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Converting wastes into added value products: from glycerol to glycerol carbonate, glycidol and epichlorohydrin using environmentally friendly synthetic routes

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ABSTRACT

Glycerol carbonate, synthesised via a non-phosgene route using glycerol and CO_2 or urea in presence of a heterogeneous catalyst, was efficiently converted into a series of derivatives through the functionalization of the –OH moiety, using high yield, high selectivity synthetic routes not affecting the carbonate functionality. So, for example, glycerol carbonate was converted into epichlorohydrin, a product that has a large industrial application, under very mild conditions, using a two-step reaction with a 98% yield and 100% selectivity. The high yield and mild reaction conditions (very often close to the ambient conditions) make the environmentally friendly synthetic approach described in this work of potential applicative interest. All compounds prepared were fully characterized.

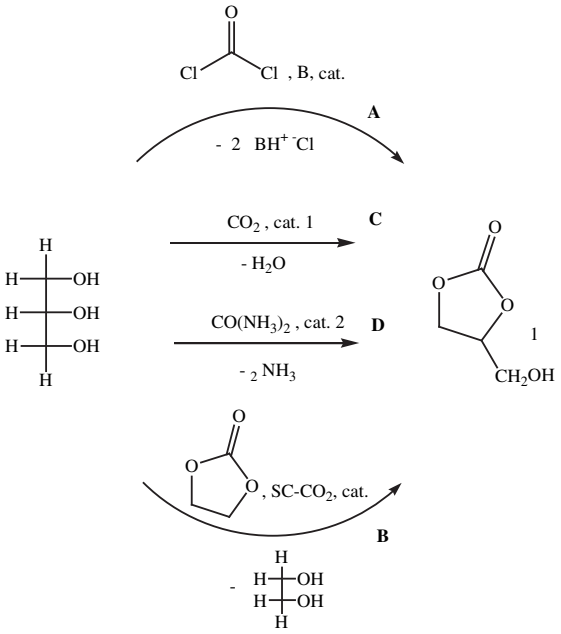
1. Introduction

The production of glycerol is increasing worldwide because of the boost of the production of biofuels from lipids. There is, thus, a need for finding new uses of the polyol in order to prevent its accumulations as a waste. Several routes are under screening and the conversion into the relevant carbonate is one of the possible options as large volumes of the latter can be utilized either directly or indirectly. In fact, besides the direct use of the carbonate itself, it is possible to search for new ways of expanding its application as starting material for new and old compounds.

Glycerol carbonate (**1** Scheme 1) is a bifunctional compound employed as solvent[1] or surfactant[2] or else in the synthesis of polyurethanes[3] and polycarbonates.[4]

Due to its low toxicity, vapour pressure and flammability, good biodegradability and moisturizing ability, glycerol carbonate also possesses the right characteristics of a wetting agent for cosmetic clays or a carrier for drugs. The actual synthetic routes to glycerol carbonate (Scheme 1) are based on:

(i) the reaction of glycerol with phosgene[5] (route A)
(ii) the transesterification with other carbonates[6] (route B)



Scheme 1. Different synthetic routes to glycerol carbonate, **1**.

Recently, the direct carboxylation with CO_2[7] (route C, in which two wastes are converted into an added value product) and the glycerolysis of urea[8] (route D, in which urea is used as an activated

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form of CO_2) have been described as new clean routes that may find industrial exploitation.

The hydroxyl functionality of glycerol carbonate allows its derivatization in many different ways to afford either known or new compounds. For example, the –OH moiety has been reacted with either anhydrides[9,10] to form ester linkages, or with isocyanates to form urethanes.[11,12]

In this paper we describe: (i) the utilization of some new catalysts active in the direct carboxylation of glycerol and in the reaction with urea; (ii) the functionalization reactions of the hydroxymethyl group of glycerol carbonate for the production of halogenated- and thionyl chloride-derivatives that can either give origin to new products or afford known compounds through alternative routes, which are cleaner and safer than those on stream. A reaction of interest is, for example, the production of glycidol and epichlorohydrin under controlled and safe conditions.

2. Results and discussion

In our previous studies[7a,8a] we have developed new synthetic routes to glycerol carbonate based on either the direct carboxylation of glycerol with CO_2 or the use of urea. The former route (route C in Scheme 1) converts two wastes into added value products, and the latter (route D in Scheme 1) results to be an indirect use of CO_2 again, considered that urea, when reacted with glycerol, releases NH_3, that is, recovered and can be converted back to urea by reaction with CO_2. We describe in this paper new synthetic approaches to glycerol carbonate and its conversion into useful chemicals, usually prepared through more harsh synthetic procedures that are not very selective. Both the use of two wastes, such as glycerol and CO_2 and particularly the mild and safe working conditions, coupled to the high yield and selectivity of the processes carried out in presence of heterogeneous catalysts, when necessary, attach environmental value to the synthetic procedures described in this paper.

