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Glycidol syntheses and valorizations: boosting the glycerol biorefinery

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Glycidol syntheses and valorizations: boosting the glycerol biorefinery

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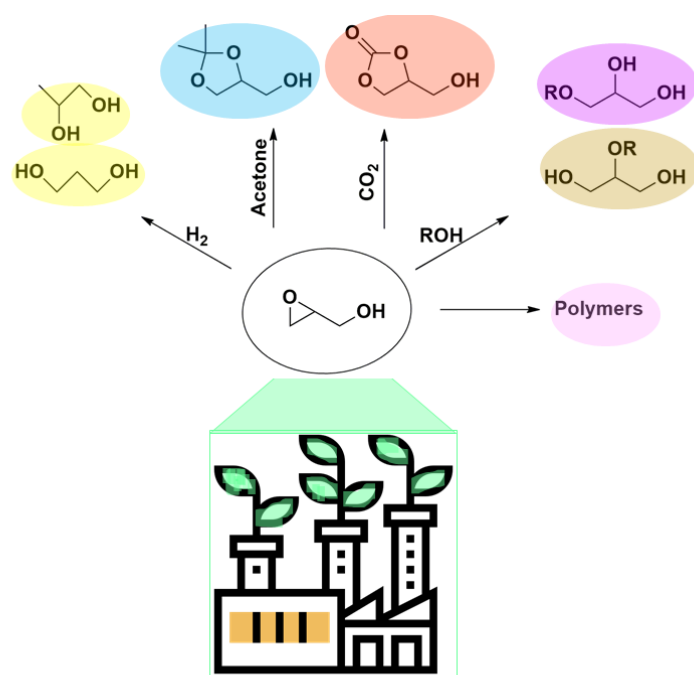
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Glycerol biorefinery

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1 **Abstract**

2 The synthesis of bio-based functional molecules and their further conversion to value-added products
3 are among the most investigated research fields within the green chemistry community. In this work,
4 we review the preparation of bio-based glycidol and its use as starting material for other chemicals.
5 Herein, we discuss the catalytic approach for the synthesis of several classes of glycidol-derived
6 organics characterized by relevant industrial applications. In detail, glycidol conversion to 1,2 and
7 1,3-propanediol, glycerol carbonate, solketal, monoalkyl glyceryl ethers and polymers is reported and
8 future perspectives in this context are proposed.

9

10 **Keywords:** glycidol; waste valorization; catalysis; life cycle assessment; green chemistry.

11

12 **Highlights:**

- 13 - Bio-based reaction pathways for glycidol preparation are reviewed
- 14 - Glycerochemistry as a valuable example of the 7th principle of green chemistry
- 15 - Glycidol conversion into value-added chemicals is discussed

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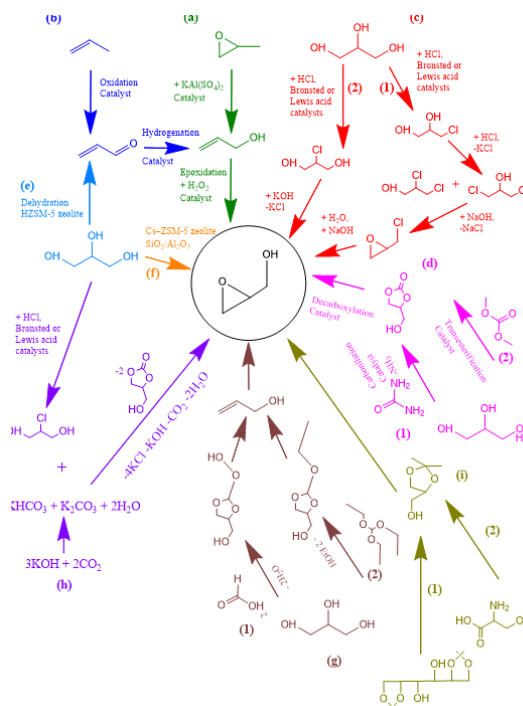
1. Synthetic pathways for glycidol preparation

