ChemPlusChem

Research Article
doi.org/10.1002/cplu.202500203

Chemistry Europe
European Chemical Societies Publishing

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# A Sequential Catalytic Carbonation–Hydrolysis–Diol Dehydrogenation Reaction of Epoxides

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The design of cascade reactions in synthetic programs is of interest, particularly if the individual steps involve catalyzed reactions, and simple and highly available molecules such as carbon dioxide ($CO_2$), water ($H_2O$), and dihydrogen ($H_2$) are employed. Herein, a three-step sequential reaction is shown from epoxides to dehydrogenated diols, catalyzed by a combination of commercially available ionic liquids and supported Pt species on charcoal (Pt/C) in low amounts (<0.05 mol%). The process involves first carbonation of epoxides with $CO_2$, followed by the opening of the carbonate with $H_2O$, and then an acceptor-less dehydrogenation reaction of the resulting diol to release $H_2$. The inclusion of this last step in the one-pot synthesis of diols from epoxides is, to the knowledge, unprecedented. Reactive and kinetic experiments for each individual step reveal the key role of $CO_2$ to avoid epoxide polymerizations and enable the synthesis of a clean diol for the final dehydrogenation reaction.

## 1. Introduction

Epoxides are the second most produced organic functional groups (>20 MTon annually) in the chemical industry after alkenes (>200 MTon), the former produced from the latter.[1–4] **Figure 1** shows that this is not surprising since the epoxide functionality, apart from its direct application in diverse markets such as glues and insulating materials, is convenient to handle the synthesis of other organic groups of industrial interest.[5,6] Two of these functional groups are carbonates (route a) and diols (route b), related between them by the acceptance/release of $CO_2$ and $H_2O$. Therefore, epoxides can be converted either to carbonates after $CO_2$ addition (carbonation reaction)[7,8] or diols after direct $H_2O$ addition (hydrolysis or hydration reaction).[9,10] A third way that ligates carbonates and diols would involve the indirect hydration reaction of epoxides after a previous carbonation reaction (route c).[11–13] This reaction is currently exploited at industrial scale in the so-called OMEGA (only monoethylene glycol advantage) process, where ethylene epoxide is first converted to ethylene carbonate by carbonation reaction with $CO_2$, to then by hydrolyzed to monoethylene glycol after hydrolysis with $H_2O$.[12] The epoxide/carbonate/diol reaction sequence is being investigated deeply and a variety of catalytic systems have been recently published.[14] However, the extension of this reaction sequence to further transformations of the diol is not obvious and much little attention has been paid,[15] despite telescoped reactions in cascade are of interest from an efficient and sustainable point of view.[16–18]

The metal-catalyzed, oxidant-free dehydrogenation of diols to ketones and carboxylic acids is an organic transformation that produces $H_2$ as the sole by-product, thus is of interest not only from the synthetic but also from the energetic point of view.[19,20] The dehydrogenation reaction has been reported to occur in the presence of water,[21] which in principle suggests that might be compatible with the hydration of either the epoxide or the carbonate, thus engageable with the latter to obtain the dehydrogenated products from epoxides. However, it is difficult to find in the literature this approach since the dehydrogenation reaction usually requires fragile soluble metal complexes as catalysts and a strong aqueous basic media,[22,23] which in principle are incompatible conditions with epoxides since the metal-containing alkaline medium tends to polymerize the epoxide starting material or promote other undesired reactions.[24–26] Therefore, only a judicious choice of catalyst combination and a subtle window of reaction conditions might drive epoxides to dehydrogenated diol products.

Here, we show that the sequential carbonation/hydrolysis/dehydrogenation of epoxides is possible if a chloride-containing and nonacidic ionic liquid is employed in combination with reduced platinum on charcoal as catalysts during the different steps of the synthesis, in the presence of controlled amounts of $H_2O$ and only if $CO_2$ is used as an intermediate reagent, since otherwise the direct hydration of the epoxide does not give the desired intermediate diols. Although the final products obtained are a combination of aldehydes, carboxylic acids, and polymers, the results here shown open the way to telescope the dehydrogenation reaction with the synthesis of diols from epoxides, involving fundamental molecules such as $CO_2$, $H_2O$, and $H_2$.

