-mass spectrometry (GC-MS) on an Agilent 6890 N gas chromatograph coupled to an Agilent 5973 MSD mass spectrometer using HP-5 MS capillary column of 30m X 0.32mm X0.25μm dimension. 77% conversion of glycerol was converted, with 58% selectivity to glycidol.

Example 4:

0.217 mmol of [Me-DABCO][OH] catalyst with respect to GL was charged to the 50 ml round bottom flask containing GL 2 g, (21.73 mmol) and dimethyl carbonate (DMC) 5.87g, (65.21 mmol). The reaction was carried out at 80^0C for 180 min. The reaction mixture was cooled, a sample was taken out for analysis and it was diluted with N, N-dimethylformamide. The products were analyzed by gas chromatography on an Agilent 6890 gas chromatograph with HP-Innowax capillary column (30.0mX0.53mmX1.00μm film thickness). Identification of products was done using gas chromatography-mass spectrometry (GC-MS) on an Agilent 6890 N gas chromatograph coupled to an Agilent 5973 MSD mass spectrometer using HP-5 MS capillary column of 30m X 0.32mm X0.25μm dimension. 80% conversion of glycerol was converted, with 11% selectivity to glycidol.

Example 5:

0.217 mmol of [TMA][HCO_3] catalyst with respect to GL was charged to the 50 ml round bottom flask containing GL 2 g, (21.73 mmol) and dimethyl carbonate (DMC) 5.87g, (65.21 mmol). The reaction was carried out at 80^0C for 90 min. The reaction mixture was cooled, a sample was taken out for analysis and it was diluted with N, N-dimethylformamide. The products were analyzed by gas chromatography on an Agilent 6890 gas chromatograph with HP-Innowax capillary column (30.0mX0.53mmX1.00μm film thickness). Identification of products was done using gas chromatography-mass spectrometry (GC-MS) on an Agilent 6890 N gas chromatograph coupled to an Agilent 5973 MSD mass spectrometer using HP-5 MS capillary column of 30m X 0.32mm X0.25μm dimension. 83% conversion of glycerol was converted, with 67% selectivity to glycidol.

Example 6:

0.217 mmol of [TBA][HCO_3] catalyst with respect to GL was charged to the 50 ml round bottom flask containing GL 2 g, (21.73 mmol) and dimethyl carbonate (DMC) 5.87g, (65.21 mmol). The reaction was carried out at 80^0C for 90 min. The reaction mixture was cooled, a sample was taken out for analysis and it was diluted with N, N-dimethylformamide. The products were analyzed by gas chromatography on an Agilent 6890 gas chromatograph with HP-Innowax capillary column (30.0mX0.53mmX1.00μm film thickness). Identification of products was done using gas chromatography-mass spectrometry (GC-MS) on an Agilent 6890 N gas chromatograph coupled to an Agilent 5973 MSD mass spectrometer using HP-5 MS capillary column of 30m X 0.32mm X0.25μm dimension. 86% conversion of glycerol was converted, with 58% selectivity to glycidol.

Example 7:

0.217 mmol of [TEA][OH] catalyst with respect to GL was charged to the 50 ml round bottom flask containing GL 2 g, (21.73 mmol) and dimethyl carbonate (DMC) 5.87g, (65.21 mmol). The reaction was carried out at 80^0C for 90 min. The reaction mixture was cooled, a sample was taken out for analysis and it was diluted with N, N-dimethylformamide. The products were analyzed by gas chromatography on an Agilent 6890 gas chromatograph with HP-Innowax capillary column (30.0mX0.53mmX1.00μm film thickness). Identification of products was done using gas chromatography-mass spectrometry (GC-MS) on

an Agilent 6890 N gas chromatograph coupled to an Agilent 5973 MSD mass spectrometer using HP-5 MS capillary column of 30m X 0.32mm X0.25μm dimension. 89% conversion of glycerol was converted, with 43% selectivity to glycidol.

Example 8

0.217 mmol of [TBA][OH] catalyst with respect to GL was charged to the 50 ml round bottom flask containing GL 2 g, (21.73 mmol) and dimethyl carbonate (DMC) 5.87g, (65.21 mmol). The reaction was carried out at 80^0C for 90 min. The reaction mixture was cooled, a sample was taken out for analysis and it was diluted with N, N-dimethylformamide. The products were analyzed by gas chromatography on an Agilent 6890 gas chromatograph with HP-Innowax capillary column (30.0mX0.53mmX1.00μm film thickness). Identification of products was done using gas chromatography-mass spectrometry (GC-MS) on an Agilent 6890 N gas chromatograph coupled to an Agilent 5973 MSD mass spectrometer using HP-5 MS capillary column of 30m X 0.32mm X0.25μm dimension. 90% conversion of glycerol was converted, with 53% selectivity to glycidol.

Example 9:

0.217 mmol of [TMA][OH] catalyst with respect to GL was charged to the 50 ml round bottom flask containing GL 2 g, (21.73 mmol) and dimethyl carbonate (DMC) 5.87g, (65.21 mmol). The reaction was carried out at 80^0C for 90 min. The reaction mixture was cooled, a sample was taken out for analysis and it was diluted with N, N-dimethylformamide. The products were analyzed by gas chromatography on an Agilent 6890 gas chromatograph with HP-Innowax capillary column (30.0mX0.53mmX1.00μm film thickness). Identification of products was done using gas chromatography-mass spectrometry (GC-MS) on an Agilent 6890 N gas chromatograph coupled to an Agilent 5973 MSD mass spectrometer using HP-5 MS capillary column of 30m X 0.32mm X0.25μm dimension. 95% conversion of glycerol was converted, with 51% selectivity to glycidol.

Example 10:

The effect of GL to DMC mole ratio on the catalyst activity was studied by varying GL: DMC molar ratio in the range of 1:3, 1:2, 1:1, 2:1, and 3:1 respectively keeping other conditions constant and the results are

presented in Table 2. GL and DMC quantity of 21.7 mmol was used in the experiment carried out with GL:DMC ratio of 1:1. In other experiments, the quantity of one of the reactant was varied keeping the quantity of other reactant constant at 21.7 mmol, depending on the GL:DMC ratio investigated. From the results it was observed that conversion of GL was very low at GL:DMC ratio of 1:1. Only 45% conversion of GL was observed at GL:DMC ratio of 1:1. With increase in either GL or DMC concentration, conversion increased significantly. High conversion (97%) were observed at GL:DMC ratio of 1:3, compared to only 55 % at GL:DMC molar ratio of 3:1. GD selectivity was not affected by a change in GL:DMC ratio.

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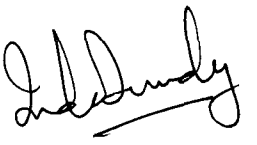

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