Review

En Route to CO$_2$-Based (a)Cyclic Carbonates and Polycarbonates from Alcohols Substrates by Direct and Indirect Approaches

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Abstract: This review is dedicated to the state-of-the art routes used for the synthesis of CO$_2$-based (a)cyclic carbonates and polycarbonates from alcohol substrates, with an emphasis on their respective main advantages and limitations. The first section reviews the synthesis of organic carbonates such as dialkyl carbonates or cyclic carbonates from the carbonation of alcohols. Many different synthetic strategies have been reported (dehydrative condensation, the alkylation route, the "leaving group" strategy, the carbodiimide route, the protected alcohols route, etc.) with various substrates (mono-alcohols, diols, allyl alcohols, halohydrins, propargylic alcohols, etc.). The second section reviews the formation of polycarbonates via the direct copolymerization of CO$_2$ with diols, as well as the ring-opening polymerization route. Finally, polycondensation processes involving CO$_2$-based dimethyl and diphenyl carbonates with aliphatic and aromatic diols are described.

Keywords: carbon dioxide; alcohols; (a)cyclic carbonates; polycarbonates

1. Introduction

Today, our modern society is facing climate change and ocean acidification caused by the continuous increase in CO$_2$ levels within the atmosphere. Our annual anthropogenic emissions are now approaching 40 Gt/year, and it is recognized that alongside other gases, including water vapor, methane and fluoro-compounds, CO$_2$ has become a major contributing factor to the greenhouse effect [1–3]. Legally binding obligations, governmental incentives and demands from industrial stakeholders are now strong drivers to fight global warming and to shift our societal paradigm based on fossil resources towards a more sustainable and circular vision, including CO$_2$ utilization. Traditionally seen as a waste, CO$_2$ may paradoxically become the key to "greening" our economy. Unlike biomass, the growth of which is inter-seasonal and requires multi-step post-treatment (extraction, fractionation, fermentation, etc.) prior to valorization, CO$_2$ is a cheap and renewable carbon source that is regenerated instantaneously and locally. This resource may undergo numerous chemical processes and syntheses to design existing organic molecules or polymers or new (sophisticated) ones [4–6].

However, the main thermodynamic barrier to the large scale utilization of CO$_2$ as a C1 building block lies in its stability, having a standard enthalpy of formation of $\Delta_f H° = -394$ kJ/mol [7]. To surpass this chemical inertness, the use of high-energy (co)reactants and the development of new catalytic methods and external energetic inputs are required to turn CO$_2$ into valuable products.

The production of salicylic acid via the Kolbe–Schmitt process, urea from ammonia and CO_2 or polyols by ring-opening copolymerization of oxiranes with CO_2 are just few examples of competitive products that have already been trademarked in the chemical industry.

CO_2 is also being used to fabricate the next generation of fuels and to store renewable energy via the so-called power-to-fuel technology. Its electrochemical reduction provides carbon monoxide, a key molecule in the Fischer–Tropsch process to produce alkanes. Numerous studies have revisited Sabatier's reaction, which has been known for more than a century, to fabricate synthetic methane from renewable H_2, while the partial hydrogenation of CO_2 provides methanol. A myriad of sophisticated molecules are also accessible from the chemical conversion of CO_2 via C-O or C-N bond formation. This route, as reviewed by others, is very promising, as (highly) reactive organic precursors counterbalance the low reactivity of CO_2. The (photo)catalytic carboxylation of alkanes, alkenes or alkynes provides a diverse portfolio of carboxylic acids. The methylation of primary amines or the formylation of secondary ones is conducted with CO_2 and a reductant (H_2, $PhSiH_3$, etc.).

The (a)cyclic organic carbonates and carbamates with ample structural diversity are fabricated with a high level of selectivity and a 100% atom economy pathway via non-reductive catalytic transformations of CO_2 with oxiranes [8–11], aziridines [12] and amines [13]. The insertion of CO_2 within epoxides is by far the most extensively explored transformation process for CO_2, as it provides 5-membered cyclic carbonates used as solvents, electrolytes for Li-ion batteries or intermediates in fine organic chemistry and polymer sciences. Despite being very attractive and easily produced via facile oxidation of olefins, including natural ones derived from vegetable oils or terpenes, epoxides display acute toxicity, as they act as alkylating agents capable of binding with DNA [14,15]. In this context, the replacement of epoxides with safe and easy-to-handle (renewable) substrates to synthesize organic carbonates and polycarbonates is now gaining huge interest in the scientific community.