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*Supporting information for this article is available on the WWW under https://doi.org/10.1002/cplu.202500203*

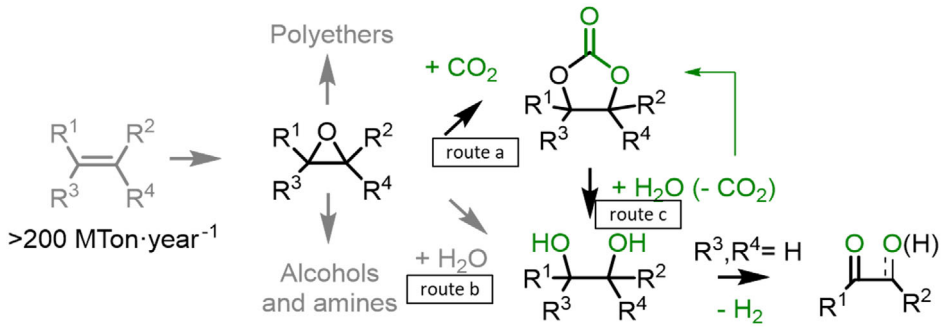



**Figure 1.** Megaton synthetic route of epoxides from alkenes and subsequent transformations into carbonates (route a) and diols (route b), and the sequential three-step reaction here reported which includes a final dehydrogenation reaction (route c).

## 2. Results and Discussion

### 2.1. Acceptor-Less Dehydrogenation Reaction of Diols

Our studies started with the last step of the sequential route, that is, the dehydrogenation reaction, in order to find different options of the reaction conditions to later couple with the epoxide-to-diol reaction sequence. Ideally, we sought to use reagents and systems that do not interfere with the previous steps of the synthesis, and we find that a common catalyst in the literature for this reaction is supported by platinum,[21] which is commercially available in different forms, either supported on alumina or charcoal. Thus, we tested the latter under different reaction conditions, starting with the solvent-free reaction, and the results are shown in **Figure 2**.

Different diols **1-8** reacted after 4 h reaction time under the solvent-free conditions. The same results were obtained with the commercial Pt/C catalyst and with a home-made Pt/C catalyst (see the Supporting Information, for experimental details), thus both can be used indistinctly.[27] The conversion for each diol was obtained after filtering off the solid Pt/C catalyst and quenching/extracting the reaction mixture with water/ethyl acetate, in order to remove the KOH, and are given as an average of the corresponding gas chromatography (GC) and $^1$H nuclear magnetic resonance ($^1$H NMR) analyses (after reaction reproduction). Mass balances were calculated using an internal standard (see Supporting Information for experimental details). The first observation we find is that the reaction requires open flask reaction conditions to proceed since when the release of $H_2$ was hampered either by trying to measure the $H_2$ volume with an inverted burette filled with water or by employing an autoclave reactor with a manometer, the reaction stopped at $<$5% conversion. For that reason, the dehydrogenation reactions were carried out in two-necked conventional round-bottomed glassware flasks connected to an open reflux. It can be seen in Figure 2 that the simple linear-chain terminal diols **1–4** reacted in moderate conversions under those conditions (35–74%), but, in contrast, the smaller allyl diol **5** and dimethyl diol **6** reacted in higher