CeO_2 loaded with either Al_2O_3 [CeO_2/Al_2O_3] or Nb_2O_5 [CeO_2/Nb_2O_5] were used as catalysts for the direct carboxylation of glycerol in a biphasic system, while TS1 was used in the reaction of glycerol with urea. All the heterogeneous catalysts can be easily recovered and re-used.

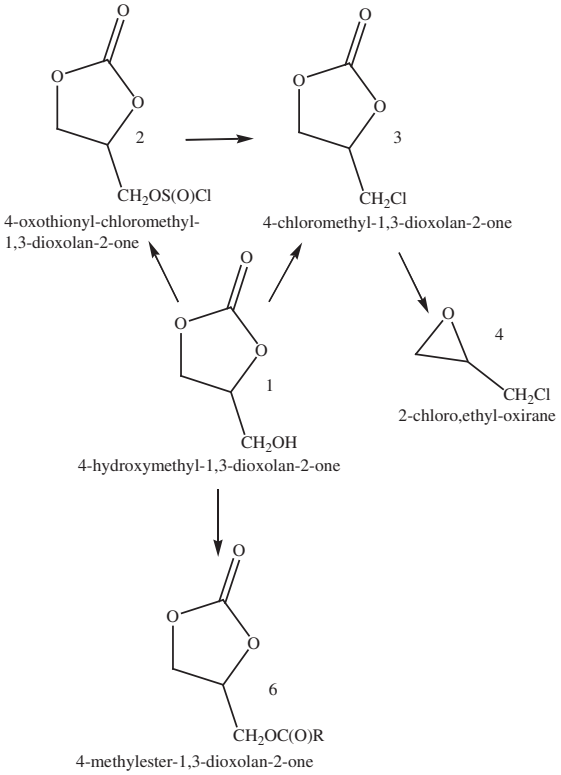
The CeO_2-based catalysts, that we have found to be active in the carboxylation of methanol and ethanol[13,14] afforded a good performance also in the direct carboxylation of glycerol in a biphasic system using tetra(ethylenglycol)dimethylether-TEGDME as solvent under 5 MPa of CO_2. The conversion yield is much better than that found when $^nBu_2Sn(OMe)_2$ was used as catalyst.[7a] We have also used the same conditions described in a report in the literature[7b] saying that glycerol in the presence of methanol is carboxylated to a 32% conversion at 353 K using the catalyst described in our work.[7a] Indeed, using such conditions with either the tin catalyst[7] or using the CeO_2-based catalysts described here, neither glycerol nor methanol were carboxylated in a detectable amount. As a matter of fact, if glycerol is heated at 353 K under a CO_2 pressure of 1.8 MPa, glycerol carbonate is not observed at all: a much higher temperature is needed for its conversion, that is, observed only above 453 K.

The use of urea as carbonylating agent instead of CO_2 improves the thermodynamics of the reaction, as urea can be considered an activated form (ΔG=−334 kJ/mol) of CO_2 (ΔG=−395 kJ/mol). TS1 is quite active in catalysing such reaction to afford **1** very selectively with a ca. 60% conversion of glycerol. The catalyst shows a good recoverability under the reaction conditions at least for a few cycles. After four–five cycles the catalyst starts to be slowly micro-pulverized because of mechanical stresses, that may cause a slight loss of TS1.

Such routes of conversion of glycerol represent an extension of our previous findings and add new opportunities to the tool-box for the carboxylation of glycerol in the absence of phosgene and other organic carbonates.

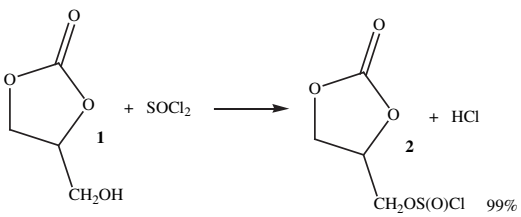
Avoiding the use of phosgene, a highly toxic agent banned in several countries, brings a good deal of safety to the chemical industry. Concerning the organic carbonates, it must be emphasized that they are prepared from phosgene (acyclic carbonates) or from epoxides (cyclic carbonates). The availability of the latter is linked to the market of hydrogen peroxide (all other routes being strongly polluting).[14b]

Glycerol carbonate obtained in such phosgene-free and organic-carbonate-free routes has been cleanly converted into a few derivatives, as reported below. Scheme 2 shows the compounds obtained in this work through the functionalization of the hydroxymethyl moiety $-CH_2OH$ of **1**. Of particular interest is the synthesis of epichlorohydrin, that is, carried out under mild and very selective conditions.