The use of biobased building block for the preparation of chemicals is one of the 12 principles of green chemistry developed by Anastas and Warner [1] and to date one of the major investigated research fields within the green chemistry community [2–6]. Glycerol valorization through catalysis (glycerochemistry) represents a valuable example with several repercussions at industrial level [7]. Among glycerol derivatives, following the benign-by-design approach [8,9], we recently proposed the preparation of glycidol. Glycidol (2,3-epoxy-1-propanol) is a versatile molecule with high reactivity due to oxiranic and alcoholic functionalities. Tab.1 collects the main chemical-physical properties.

Table 1. Glycidol chemical-physical properties.

Its current market value reaches USD 20 per kg [10], with a global size over USD 130 million (2019) and an expected projection up to USD 180 million in 2026 [11]. Glycidol market is segmented by purity grades, among those 96% will dominate (with more than USD 67 million by 2026 [11]) due to its applications in laundry detergents, disinfectants and cosmetic preparations. In addition, glycidol increasing usage in skin creams, moisturizing lotions and shampoos may raise its demand in the next few years [11]. Glycidol importance is also highlighted by the development of new laboratory pilot scale plant. Green Lizard Technologies has introduced a two-stage production pathway for producing glycidol from glycerol carbonate. They are proceeding with scaling up the technology to achieving 100kg/day production [12]. Further details on initiatives, process conditions and technologies were published in a recent review [10].

1 Glycidol preparation from biomass, instead its fossil-based production, and its further conversion to
 2 value-added products could represent viable opportunities to boost the glycerol biorefinery.



3 **Figure 1.** Main synthetic routes for glycidol preparation.

4 Figure 1 summaries the main routes for obtaining glycidol. Two are the most diffused syntheses
 5 worldwide. First, allyl alcohol (AA) epoxidation with H_2O_2 and tungsten oxide/salts of tungstic
 6 acid [13] or TS-1 [14,15] as catalytic system. TS-1 leads to 47% conversion with a glycidol
 7 selectivity of 92.5% [16]. AA is generally fossil-based, obtained from propylene (Fig. 1-a) or
 8 propylene oxide (Fig 1-b). The second route use bio-based glycerol as raw material, a platform
 9 molecule with a market projected to reach 4 Mt by 2027 (Global Industry Analysts Inc., 2021).
 10 Glycerol is chlorinated with gaseous HCl in the presence of Brønsted or Lewis acid catalysts [17–
 11 19] (Fig 1-c2). This alternative was developed to enhance the environmental sustainability of the
 12 Epicerol® process, method patented by Solvay to produce bio-based epichlorohydrin (ECH)
 13 [20,21]. ECH plays a great importance worldwide (around 2.2 Mt y^{-1} and 1.8–2.5 US\$ per kg
 14 [10]) given its usage as (co-)monomer (in the preparation of epoxy resins) and intermediate in the
 15 manufacture of other polymers. Within the Epicerol® process, 2-chloro-1,3-propanediol (β -MCH)
 16 stream is recovered and treated using an alcoholic solution of KOH at room temperature with high