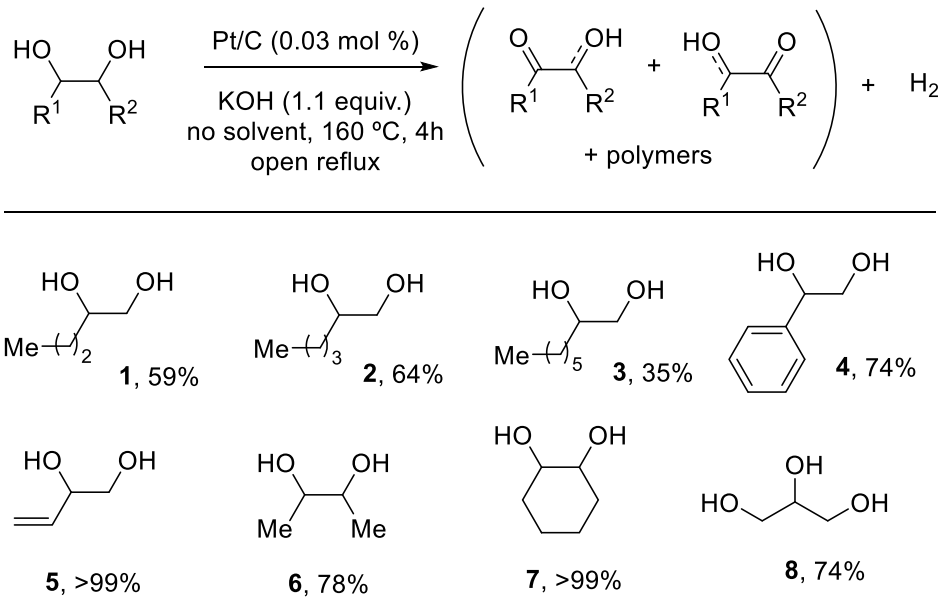


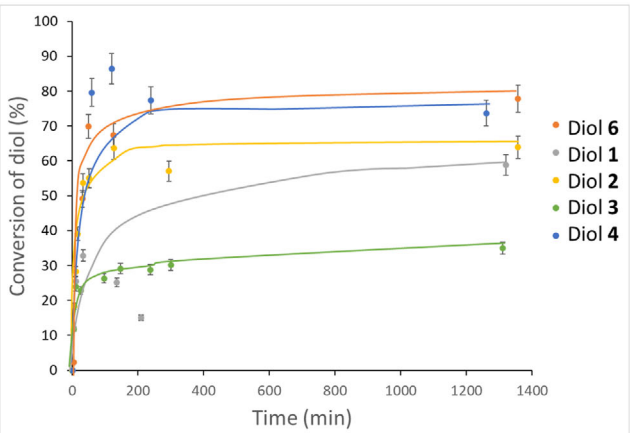

**Figure 2.** Catalytic results for the acceptor-less dehydrogenation reaction of diols **1–8**. Conversions were calculated as an average between GC and $^1$H NMR results. Reaction conditions: neat diol (1 mmol), KOH (pellets, 1.1 mmol), 5 wt% Pt on charcoal (0.03 mol% in Pt), 160 °C, open flask, or in case of **8,** connected to open reflux, allowing the leave of $H_2$ and the cooling of the product lactic acid, 4 h. Reactions were carried out by duplicate.

extent (>99% and 78%, respectively). The detailed analysis of the diol **4** by $^1$H NMR showed that some aldehyde was formed (Figure S1, Supporting Information), but that aldehyde was not 2-phenylacetaldehyde because it should be a triple peak and we only observe a singlet. We also discarded the formation of 2-hydroxy-2-phenylacetaldehyde because in this case the aldehyde signal should be a doublet. With this, we must assume that the aldehyde signal observed is due to some polymer formed. However, we were able to observe the signal at 2.62 ppm, which may correspond to the methyl group of acetophenone, obtained by dehydration of the diol.

In order to check if a correlation between linear chain length in the diol and reactivity was occurring, on the basis of a possible steric hindrance, kinetic experiments were performed, and the results are shown in **Figure 3**. It is noteworthy to remark here that each point in the kinetic comes from an individual reaction, after work-up and averaged GC-$^1$H NMR analysis.

The results in Figure 3 show that a correlation between linear chain length and conversion cannot be observed since the initial rates for diols **6** and **1–3** do not follow decreasing (neither an increasing) order. The phenyl-substituted diol **4** was also included in the kinetic order for the sake of comparison, and an abrupt stopping of the dehydrogenation reaction after 2 h reaction time (120 min) can be observed. This reaction stopping is not appreciated for the alkyl derivatives, and they continue reacting until 4 h reaction time, when the conversion levels off. It must be noticed here that some experimental points deviate from the averaged line (see for instance diol **1**); however, this can be accepted considering that they are the result of individual multiphase reactions (heterogeneous Pt/C catalyst, solid KOH, and liquid diol) after aqueous extractions. In any case, the initial turnover frequency ($TOF_0$) for the Pt catalyst is very high for an organic reaction in liquid phase since addressing the highest initial rate (diol **2**, 2.3 $min^{-1}$) with a 0.03 mol% of Pt, a $TOF_0 = 6736\ h^{-1}$ was obtained when considering the reachable external Pt atoms on the supported nanoparticles (19%).[28] For that calculation, the Pt/C catalyst was characterized by powder X-ray diffraction (PXRD, Figure S2, Supporting Information) and scanning transmission electron microscopy with annular dark field detector (STEM-DF, Figure S3, Supporting Information), and the percentage of atoms on the nanoparticle surface was calculated from the estimated mean diameter size (2.3 nm, Figure S3, Supporting Information bottom and Figure S4, Supporting Information). The oxidation state of the Pt/C nanoparticles was determined by XPS (Figure S5, Supporting Information) obtaining a single doublet of asymmetric spin–orbit components Pt $4f_{7/2}$–Pt $4f_{5/2}$ with two bands at binding energies BE (Pt $4f_{5/2}$) 74.8 (major peak) and 77.4 eV (minor peak), which correspond to $Pt^0$ and $Pt^{2+}$ oxidation states, respectively. The major species is Pt(0), accounting for >80%. A hot filtration test to determine if catalytically active Pt species migrated to the solution failed here due to the multiphasic nature of the reaction and the high density of the reaction mixture. For that reason, we measured the Fourier-transformed infrared spectra (FT-IR) of the used Pt/C after reaction, confirming the presence of organic compounds in the solid (Figure S6, Supporting Information left). After washing the sample three times with isopropanol, most of the organics were removed, but some signals corresponding to C—C and C—H bonds were still observed. In fact, inductively coupled plasma-emission optical spectrophotometry (ICP-OES) of the Pt/C after using showed a decrease of more than half the amount of Pt in the sample measured (1.8 wt% Pt/C). Even taking into account the remaining organics, some Pt species seem to be leached out during reaction. We reused the catalyst under the optimized reaction conditions, and the conversion observed decreased from 99% to 67% after four reuses (Figure S6, Supporting Information, right), which is remarkable in view of the complexity of the reaction, the Pt leaching, and the solid catalyst poisoning.