Scheme 2. Products of functionalization of glycerol carbonate.

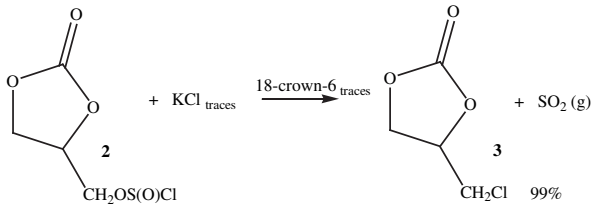
4-Oxothionylchloromethyl-1,3-dioxolan-2-one (**2**, Scheme 2) is a new compound, never described in the literature. It is a pale yellow, irritating liquid. This compound, differently from the starting carbonate, does not form hydrogen bonds. Its decomposition temperature (at 0.1 MPa) is 383 K. The surface tension (71.8 dyn/cm^3) and the density (1.73 g/cm^3) are higher than those of glycerol carbonate (44.1 dyn/cm^3 and 1.42 g/cm^3, respectively). Compound **2** was synthesised through a direct thio-chlorination of glycerol carbonate (Scheme 3) with >98% yield.



Scheme 3. Thio-chlorination of glycerol carbonate.

The reaction needs to be carried out very carefully at 315 K and under a nitrogen flow so as to avoid the formation of 4-chloromethyl-1,3-dioxolan-2-one and to assist the elimination of the hydrogen chloride formed. Compound **2** was isolated and characterized by mass spectrometry (see Experimental section) and ^{13}C NMR (Fig. 1). A signal at 154.5 ppm is attributed to the carbonylic-C and the signals at 73.2, 66.6 and 63.3 ppm are due to C4, C6 and C5, respectively.

Compound **2** is moisture sensitive and after exposure to moist air its ^{13}C NMR and FTIR spectra, show (Fig. 2) that it cleanly and quantitatively back-converts into **1**.



Scheme 5. Reaction of desulfurization of **2** to afford **3**.

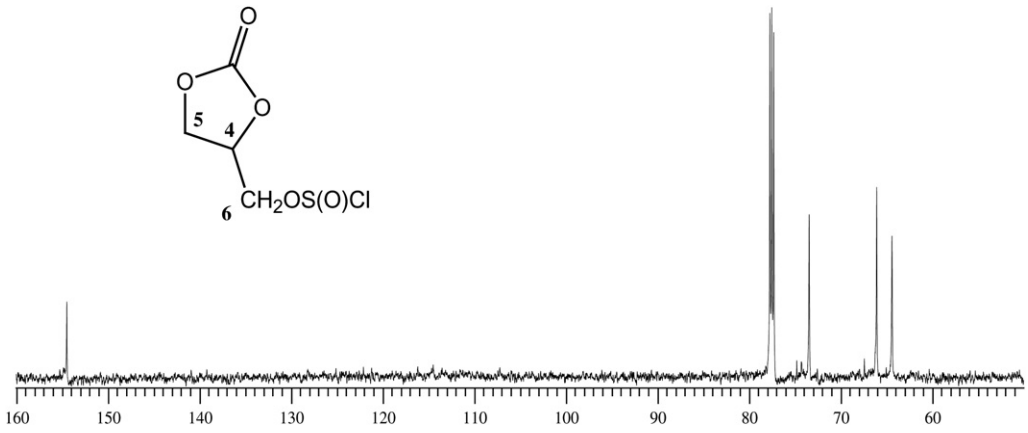


Fig. 1. $\{^1H\}-^{13}C$ NMR (100 MHz, CD_3Cl) spectrum of **2**.