yield (90%) and selectivity (99%) [17]. ECH can also be used as a platform molecule to synthesize glycidol through a first dehydration to 3-chloro-1,2-propanediol (α -MCH) (recently used for glycidol preparation via dehydrogenation using bipolar membrane electrodialysis [22]) and then a treatment with NaOH (Fig 1-c1). These latter routes (Fig. 1-c1 and c2) have substituted the main bio-based synthesis used before the concretization of the green chemistry principles [1] worldwide. They implied the conversion of D-mannitol (Fig. 1-i1) or L-serine (Fig. 1-i2) into solketal by adopting strong reaction condition (NaBH_4 , $\text{Pb}(\text{CH}_3\text{COO})_4$, LiAlH_4 , etc.;) [23]. The production of glycidol via glycerol carbonate (GC) intermediate was also investigated. This is a two-step reaction: first GC synthesis and then its decarboxylation into glycidol and CO_2 [24]. Synthesis of GC may be carried out with carbamide [24,25] (Fig. 1-d1) or dimethyl carbonate [26–29] (Fig. 1-d2) in a liquid-phase over heterogeneous catalysts. However, to reduce reaction steps and time, by avoiding high catalyst price and pressure, Kostyniuk et al. (2020) [30] proposed a gas-phase conversion of glycerol into glycidol in one-step over Cs–ZSM-5 zeolite catalyst with $\text{SiO}_2/\text{Al}_2\text{O}_3$ by achieving a maximum yield of 40.4 mol% (Fig.1 1-f). Despite that AA is mainly fossil-based, it can be obtained also from bio-based glycerol in a three stages conversion, with a first dehydration to acrolein over an acidic catalyst such as HZSM-5 zeolite (Fig. 1-e) [31,32]. The conversion of glycerol into AA was also proposed by Tshibalonza and Monbaliu (2017) [33,34] who implemented the classical deoxydehydration towards AA by combining continuous-flow conditions in a microfluidic continuous-flow reactor and a dynamic reactive feed solutions by mixing glycerol with formic acid (Fig. 1-g1), triethyl orthoformate (TEOF, Fig.1 1-g2), or a combination of both. Best results (86% yield) were achieved by mixing glycerol, TEOF (1 equiv.) and formic acid (10 mol%) at 250°C. Monbaliu et al. (2019) [35] discussed the glycerol upgrading to a mixture of glycidol and ECH using a two-step continuous flow setup. The first step involves the hydrochlorination reaction and allows the rapid generation of chlorohydrins using concentrated aqueous hydrochloric acid and pimelic acid as catalyst. The second step relies on the dechlorination of the chlorohydrins in the presence of a concentrated aqueous solution of

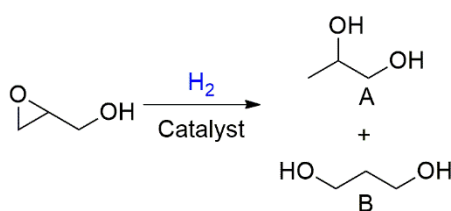
NaOH. Both steps are directly concatenated and are further improved with the addition of an extraction unit to favour the separation between glycidol and ECH. Literature also reports an indirect solvent-free synthesis for obtaining GC and glycidol from glycerol and CO₂ (Fig. 1-h) through the reaction of β -MCH and potassium (hydrogen) carbonate [36]. An 80% GC yield together with a production of 0.56 mol glycidol/mol GC were obtained with 3:1 β -MCH/K₂CO₃ molar ratio at 80 C° per 30 min. This alternative could be integrated with direct capture from air or into industries with intensive carbon emission (both biogenic and fossil).

2. Glycidol conversion to value-added chemicals

2.1 1,2 and 1,3-propanediols

An investigated route for glycidol conversion is the hydrogenolysis to propanediols (1,2-propanediol (1,2-PD) and 1,3-propanediol (1,3-PD)) as depicted in Fig.2. 1,2-PD finds application as precursor of polyethers, propylene [37], unsaturated polyester resins while 1,3-PD is an important monomer in the synthesis of polypropylene terephthalate and polyesters [38]. Only few studies reported on the efficient and selective conversion of glycidol to 1,2-propanediol. Sajiki and his group achieved 89% conversion of glycidol to 1,2-PD with 100% selectivity using Pd/C-ethylenediamine complex in methanol using H₂ pressure of 1 bar [39]. Recently, glycidol hydrogenolysis has been investigated [40] using various supported metals as heterogeneous catalysts under mild reaction conditions (80°C, 8 bar of H₂, ethanol as solvent). In this study, total conversion and selectivity of 99.2% towards 1,2-PD were achieved in 6 h. The catalytic productivity of Pd/C was improved by the use of the acidic resin Amberlyst-15 that permits to reach a TOF value of 162 h⁻¹. 1,2-PD is obtained with high yields and selectivity (> 99%) in only 1 h under mild reaction conditions. The catalytic system (Pd/C + Amberlyst-15) shows also a good recyclability also after seven reaction cycles reaching high performances in term of conversion and selectivity [41]. Catalytic hydrogenolysis of glycidol to 1,3-propanediol has been investigated with different heterogeneous catalytic systems based on non-noble metals. Gebretsadik et al. [42] used a Ni-based