Alcohols are ubiquitous scaffolds with low toxicity made from multiple synthetic and natural sources. This makes them ideal candidates within the field of CO_2 transformation to replace epoxides. This review provides an overview of the progress made in the synthesis of (a)cyclic and polymeric carbonates from alcohols substrates. The first section is dedicated to the main pathways that are used to upgrade CO_2 with mono-, di- or polyols; haloalcohols; or allylic or propargylic alcohols into organic scaffolds, and is complemented by mechanistic guidelines. The second section highlights the synthesis of polycarbonates either by direct polycondensation of CO_2 with alcohols or via the polymerization of CO_2-sourced monomers through ring-opening or step-growth methods. An overview of the most relevant routes discussed in this review for the direct coupling of CO_2 with alcohols to produce (a)cyclic carbonates and polycarbonates is presented in Scheme 1.
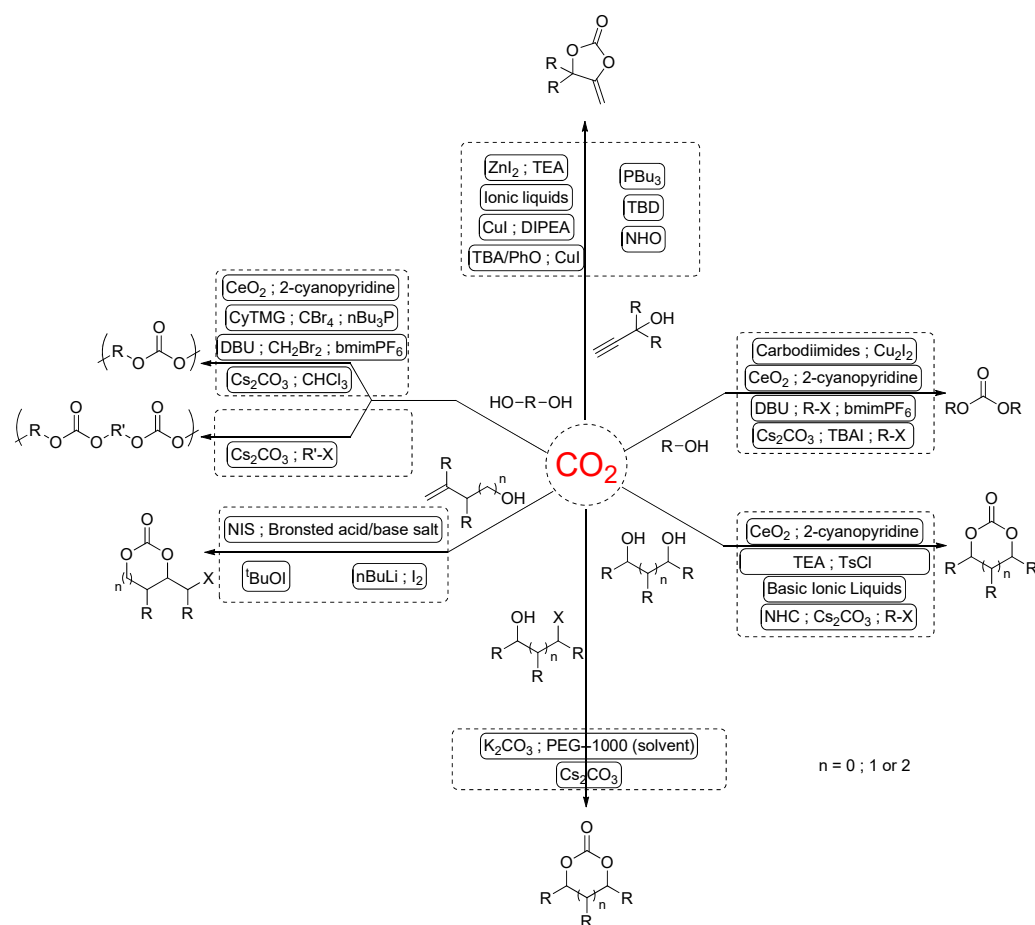
Scheme 1. Main strategies used to afford (a)cyclic carbonates and polycarbonates from the coupling of alcohols and CO_2.