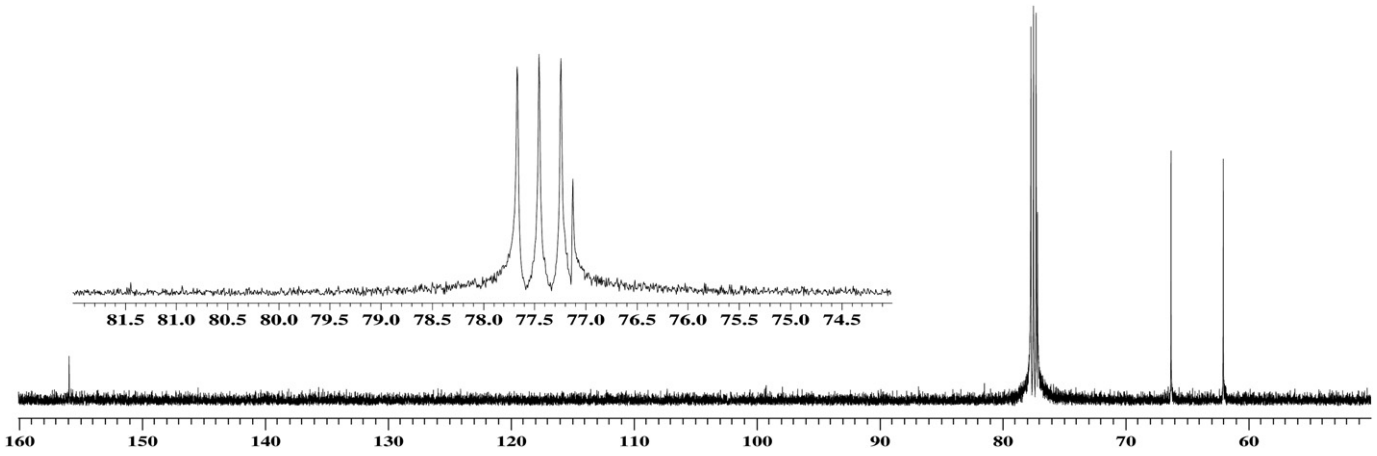
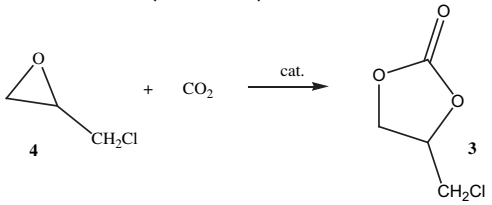


Fig. 2. $\{^1H\}-^{13}C$ NMR (100 MHz, CD_3Cl) spectrum of **2** after exposure to air: **2** is converted back to **1**.

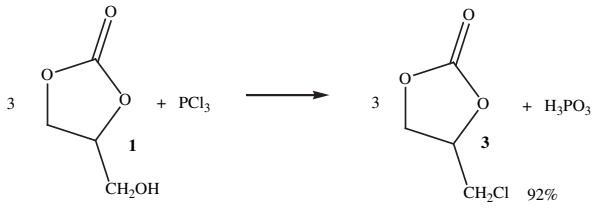
Compound **2** can be advantageously used for the synthesis of compounds, such as 4-chloromethyl-1,3-dioxolan-2-one **3**, that is, a good intermediate for organic syntheses.[15]

The synthesis of the latter is presently mainly based on the cycloaddition of carbon dioxide to epichlorohydrin **4** (Scheme 4),[16] that requires the preliminary synthesis of **4**, obtained by high temperature oxo-chlorination of propene followed by further work-up with $Ca(OH)_2$ at 373 K[17]

In order to avoid complex synthetic procedures that are not selective, we synthesised **3** by desulfurization of **2** (Scheme 5) or by direct chlorination of **1** (Scheme 6).



Scheme 4. Carboxylation of epichlorhydrin.

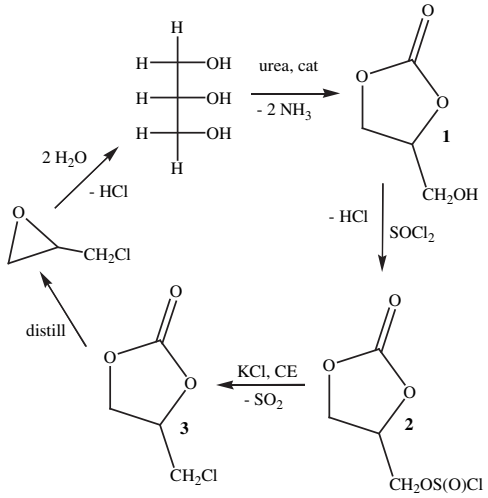


Scheme 6. Direct chlorination of glycerol carbonate to afford **3**.

Both reactions proceed with a >92% yield. In particular, the desulfurization of **2** was carried out with a >99% yield and in milder conditions than those used for the carboxylation of the epichlorohydrin. The catalytic use of KCl and crown-ether (<1%) make the desulfurization reaction very clean and fast also under mild conditions (298 K and 0.1 MPa). The formed SO_2 can directly be removed from the reaction medium with a nitrogen flow and condensed at low temperature (and eventually re-used).

If the direct chlorination of **1** is made using PCl_3, **3** can be separated from the formed phosphoric acid by using toluene that selectively extracts **3**.