1 catalyst supported on an acid mesoporous saponite for this reaction. The effect of Ni loading was
 2 investigated , and the authors reported 29% of conversion using 40% wt Ni and a selectivity (1,3-
 3 PD/1,2-PD = 0.97) comparable to that obtained with noble-metal based catalysts at higher
 4 temperatures and for longer times; furthermore, Ni- and Cu-based mono- and bi-metallic catalysts
 5 modified with different acid oxides MO_x (M=Mo, V, W, and Re) were used to modulate the acidity
 6 of the catalyst [43]. Herein, the best results (46% yield of 1,3-PD and a 1,3-PD/1,2-PD ratio of 1,24)
 7 were reported in the presence of monometallic Ni catalyst at 40% wt modified with 7% wt Re.
 8 The same group, investigated a Ni-Cu alloy based catalytic system and observed that the presence of
 9 an appropriate amount of Cu allowed the control of the hydrogenation capacity of Ni favouring the
 10 formation of 1,3-propanediol. [44] Recently, Sun et al. [45] developed a carbon film encapsulated
 11 Co nanoparticle catalyst for glycidol hydrogenolysis to 1,3-PD characterized by high productivity
 12 and selectivity towards 1,3-PD (50,4% of 1,3-PD obtained at 140 °C, 2 MPa H_2 and 4 h).



Main results

<i>Sajiki et al 1999</i> ^[31]	<i>Cucciniello et al 2017</i> ^[33]	<i>Gebretsadik et al 2017</i> ^[35]	<i>Sun et al 2019</i> ^[37]
Catalyst = Pd/C(en)	Catalyst = Pd/C; Amberlyst-15	Catalyst = NiCu (6:1)/S	Catalyst = Co@NC
Load 10% wt	Load 10% wt; 1% wt	Load 24% wt	Load 10% wt
1 atm H_2	8 bar H_2	50 bar H_2	20 bar H_2
t = 22 h	t = 1 h	t = 4 h	t = 4 h
Yield = 89 %; A = 100 %	Yield = 100 %; A = 100 %	Yield = 77 %; B = 17 %	Yield = 43 %; B = 50 %

Figure 2. Glycidol hydrogenolysis to 1,2 and 1,3-propanediols.

2.2 Glycerol carbonate and solketal

17 Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one; GC) is one of the most valuable molecules
 18 for the possibility to be used as a solvent, lubricant, coating agent and ingredient in

1 pharmaceutical/personal care. In addition, thanks to its chemical structure, it serves as building block
2 in organic and polymer chemistry [46–49].

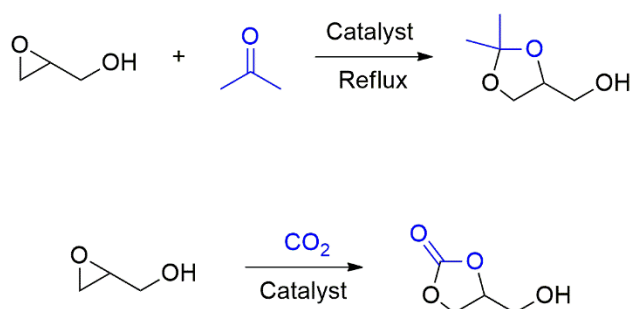
3 The cycloaddition of CO₂ to glycidol is potentially a 100% atom economical and environmentally
4 friendly way to produce GC (see Fig.3).