In view that the conversion was not complete in most cases and that a plateau was observed in the different kinetic profiles, we then performed tests to study a potential product inhibition suffered by the catalyst. The results (Figure S7, Supporting Information) show that the addition from the beginning of the reaction of one of the oxidative products, in this case commercially available (thus in pure form and in equimolar amounts) 2-hydroxyacetophenone, gave a similar initial rate to the original




| Diol | $v_0$ ($min^{-1}$) |
|---|---|
| 4 | 1.3(3) |
| 6 | 1.4(7) |
| 1 | 0.8(7) |
| 2 | 2.3(6) |
| 3 | 1.9(8) |

**Figure 3.** Kinetic results for the Pt/C-catalyzed dehydrogenation reaction of diols **1–4** and **6**. Conversions were calculated as an average between GC and $^1$H NMR results. Reaction conditions: diols **1–4** or **6** (1 mmol), KOH (pellets, 1.1 mmol), 5 wt% Pt on charcoal (0.03 mol% in Pt), 160 °C, open vial. Each point is the result of an individual reaction after work-up, error bars account for a 5% uncertainty. Lines are a guide to the eye.

reaction (1.55 and 1.33 $min^{-1}$, respectively). The conversion is complete when 2-hydroxyacetophenone is added from the beginning, which could be due to a faster polymerization in the presence of some artificially added initial product. However, when we added fresh Pt/C to the reaction mixture after arriving to the plateau (at 240 min), in order to measure the conversion at 1260 min reaction time, this conversion is the same (72% vs 74% conversion with fresh added Pt/C catalyst), which strongly supports the rapid poisoning of the Pt/C catalyst after product formation. A third piece of evidence for the deactivation of the catalyst with time is that reactions performed in closed vials or connected to an inverted burette filled with water to measure the $H_2$ formed (see Figure S7, Supporting Information) did not show any conversion since the Pt/C catalyst must be able not only to dehydrogenate the reactant but also to efficiently remove the $H_2$ formed, otherwise the catalyst gets poisoned and the reaction does not proceed. All these results, together, agree well with the observed presence of organic contaminants in the used Pt/C catalyst and its progressive deactivation throughout the reuses (see above).

The good yield for the internal diol **6**, despite not having the higher initial rate (see Figure 3 above), suggests that internal diols could be more reactive for the reaction. To check this, cyclohexanediol **7** was tested and complete conversion (see Figure 2). Then, glycerol **8** was tested, to give a 74% conversion, in this case with good selectivity to the single product lactic acid **9** as assessed by $^1H$ and $^{13}C$ NMR analyses (>95%, Figure S8 and S9, Supporting Information).[29] In view that yield and not only conversion of the reaction could be followed for glycerol **8**, the solvent scope and the presence or not of catalytically active Pt species in solution during the dehydrogenation reaction were assessed at this point. First, different solvents able to bear the reaction conditions (160 °C and KOH) were tested, including polyethylene glycol (with $M_n = 400$ to be in the liquid state at room temperature, PEG-400), *N*-methyl pyrrolidone (NMP), 1,2-dichlorobenzene (DCB), and *N*-butyl-*N*-methylmethylimidazolium chloride ([bmmimCl]). The latter is an ionic liquid with the acid H removed (substituted by a methyl group). While PEG-400 is able to dissolve the KOH, the conversion to **9** was just 8%, but, in contrast, NMP gave and intermediate 46%, DCB gave an 80%, and [bmmimCl] gave a 90% yield of **9** when the amount of Pt/C was increased (0.6 mol%, Figure S10, Supporting Information). The results with DCB and [bmmimCl] are very similar or even better to the solvent-free reaction (74%), and since KOH is not soluble in these solvents, these results showcase that the solubility of KOH has little influence on the reaction outcome. It has to be remarked here that the reported result in $H_2O$ as a solvent, under similar reaction conditions, is similar to NMP (49% yield of **9**).[21] The conversion of **8** was <5% if Pt/C was not added to the reaction mixture, for any solvent or under the solvent-free conditions, confirming the need for the Pt catalyst for the dehydrogenation reaction to proceed. Second, since DCB as a solvent gives similar results to the solvent-free reaction, the presence of catalytically active Pt species in solution was assessed with glycerol **8** after adding a quencher for soluble Pt species (the solid KOH in the reaction mixture still hampered a classical hot filtration test). The corresponding kinetic experiments with $PPh_3$ (Figure S11, Supporting Information) show that the reaction proceeds with exactly the same initial reaction rate in the presence or not of $PPh_3$, and only the reaction profile decays at >40% yields, which strongly indicates that the catalytically active Pt species are supported on the charcoal during reaction and not in solution.[30]