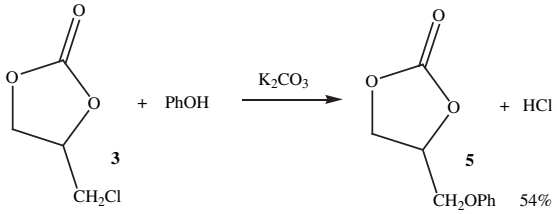
Interestingly, starting from **3** we easily obtained **4** by distillation under vacuum at 353 K with an almost quantitative yield. The overall conversion yield of glycerol into epichlorohydrin is close to 70%. This route based on glycerol, that is, converted into the carbonate using urea (Scheme 7), represents an interesting alternative synthetic methodology for epichlorohydrin, that is, a colourless highly reactive compound used in the production of plastics, elastomers and epoxy resins.[18]



Scheme 7. Reaction-chain for the synthesis of epichlorohydrin from glycerol.

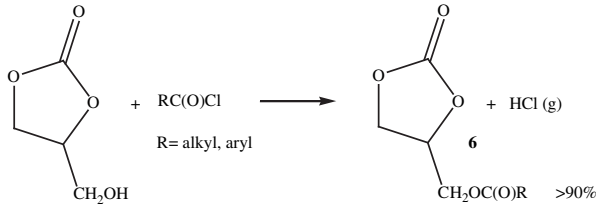
Interesting classes of compounds obtained from glycerol carbonate are ethers[19,20] and esters[21–23] that find application as intermediates for pharmaceuticals.[19]

Compound **3** can be easily converted into the relevant phenoxyl ether (Scheme 8) with a 54% yield of conversion that represents an improvement of the routes reported in the patent and scientific literature[19,20] that are based on the reaction of CO_2 and epoxides. In the latter processes the catalyst always contaminates the product.



Scheme 8. Etherification of 4-chloro glycerol carbonate.

The esters of cyclic carbonates find application in demolding thermoplastic polycarbonates[21] or in urethane coatings.[22] The main synthetic approach for esters is based on the reaction of CO_2 with substituted epoxides[23] or on the reaction of the –OH moiety of the carbonate with Ac_2O.[22] We have performed the esterification of glycerol carbonate with different acyl chlorides (Scheme 9) or



Scheme 9. Esterification of glycerol carbonate.

anhydrides under very mild conditions and often with an almost quantitative conversion.

The results reported in the Experimental section demonstrate that, will the nucleophile being the same in all reactions, the steric and electronic factors of the reagents play a prominent role, but the conversion yield is always >92%. The acyl chlorides show a higher activity compared to aroyl chlorides, which is what one expects considering the electronic factors. In the alkylic series, this factor was overturned from **6c** to **6d** because of the steric hindrance of the dimethyl moiety in **6d**. All the isolated ester species, were fully characterized and stable in the air.

3. Conclusions

New catalysts active in the carboxylation of glycerol to glycerol carbonate are described using heterogeneous catalysts. The carbonate obtained with the exclusion of the use of phosgene or other organic carbonates (often prepared from phosgene or using epoxides that require hydrogen peroxide for their synthesis) have been converted into known or new compounds. In this way, molecules, such as epichlorohydrin, which may have a large application, were obtained by using simple and safe synthetic routes. All the reactions described in this paper require very simple manipulations and are characterized by a very high yield (often almost quantitative) and 100% selectivity. These processes open the way to new synthetic methodologies, which do not require either phosgene or epoxides and use two wastes, such as the abundant glycerol and carbon dioxide as starting material for the synthesis of several chemicals.

4. Experimental section

4.1. Chemical reagents

All reagents and solvents were RP grade purchased by Aldrich. Starting glycerol carbonate was prepared as reported in Ref. 1. The infrared spectra were obtained using a SHIMADZU IR Prestige 21 spectrometer placing the sample between KBr disks, neat or dispersed in Nujol. The reaction liquid and/or gas products were analyzed using a gas chromatograph HP 6850 series equipped with a capillary column ZB-WAX (30 m×0.25 mm) and with a flame ionization detector. The gas-mass analyses were conducted with a GC–MS Shimadzu QP5050 equipped with the same column as the gas chromatograph. The ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker spectrometer operating at 600 MHz with deuterated toluene (C_7D_8), deuterated chloroform ($CDCl_3$) or deuterated methylene chloride (CD_2Cl_2) as solvent and tetramethylsilane (TMS) as the internal reference at 298 K. TS1 was a gift of ENI-IT.

Surface characterization was carried out using Pulse Chemisorb Micrometrics 2750 Instrument. The acid and basic sites of the catalysts were determined by TPD of NH_3 and CO_2, respectively. BET surface analyses were performed using a 30%N_2/70%He gas mixture.