5 A major advance in this field was achieved in the 2016 when Capacchione et. al. first observed that
6 the reactivity of glycidol in the presence of tetrabutyl ammonium bromide (TBAB) is exceedingly
7 higher compared to propylene oxide (PO) and methyl-glycidyl ether as substrate [50] . In particular
8 using 5 mol% of TBAB at 60 °C and 1 MPa of CO₂ pressure it was possible to convert in a virtually
9 quantitative yield to GC. Under the same reaction conditions PO is converted to PC only in 4% yields.
10 Such peculiar behavior was clearly due to the presence of the hydroxy functionality in the glycidol
11 molecule. DFT calculation show that the presence of these dimers, formed via hydrogen-bond, is the
12 keystone for the facile obtaining of GC from glycidol.

13 In the same year the group of Kleij reported on the halide free conversion of glycidol to GC catalyzed
14 by the aluminum aminotriphenolate catalyst. Also, in this case the presence of the hydroxy group was
15 pivotal to explain the reaction pathway. In fact, the hydroxy group is involved in the activation of
16 CO₂ trough the formation of a transient hemi-carbonate that can open the oxirane ring by forming
17 GC without adding external nucleophile under mild reaction conditions. 93% of isolated yield was
18 observed with 1% of catalyst loading at 75 °C/1 MPa of CO₂ in methylethylketone(MEK) as solvent
19 [51,52]. In 2021, Kleij et al. reported the first continuous flow preparation (48 h without any
20 noticeable loss of catalytic performance) of glycerol carbonate (17.3 g (147 mmol); TON, 99;
21 productivity, 2.04 mmol h⁻¹ mmolcat⁻¹) using an immobilized organocatalyst (TBD@Merrifield).
22 The latter mediates the coupling of glycidol and CO₂ under comparative mild reaction and halide-
23 free conditions [53].

24 Another useful cyclic organic compound, solketal (2,2-dimethyl-1,3-dioxolane-4-methanol) can be
25 obtained from glycidol (see Fig.3). It finds application as flavoring agent, surfactant and fuel additive.

1 The use of glycidol as starting materials was scarcely investigated and, in particular, the examples
 2 reported in literature were focused on the use of homogeneous Lewis acid catalysts such as RuCl_3 [54],
 3 $\text{Fe}(\text{CF}_3\text{COO})_3$ [55] and $\text{Er}(\text{OTf})_3$ [56]. In this scenario the use of a heterogeneous and recyclable
 4 catalyst is highly desirable. This result was recently achieved through the commercially available
 5 Nafion NR50 in refluxing acetone gives good conversion (79%) and selectivity (88%) to the desired
 6 product [57].

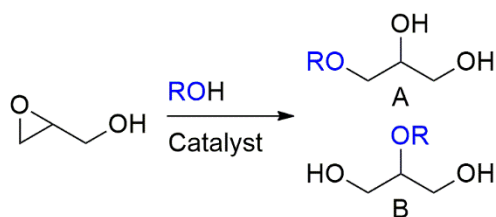


Glycerol carbonate		Main results	Solketal
<i>Capacchione et al 2016</i> ^[42]	<i>Kleij et al 2021</i> ^[56]	<i>Procopio et al 2005</i> ^[48]	<i>Cucciniello et al 2018</i> ^[48]
Catalyst = TBAB	Catalyst = TBD@Merrifield	Catalyst = $\text{Er}(\text{OTf})_3$	Catalyst = Nafion NR50
Load = 5 mol%	Load = 0,30 mmol%	Load = 1 mol%	Load = 10 wt%
10 bar CO_2	5 bar CO_2	27 eq. Ketone	43 eq. Ketone
Carbonate yield = >99 %	Carbonate Yield = 88 %	Solketal Yield = >99 %	Conversion = 79 %
			Selectivity (Solketal) = 88 %

8 **Figure 3.** Glycidol conversion to glycerol carbonate and solketal.