As a partial summary of the aforementioned results, we can say that the dehydrogenation reaction catalyzed by Pt/C proceeds for a variety of diols in moderate to excellent conversions, with Pt/C as a catalysts and KOH as a base in different solvents, including DCB, [bmmimCl] and solvent-free reaction conditions. At this point, we focused in the previous reaction in our targeted reaction sequence, that is, the hydration of the epoxide.

## 2.2. Hydration Reaction of the Epoxide

### *2.2.1. Direct Hydration*

The first logical approach here was, in our opinion, to try a direct hydration of the epoxide under the aqueous basic reaction conditions found for the dehydrogenation reaction, although these conditions might lead to undesired by-reactions. We chose the cyclohexane epoxide **10** of the more reactive diol **7** as starting material and, as Figure 7 shows, the hydration reaction did not work but a self-coupling of the epoxide **10** occurred, leading to product **11** in >95% yield after deprotonation of the β-carbon atom. This result makes sense considering that the direct hydration of epoxides is normally performed with acid catalysts,[31] in order to activate the epoxide toward the opening with the weak water nucleophile, thus our basic conditions here trigger undesired pathways **Figure 4**.

The revision of the literature on direct epoxide hydration reaction under basic or neutral conditions[32–34] leads us to find

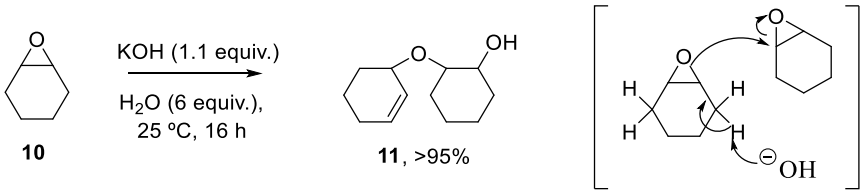



**Figure 4.** Results for the attempt of the direct hydration reaction of the cyclohexane epoxide **10** to cyclohexane diol **7** under basic aqueous conditions, with the plausible simplified mechanism for the by-reaction found, to give 2-(cyclohex-2-en-1-yloxy)cyclohexan-1-ol **11**. The yield was calculated as an average between GC and $^1H$ NMR results. Reaction conditions: epoxide **10** (1 mmol), KOH (pellets, 1.1 mmol), $H_2O$ (6 mmol),) 25 °C, 16 h. The reaction was carried out by duplicate.

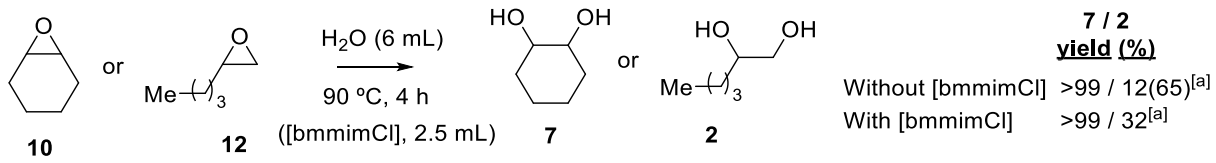



**Figure 5.** Results for the direct hydration reaction of cyclohexane epoxide **10** or 1-hexene epoxide **12** to cyclohexane diol **7** or 1,2-hexanediol **2** in hot water, either in the presence or not of the ionic liquid [bmmimCl]. Yields were calculated as an average between GC and $^1$H NMR results. Reaction conditions: epoxide (1 mmol), $H_2O$ (6 mL), ([bmmimCl], 2.5 mL), 90 °C, 4 h. The reactions were carried out by duplicate. [a]After 16 h reaction time.