4.2. Synthesis of CeO_2/Al_2O_3 and CeO_2/Nb_2O_5

These mixed oxides were synthesised as reported in Refs. 13a,b. Below we report the acid/base properties and the BET surface of the calcinated catalysts (2 h at 823 K).

Catalyst: Al_2O_3/CeO_2[13a]
BET: 81 m^2/g
Acid/basic sites ratio: 0.53
Catalysts: Nb_2O_5/CeO_2[13b]
BET: 36 m^2/g
Acid/basic sites ratio: 1.09

4.3. Direct carboxylation of glycerol in TEGDME using modified-ceria catalysts

Glycerol (4 g, 43 mmol) were transferred into a conditioned reactor together with tetra(ethylene glycol)dimethyl ether-TEGDME (10 mL) and mixed oxide (ca. 20 mg) in order to have a catalyst/glycerol ratio equal to 0.3% in mol. The reactor was placed in a stainless steel autoclave charged with 5 MPa of CO_2. The reaction was carried out for 15 h at 453 K under stirring.

At the end of the reaction, the organic phase was analyzed with a gas chromatograph using biphenyl ether as internal standard. The catalyst was recovered by filtration, washed with methanol, dried at 423 K for 15 min and used again in a new reaction cycle. The same catalyst was recycled at least three times without any loss of activity. The conversion of glycerol into glycerol carbonate was equal to 2.5% with an apparent TON of 8 in each of the three consecutive cycles of reaction. After a few cycles a total conversion of 10% glycerol was observed. This value is higher than that obtained using heterogenized Sn-catalysts.[7a]

The addition of methanol[7b] did not improve the conversion of glycerol also at 453 K. Lower yields were observed at lower temperature. No reaction was observed at all below 400 K, in presence or absence of methanol. This is in line with the fact that the direct synthesis of dimethylcarbonate from methanol and CO_2 is observed only at 413 K.

4.4. Reaction of glycerol with urea using TS1 as catalyst

The catalyst TS1 was preliminarily calcinated for 3 h at 773 K. Glycerol (5.1087 g, 55 mmol), powdered urea (1.6521 g, 27.5 mmol) and the catalyst (0.0318 g) were placed in the reactor. A vacuum system (20 Pa) for the removal and capture of ammonia during the reaction was connected to the head of the reactor. The reaction was allowed to proceed for 3 h at 418 K under stirring after which the reactor was cooled to room temperature. Glycerol carbonate was extracted using CH_3CN in which neither glycerol nor urea was soluble and analyses were performed by gas chromatography, FTIR and NMR on the extracts. The conversion of glycerol into glycerol carbonate was equal to 58%. This reaction was also performed using a 1/1 glycerol/urea molar ratios, with a 3% w/w catalyst. The glycerol conversion yield was 36%. In order to optimize the glycerol use, a glyecrol/urea molar ratio as close as possible to 1 was used by adopting a technique in which starting with a 2:1 glycerol/urea molar ratio, urea was slowly added over 3 h until a 1/1 M ratio was reached.

The glycerol conversion yield was monitored to be close to 60% with 100% selectivity.

4.5. Synthesis of 4-oxothionylchloromethyl-1,3-dioxolan-2-one, 2

Thionyl chloride (3 mL, 41.20 mmol) were placed in a three-necked flask equipped with a condenser under a nitrogen flow and 4-hydroxymethyl-1,3-dioxolan-2-one (1 mL, 11.86 mmol) was added dropwise with stirring. A trap of triethylamine for the neutralization of hydrogen chloride formed during the reaction was placed on the top of the condenser. The addition of carbonate was carried out at room temperature and the reaction was allowed to proceed for 1 h after the addition was completed. The excess of thionyl chloride was eliminated under vacuum at 40 °C and recovered and the final liquid was analyzed by gas chromatography, mass spectrometry and ^{13}C NMR and shown to be pure **2** (2.36 g, 99.1%).

^{13}C NMR (C_7D_8, 100 MHz): δ=154.5, 73.2, 65.6, 63.3 ppm attributed as in Fig. 1. Anal. Calcd for $C_4H_5ClO_5S$: C, 23.94; H, 2.59; Cl, 17.68; O, 39.90; S, 15.99. Found: C, 23.88; H, 2.65; Cl, 17.61; S, 15.65. MS: *m*/*z* 87 (loss of CH_2Cl), 57 (loss of Cl and CO_2), 49 (CH_2Cl^+), 43 (loss of CO_2 from fragment 87), 29 (CHO^+ derived from fragment 57).