9 2.3 Monoalkyl glyceryl ethers (MAGEs)

10 MAGEs are one of the most interesting products that can be obtained through the nucleophilic ring-
 11 opening reaction of glycidol. The nucleophilic attack takes place preferably to the less hindered C3
 12 carbon of glycidol with the consequential formation of two regioisomers (see Figure 4).



Main results

<i>Cucciniello et al 2016</i> ^[50]	<i>Pires et al 2017</i> ^[56]	<i>Cucciniello et al 2018</i> ^[54]	<i>Capacchione et al 2019</i> ^[55]
Catalyst = Al(OTf) ₃	Catalyst = KOH	Catalyst = Nafion NR50	Catalyst = [OSSO]-Fe(III)-triflate
Low load 0.01 mol%	High load. 20 mol%	Low load 0.5 mol%	Low load. 0.05 mol%
9 eq. ROH	15 eq. ROH	9 eq. ROH	9 eq. ROH
9 Examples	7 Examples	11 Examples	16 Examples
A = 66-78 %	A = 30-93 %	A = 72-95 %	A = 84-96 %

Figure 4. Glycidol conversion to monoalkyl glyceryl ethers (MAGEs).

Varying the R group, MAGEs find applications in several industrial areas (C₁-C₆ solvents, C₁-C₂₄ detergents and surfactants, C₁-C_x additives for lubricants, inks, etc., C₄-C₁₈ cosmetics). The first relevant and recent example of glycidol conversion to MAGEs was reported in 2016 by the ring opening of glycidol with alcohols (C₁-C₈) in the presence of Lewis acids [58]. Glycidol is quantitatively converted with high selectivity (99%) into MAGEs in 1 h and under very mild reaction conditions (80°C and 0.01 mol% catalyst loading) using Al(OTf)₃, Fe(OTf)₃ and Bi(OTf)₃ as catalyst. Results were also discussed and boosted through a simplified LCA [59,60] comparing the environmental performance of the proposed innovative route with that of the most investigated pathway from glycerol [61]. In 2018, the first example of acid heterogeneous catalyst for MAGEs preparation from glycidol was reported and the best results were obtained using (stable and recyclable) Nafion NR50 under mild reaction conditions (80°C, 3 h, 0.5 mol% catalyst) [62]. The regioselective and homogeneous version of the Fe(III)-based catalyst was reported in 2019 with the preparation of Fe(III)-triflate complex, bearing a bis-thioether-di-phenolate [OSSO]-type ligand. In this case, the reaction proceeded with high activity (initial turnover frequency of 1680 h⁻¹ for EtOH) and selectivity (>95%) toward the formation of twelve monoalkyl glyceryl ethers (MAGEs) in a regioselective fashion (84–96% yield of the non-symmetric regioisomer) [63]. MAGEs preparation from glycidol was also reported under basic conditions using 20 % mol of KOH with good yields

(regioselectivity strongly depended on the alcoholic substrate, ranging from) and heterogeneous IRA-400 [64]. Guaiafenesin and mephenesin represent two interesting examples of MAGEs useful as drugs which was synthesized by glycidol ring-opening with phenols (guaiacol and o-cresol). Yadav et al. reported the guaiafenesin (selectivity 86 % at guaiacol conversion of 92%) synthesis in the presence of calcined hydrotalcite at 120°C in 4 h [65]. Recently, bio-glycidol conversion to surfactants has been reported through glycidol etherification with long-chain alcohols (n-octanol, n-decanol and n-dodecanol) catalyzed by $\text{Al}(\text{OTf})_3$ reaching initial turnover frequency up to 2633 h^{-1} in the case of octanol [66]. The critical micelle concentration was determined for all bio-surfactants using the pyrene method (octylglyceryl ether: 0.97 ± 0.02 mM; decylglyceryl ether: 0.85 ± 0.03 mM; dodecylglyceryl ether: 0.71 ± 0.04 mM). Furthermore, this class of MAGEs has been tested innovatively in combination with xanthan gum for water-based lubricants. Results clearly demonstrated that alkyl glyceryl ethers showed a significantly improved performance (higher friction reduction) with increasing the alkyl chain length through interaction with xanthan gum which favors ether dispersion and adsorption on metal surfaces [67].