a report on the opening of epoxides in neat hot water.[32] This reactivity is based on the self-ionization of water after increasing the temperature, which lowers the -log Kw (Kw is the self-ionization constant of water) value form 14 at 25 °C to 12.2 at 100 °C, thus one order of magnitude higher. In our hands, this direct hydration reaction indeed worked for epoxide **10**, to give diol **11** in >95% yield after 4 h reaction time at 90 °C. Then, the addition of one of the solvents employed in the dehydrogenation reaction studies ([bmmimCl]) was attempted since this ionic liquid could also catalyze the formation of carbonates (see ahead). The result, also shown in **Figure 5**, was exactly the same than without [bmmimCl] (>99% yield of diol **7** after 4 h), and kinetic results confirmed that 4 h was the required time for the complete conversion of **10** (Figure S12, Supporting Information); thus, the addition of [bmmimCl] did not affect to the hydration reaction.

The amount of water could be decreased either after increasing the amount of ionic liquid (Figure S13, Supporting Information) or after fixing the amount of ionic liquid at 2.5 mL and decreasing the amount of water (Figure S14, Supporting Information), to achieve complete conversion to product **7** at 7–20 wt% water amounts.[35,36] However, the change of the epoxide to 1-hexene epoxide **12** significantly decreased the conversion of the hydration reaction with hot water, to give 1,2-hexanediol **2** in just a 12% yield after 4 h reaction time (see Figure 5). A kinetic study (Figure S15, Supporting Information) showed that the yield for this direct hydration reaction can be increased with time, to achieve a 65% of **2** after 16 h (see Figure S9, Supporting Information), but the addition of the ionic liquid halved the yield to 32%. Attempts to find a suitable combination of water + ionic liquid to increase the conversion of the linear epoxide **12** allowed to achieve a 70% yield of **2**, but not more, and the yield for the cyclic diol **7** was systematically superior for every condition tried (Figure S16, Supporting Information).

The earlier results indicate that the direct hydration of epoxides under basic or neutral reaction conditions, compatible with the subsequent dehydrogenation reaction, is significantly hampered by the lack of acidity in the reaction system. Reactions in diluted HCl (Figure S17, Supporting Information) confirm the need of acidity to bring epoxides **10** and **12** to the corresponding diols quantitatively. Thus, an alternative hydration through a carbonate intermediate was envisaged here.

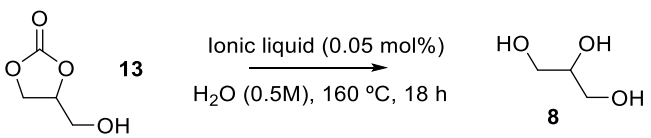
### *2.2.2. Indirect Hydration (Hydrolysis of Carbonates)*

The hydrolysis of carbonates to diols has been reported to occur with chloride salt catalysts in water.[37] These conditions

**Table 1.** Results for the hydrolysis reaction of glycerol carbonate 13 in the presence of the ionic liquid chlorides. Yield was calculated as an average between GC and $^1$H NMR results. Reaction conditions: carbonate 13 (1 mmol), ionic liquid (0.05 mol%), $H_2O$ (0.5 M), 160 °C, 18 h. The reactions were carried out by duplicate.

| Entry | Catalyst | Yield to 8 [%] |
|---|---|---|
| 1 | None | 29 |
| 2 | *N*-butyl-*N*-methylmethylimidazolium chloride ([bmmimCl]) | 91 |
| 3 | *N*-butyl-*N*-methylmethylimidazolium nitrate ([bmmim$NO_3$]) | 20 |
| 4 | *N*-butyl-*N*-methylmethylimidazolium hexafluorophosphate ([bmmim$PF_6$]) | 22 |
| 5 | *N*-butyl-*N*-methylimidazolium chloride ([bmimCl]) | 78 |
| 6 | *N*-ethyl-*N*-methylimidazolium bromide ([emimBr]) | 44 |

are in principle compatible with the dehydrogenation reaction since the ionic liquid [bmmimCl] can be employed as a solvent for the latter. Thus, we tested the hydrolysis reaction of the commercially available glycerol carbonate **13** in the presence of different ionic liquid chlorides at the same reaction temperature (160 °C) to the dehydrogenation reaction, not only because the compatibility of the ionic liquid but also because the latter are also good catalysts for the carbonation reaction of epoxides, which will enable a complete sequential reaction from epoxides to dehydrogenated products. **Table 1** shows the results for the hydrolysis reaction of carbonate **13**, and it can be seen that a 0.05 mol% of [bmmimCl] is able to catalyze the hydrolysis reaction, to give a 91% yield of glycerol **8** (see the $^1$H, $^{13}$C NMR, and the distortionless enhancement by polarization transfer, DEPT, spectra in Figure S18, Supporting Information), while the noncatalyzed reaction only gave a 29% (entries 1 and 2). Remarkably, either if the anion of bmmim (entries 3 and 4) or the imidazolium part (entries 5 and 6) are varied, the yield is significantly lower, in some cases in the blank range. These results support the suitability of the nonacidic, C-methyl substituted imidazolium ionic liquid [bmmimCl] to perform not only the hydrolysis reaction but also to be present during the dehydrogenation reaction (see earlier).