4.6. Synthesis of 4-chloromethyl-1,3-dioxolan-2-one, 3 by desulfurization of 2

To liquid 4-oxothionylchloromethyl-1,3-dioxolan-2-one (1.84 g, 11.75 mmol), toluene (solvent, 3 mL), crown-ether 18-crown-6 (152.20 mg, 0.576 mmol) and KCl (49.40 mg, 0.576 mmol) were added. The suspension was heated for 3 h at 60 °C in a system that allowed the removal of the formed SO_2. The conversion of the sulfonyl chloride into the chloromethyl derivative was >99%.

The liquid phase was separated from KCl and CE by filtration. The final liquid was evaporated in vacuum at 20 °C so to remove toluene. The residual liquid was analyzed by gas chromatography, mass spectrometry and ^{13}C NMR and shown to be pure **3**.

^{13}C NMR (C_7D_8, 100 MHz): δ=155, 75, 67, 44.8 ppm attributes to C2, C4, C6 and C5, respectively. Anal. Calcd for $C_4H_5ClO_3$: C, 35.19; H, 3.67; Cl, 25.95; O, 35.19. Found: C, 35.06; H, 3.60; Cl, 25.75%. MS: *m*/*z* 87 (loss of CH_2Cl), 57(loss of C1 and CO_2), 49 (CH_2Cl^+), 43 (loss of CO_2 by fragment 87), 29 (CHO^+ derived by the fragment 57).

4.7. Synthesis of 4-chloromethyl-1,3-dioxolan-2-one, 3 by direct chlorination of 1

To a solution of 4-hydroxymethyl-1,3-dioxolan-2-one (2.10 g, 17.78 mmol) in CH_2Cl_2 (5 mL), the stoichiometric amount of PCl_3 according to Scheme 6 (0.81 g, 5.93 mmol) was added dropwise and the reaction was allowed to proceed at 40 °C for 3 h. At the end of the reaction the product was extracted with toluene (3×3 mL), toluene was evaporated in vacuum at 20 °C and the remaining liquid (2.23 g, 92% of 4-chloromethyl-1,3-dioxolan-2-one) was analyzed by gas chromatography, mass spectrometry and ^{13}C NMR and shown to be pure **3**.

Anal. Calcd for $C_4H_5ClO_3$: C, 35.20; H, 3.66; Cl, 25.97; O, 35.17. Found: C, 35.1; H, 3.60; Cl, 25.90. The GC–MS and NMR data obtained were the same as for the compound obtained in the previous reaction.

4.8. Synthesis of 2-chloromethyloxirane, 4 by decarboxylation of 2

4-Chloromethyl-1,3-dioxolan-2-one obtained as described in the reactions above was subjected to a vacuum distillation at 80 °C. The distilled fraction was analyzed by infrared spectroscopy, mass spectrometry and nuclear magnetic resonance. The conversion of **2** into **4** was >99%.

IR: ν_{max}/cm^{-1} 3063m, 3004s, 2963m, 2926m, 1519w, 1480m, 1448m, 1433s, 1398s, 1277s, 1267s, 1266s, 1209w, 1137w, 1092w, 962s, 927s, 906m, 854s, 844s, 836s, 761s, 738s, 723s, 696m, 444m. ^{13}C NMR ($CDCl_3$, 100 MHz) 51.3, 46.9, 45.5. MS: *m*/*z* 94 (mol. ion+2), 92 (mol. ion), 57 ($CH_2(O)CHCH_2^+$), 51 (CH_2Cl^+), 49 (CH_2Cl^+), 64 (−CO), 28 (CO^+).

4.9. Synthesis of 4-phenoxymethyl-1,3-dioxolan-2-one, 5

4-Chloromethyl-1,3-dioxolan-2-one (1.1223 g, 7.38 mmol) in CH_2Cl_2 (4 mL), phenol (0.6948 g, 7.38 mmol) and an excess of K_2CO_3 were placed in a flask under a nitrogen flow. The reaction was carried out for 3 h under reflux. At the end of the reaction the excess of the potassium carbonate was removed by filtration and the obtained solution was analyzed by ^{13}C NMR. The solvent was eliminated under vacuum and elemental analyses were performed on the residual liquid (0.77 g, 54%).

^{13}C NMR ($CDCl_3$, 100 MHz): δ=162.7 (C_1 Ph), 155.4 (–CO), 129.3 (C_3 Ph), 124.1 (C_4 Ph), 118.2 (C_2 Ph), 74.2 (C_4 glycerol carbonate moiety), 66.6 (C_6 glycerol carbonate moiety), 63.7 (C_5 glycerol carbonate moiety). Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.15; O, 32.99. Found: C, 61.06; H, 5.04.