2.4 Polymers

Poly(glycidyl-ether)s are sustainable and biodegradable polymers that can be obtained by anionic polymerization of glycidol and protected glycidols. Glycidol reactivity has been exploited in anionic polymerization where the epoxide group is involved in propagation reaction, whereas the hydroxyl moiety is responsible for chain transfer reactions [68,69]. Therefore, the polymerization of unprotected glycidol always leads to branched polymers with moderate molecular weights [70]. Linear poly(glycidol), instead, could be obtained only by polymerization of the monomer with protected $-\text{CH}_2\text{OH}$ groups to avoid chain transfer reactions [71]. Linear polymers with high M_n (up to 85000) were obtained by polymerization of 1-ethoxyethylglycidyl ether [72], which can be synthesized through reaction of glycidol with vinyl ethyl ether, catalysed by p-toluenesulfonic acid [73]. After the polymerization, the $-\text{CH}_2\text{OH}$ groups can be deprotected by acid hydrolysis. Moreover,

1 protective group can be chosen properly to obtain functionalized polyglycidols for different
2 applications, accordingly to the moiety on the side chains [74–76]. For example, both neutral and
3 anionic pendants have been considered for the application of derivatised poly(glycidyl-ether)s as
4 electrolytes for electrochemical devices (e.g. batteries, fuel cells, solar cells). [75,76]

5 **2.5 Other relevant glycidol-derived products and future perspectives**

6 Glycidyl esters, valuable epoxy resin monomers, have been obtained through the selective
7 transformation of glycidol catalyzed by a quaternary alkyl ammonium salt by transesterification of
8 methyl esters. Mechanistic studies revealed the formation of a binding complex of glycidol and
9 quaternary alkyl ammonium salt in a nonpolar solvent and the generation of the alkoxide anion as a
10 catalyst through the ring-opening reaction of the epoxide [77]. Toda and Suga reported the synthesis
11 of oxazolidinones through glycidol reaction with isocyanates catalyzed by a phosphonium salt. 4-
12 Hydroxymethyl-substituted oxazolidinones including enantio-enriched ones were obtained in high
13 yields [78].

14 In 2021, Lozano and coworkers showed the sustainable chemo-enzymatic synthesis of glycerol
15 carbonate (meth)acrylate from glycidol and carbon dioxide enabled by ionic liquid. Glycidyl
16 (meth)acrylate was firstly synthesized by enzymatic transesterification of (meth)acrylate vinyl ester
17 with glycidol in Sponge Like Ionic Liquids as the reaction medium. The second step consisted of the
18 synthesis of glycerol carbonate acrylate, or glycidyl (meth)acrylate, as the outcome of the
19 cycloaddition of CO₂ to the obtained glycidyl acrylate or glycidyl methacrylate, respectively,
20 catalyzed by a covalently attached 1-decyl-2-methylimidazolium moiety in a solvent-free system and
21 under mild conditions (60 °C, 1–10 bar), leading to up to 100% yield after 6 h [79].

22 To sum up, glycidol valorization to value-added chemicals has been reviewed. The preparation of
23 bio-based allyl alcohol through glycerol deoxydehydration represents, to date, the major challenge to
24 speed up the transition from a fossil-based production to a renewable one. In this context, glycidol
25 obtained as glycerol derivate could increase the interest towards the glycerol biorefinery [80].

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