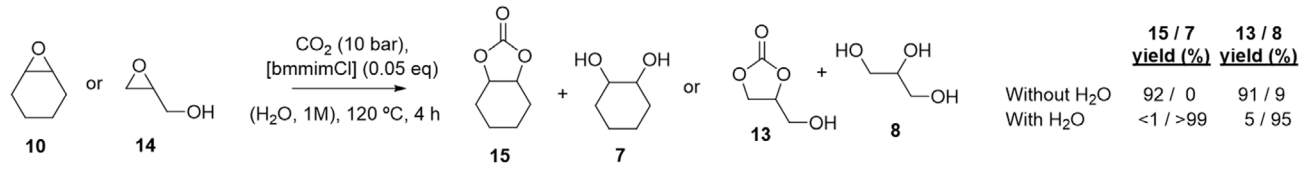



**Figure 6.** Results for carbonation reaction of cyclohexene epoxide **10** and glycidol **14** with [bmmimCl] as a catalyst (0.05 mol%), either in the presence or not of water. Yields were calculated as an average between GC and $^1$H NMR results. Reaction conditions: epoxide **10** or **14** (1 mmol), ionic liquid (0.05 mol%), $H_2O$ (1 M), 120 °C, 4 h.

### 2.3. Carbonation Reaction of Epoxides

The carbonation reaction of epoxides catalyzed by ionic liquids is profusely reported in the literature,[38–42] thus we proceed to check if the [bmmimCl]-catalyzed carbonation reaction of either cyclohexene epoxide **10** or glycidol **14**, as starting epoxides, occurred after adapting the reaction conditions to those compatible with our cascade. The results in **Figure 6** show that the carbonation reaction indeed proceeds well under anhydrous conditions with just 0.05 mol% of [bmmimCl] at 120 °C (>90% for both carbonates **15** and **13**, see NMR, DEPT, CG, and GC–MS for **15** in Figure S19, Supporting Information), and that the addition of water drives the reaction to the desired diols (>95% for both diols **7** and **8**). These results encourage us to test the sequential reaction, after $CO_2$ utilization.[43]

### 2.4. Sequential Carbonation of Epoxides–Hydrolysis–Diol Dehydrogenation Reaction

The sequential reaction was then ready to be tested, using the ionic liquid [bmmimCl] and Pt/C as catalysts in low amounts (0.05 and 0.03 mol%, respectively), and $CO_2$ as an intermediate reagent. The results are shown in **Figure 7**. The initial [bmmimCl]-catalyzed carbonation reaction was carried out under anhydrous conditions at 150 °C, to assure the complete formation of the carbonate, and only then $H_2O$ was added, after $CO_2$ release, to trigger the hydrolysis reaction at 120 °C, enough reaction temperature for a complete formation of the diol. Then, the Pt/C catalyst and KOH were added, and the reaction was heated at 160 °C. Water was not present any more in the reaction mixture and the dehydrogenation reaction proceeded in the presence of the residual [bmmimCl] catalyst. All the epoxides tested, including the epoxides **10**, **12**, **14**, and **16–18**, were quantitatively converted to a mixture of aldehydes and carboxylic acids under the indicated reaction conditions, according to the $^1$H and $^{13}$C NMR spectra of the resulting reaction mixtures, with the generation of $H_2$. In some cases, minor amounts of the intermediate diols could be observed. The reaction from the epoxide to the dehydrogenated products can also be performed in cascade, with all the reagents present in the starting mixture from the beginning of the reaction, if [bmmimCl] is added in 0.5 equivalents, and the amount of Pt/C and KOH are also increased to 3 mol% and 5.5 equivalents, respectively. In this way, glycidol **14** formed lactic acid **9** in 58% yields since over oxidations and uncontrolled polymerizations were apparently slowed. A kinetic study shows that the cascade reaction (all the reagents from the beginning) reaches up to a 68% yield to lactic acid **9** at longer reaction times (Figure S20, Supporting Information). It must be remarked here that an acid-catalyzed direct hydration of the epoxide is not possible since basic reaction conditions are applying from the beginning of the reaction. These results confirm the viability of the sequential or cascade carbonation–hydrolysis–diol dehydrogenation reaction of epoxides after applying the data acquired through the study of the individual steps. We checked the stability of the [bmmimCl] in the presence of Pt/C to discard interactions between the IL and the Pt site by FT-IR (Figure S21,