4.10. Synthesis of 4-methylbenzoate-1,3-dioxolan-2-one, 6a

4-Hydroxymethyl-1,3-dioxolan-2-one (1.1613 g, 9.83 mmol) in CH_2Cl_2 (4 mL) were placed in a flask under a dinitrogen flow. Benzoyl chloride (1.38 g, 9.83 mmol) were added and the reaction allowed to proceed for 3 h under reflux while the formed HCl was stripped away and trapped in a KOH water solution (1.90 g, 87%).

The final pure product (100% selectivity and 99% chromatographic yield) was isolated by column chromatography (the column was packed with silica and chloroform/toluene=1/1 was used as eluent) with a 92% yield.

The collected fractions were concentrated under vacuum and a white powder was obtained, which was characterized by elemental analyses, FTIR, ^{1}H and ^{13}C NMR.

IR: ν_{max}/cm^{-1} (in the range 1800–700): 1790s, 1705s, 1597m, 1475m, 1463m, 1452m, 1400m, 1319m, 1270m, 1252m, 1180s, 1175m, 1081s, 1025m, 1033m; 984m, 866m, 808w, 767m, 702s; ^{1}H NMR ($CDCl_3$, 600 MHz): δ=8.01, 7.55, 7.66 (5H, Ph), 4.61, 4.36 (2H, CH_2), 4.79, 4.28, 4.23 (3H, cyclic carbonate); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=166.4 (CO ester), 155.3 (CO carbonate), 134.3 (C_4 Ph), 132.8 (C_1 Ph), 130.0 (C_2 Ph), 128.7 (C_3 Ph), 74.2, 66.6, 63.7 (C_4, C_6 and C_5 of glycerol carbonate moiety, respectively). Anal. Calcd for $C_{11}H_{10}O_5$: C, 59.46; H, 4.50; O, 36.04. Found: C, 59.2; H, 4.50.

4.11. Synthesis of 4-phenylacetate-1,3-dioxolan-2-one, 6b

Following the same procedure reported in Section 4.10, 4-phenylacetate-1,3-dioxolan-2-one was synthesised from **1** and phenylacetyl chloride with a 92% isolated yield (99% GC-conversion, 100% selectivity).

^{13}C NMR ($CDCl_3$, 100 MHz): δ=172.2 (CO ester), 155.3 (CO carbonate), 136.1 (C_1 Ph), 130.4 (C_2 Ph), 129.4 (C_3 Ph), 127.6 (C_4 Ph), 74.2, 66.6, 63.7 (C4, C6 and C5 of the glycerol carbonate moiety, respectively), 39.7 ppm (CH_2 benzyl). Anal. Calcd for $C_{11}H_{12}O_5$: C, 61.02; H, 5.08; O, 33.90. Found: C, 60.95; H, 5.05.

4.12. Synthesis of 4-methylacetate-1,3-dioxolan-2-one, 6c

4-Hydroxymethyl-1,3-dioxolan-2-one (1.2233 g, 10.35 mmol) in CH_2Cl_2 (4 mL) were placed in a flask under a dinitrogen flow. Acetyl chloride (0.81 g, 10.35 mmol) were added and the reaction allowed to proceed for 1.5 h under reflux with HCl trapping, as described above (1.62 g, 98%). The solvent was eliminated under vacuum and a pale yellow liquid was obtained, which was characterized by elemental analyses, FTIR and ^{13}C NMR as pure ester (100% GC-conversion, 100% selectivity; 98% isolated yield).

IR: ν_{max}/cm^{-1} (in the range 1800–700): 1792s, 1714s, 1481w, 1398s, 1294s, 1280w, 1180s, 1087s, 1053s, 935m, 856w, 775m, 717m. ^{1}H NMR ($CDCl_3$, 600 MHz): δ=2.04 (3H, CH_3), 4.61, 4.33 (2H, CH_2), 4.82, 4.36 and 4.19 (H, glycerol carbonate moiety); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=171.0, 155.4, 74.5, 67.0, 63.7, 21.1. Anal. Calcd for $C_6H_8O_5$: C, 45.0; H, 5.0; O, 55.0. Found: C, 45.1; H, 5.0.

4.13. Synthesis of 4-dimethylacetate-1,3-dioxolan-2-one, 6d

4-Dimethylacetate-1,3-dioxolan-2-one was synthesised in the same way as reported in 4.10 from **1** and isobutyryl chloride with 84% isolated yield (>98% GC-conversion and 100% selectivity).

^{13}C NMR (CD_2Cl_2, 100 MHz): δ=174.0, 151.5, 74.5, 66.0, 63.7, 35.5, 18.2. Anal. Calcd for $C_8H_{12}O_5$: C, 51.06; H, 6.38; O, 42.56. Found: C, 51.0; H, 6.25.

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