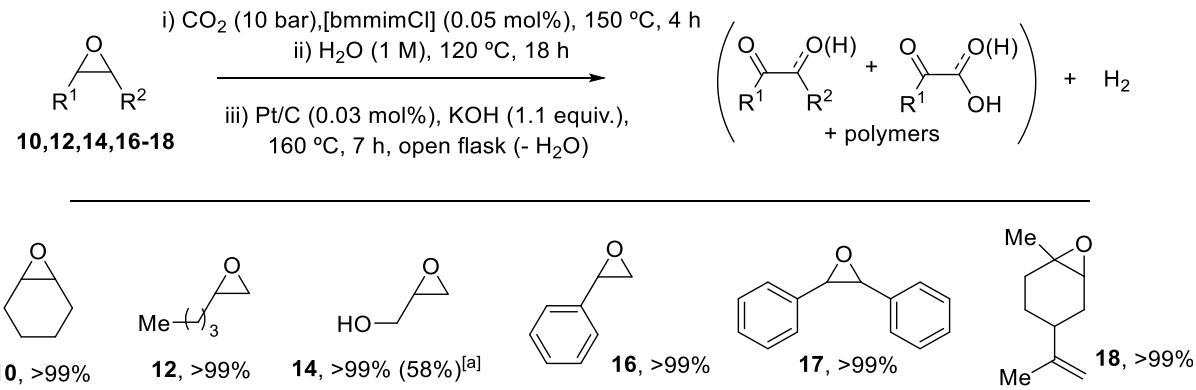



**Figure 7.** Results for the sequential carbonation–hydrolysis–diol dehydrogenation reaction of epoxides **10**, **12**, **14**, and **16–18** with the ionic liquid [bmmimCl] (0.05 mol%) and Pt/C (0.03 mol%) as a catalyst. Conversions were calculated by $^1$H NMR. Reaction conditions: epoxide (1 mmol), [bmmimCl] (0.05 mol%), $H_2O$ (1 M), and KOH (1.1 equivalents). [a]Between parentheses, yield for lactic acid **9** after performing the reaction in cascade using 0.5 equivalents of [bmmimCl], 3 mol% of Pt/C and 5.5 equivalents of KOH (notice that a 10-fold more Pt/C was required to achieve good results).

Supporting Information) and during the reaction conditions to obtain **8** by $^1$H NMR, and the results confirmed that the IL is stable even in the presence of KOH (Figure S22, Supporting Information).[44]

## 3. Conclusion

The sequential carbonation–hydrolysis–diol dehydrogenation reaction of epoxides has been achieved after studying the individual steps, from the last to the first, and finding common reaction conditions to engage the different steps. The use of a commercially available and non-acidic ionic liquid [bmmimCl] is key to catalyze the carbonation and hydrolysis reaction without perturbing the last dehydrogenation reaction, and $CO_2$ is needed as an intermediate reagent since the direct hydration of the epoxide is not possible without acidic conditions. In this way, low amounts (<0.05 mol%) of commercially available catalysts ([bmmimCl] and Pt/C) and extremely cheap KOH, in combination with simple molecules such as $CO_2$ and $H_2O$, enable the direct transformation of epoxides into dehydrogenated diol products and $H_2$.[45] These results open the way to engage not only the acceptor-less dehydrogenation reaction but also other reactions, which proceed under relatively harsh conditions, to the epoxide hydration reaction.

## Acknowledgements

This work was supported by the MICINN and MCIUN (Spain), Projects PID2020-115100GB-I00 and PID2023–148441NB–I00. Thanks are also extended to the Severo Ochoa centre of excellence program (CEX2021–001230–S). J.O.-M. thanks the MICIIN for the concession of the Ramón y Cajal contract RYC2022–036154–I (funded by MCIN/AEI/10.13039/501100011033). A.L.–T. thanks the MICINN for the concession of the FPI grant PRE2020-093338 (through SEV-2016-0683-20-3).

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** cascade reactions · dehydrogenation of diols · hydrolysis of epoxides · ionic liquids · sequential reactions

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Manuscript received: March 18, 2025
Revised manuscript received: April 25, 2025
Version of record online: May 12, 2025