2. CO_2-Based Synthons: Organic Carbonate Synthesis from the Carbonation of Alcohols

Industrially, the oxidative carbonylation of alcohols by phosgenation is the most facile and economically viable route for fabricating (a)cyclic organic carbonates. However, the toxicity of phosgene; the protective measures required for its safe transportation, storage and handling; and the large volume of chlorinated waste generated during the reaction are strong limitations that support the development of a more sustainable carbonation process. In this context, the formation of carbonates via the coupling of alcohols and CO_2 looks very attractive but remains an elusive endeavour, as this approach faces two severe limitations linked to: (i) the difficulties in identifying ways to properly activate CO_2, as it will not spontaneously react with alcohols; (ii) the formation of water as a by-product, which affects the reaction equilibrium (Scheme 2).
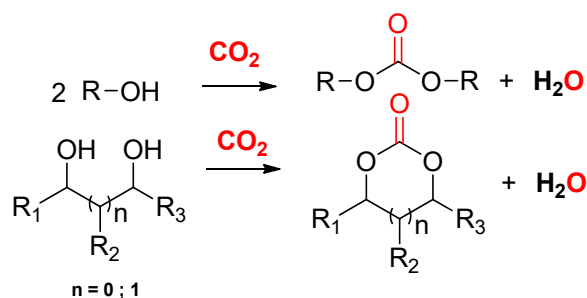
Scheme 2. The CO_2–alcohol coupling to synthetize organic carbonates.

To surpass these hurdles, three main strategies have been envisioned:

(i) The "dehydrative condensation" approach, utilizing the synergy between a catalyst, which facilitates the CO_2 fixation onto the alcohol moiety, with physical or reactive dehydrating agents to trap or consume water;

(ii) The "alkylation" strategy, involving the activation of CO_2 under the form of a hemicarbonate ion in the presence of an excess of base prior to further reaction with an alkyl halide via nucleophilic substitution. As a variant, the "leaving group" approach proposes the in situ formation of a highly reactive carbonate intermediate from the ter-reaction between CO_2, an alcohol and a dihalide, which undergoes facile transcarbonation into an acyclic carbonate;

(iii) The "protected alcohols" route, which generates in situ alcohols from ketals, trimethyl phosphates, or orthoesters via water consumption prior to reaction with CO_2

### 2.1. Synthesis of Acyclic Organic Carbonates

The synthesis of dimethyl carbonate (DMC) is by far the most widely studied pathway to illustrate the conversion of alcohols and CO_2 into useful organic scaffolds. However, the high standard Gibbs-free energy of DMC formation from methanol and CO_2 ($\Delta^R G \approx +37$ kJ/mol) indicates that the reaction is thermodynamically unfavorable, limiting the yield of the overall reaction to below 1% [16–18]. Various approaches have been proposed and optimized to produce DMC with good yields and selectivity.

2.1.1. DMC Synthesis by Dehydrative Condensation

Since the pioneering studies by Kizlink [19,20], who demonstrated the low yield but selective formation of DMC from CO_2 and MeOH using organotin catalysts, a tremendous number of metal alkoxide catalysts have been developed. Titanium-($Ti(OEt)_4$, $Ti(OBu)_4$) [21], nickel-($Ni(OAc)_2 \cdot 4H_2O$) [22], niobium-($[Nb(OMe)_5]_2$) [23] and magnesium-based catalysts [24] are some examples of homogenous systems that have proven their utility in driving the formation of the acyclic organic carbonates. Heterogeneous amphoteric metal oxide systems combining acidic and basic sites such as ZrO_2 [25–27]; ZrO_2–phosphoric acid dual catalysts [28,29], ceria oxides [30,31] and other mixed oxides [32–34]; or Cu-Fe, Cu-Ni and bimetallic oxides immobilized onto graphite oxide and graphene nanosheets [35–37] also displayed some catalytic activity. However, for all systems, the formation of water as a by-product severely limited the reaction yields (up to 5% for the $H_3PW_{12}O_{40}/Ce_{0.1}Ti_{0.9}O_2$ system [38]). Some catalysts also faced selectivity issues with the high-temperature concomitant formation of formaldehyde and carbon monoxide from CO_2 and methanol. To overcome these limitations, the utilization of metal-based catalysts that operate in synergy with "physical" or reactive desiccants or dehydration system emerged as a valuable option to push the reaction manifold toward high yield and the selective formation of DMC.

- Physical drying systems;

Membrane catalytic reactors combing a Cu catalyst immobilized onto a mixed oxide carrier (MgO-SiO_2) with hydrophilic polyimide–silica or polyimide–titania hybrid separating membranes [39] or inorganic absorbents such as molecular sieves or zeolites combined with organotin catalysts [40,41] were engineered to get rid of water and displace the reaction equilibrium towards the DMC formation. Among them, the $Bu_2Sn(OMe)_2$–3A molecular sieves provided the best DMC yields (45%) under operative conditions of 180 °C and 30 MPa of CO_2 in 80 h. This approach highlights the benefits of the desiccant for the carbonylation of methanol, with a 10-fold increase in DMC yield [40,42]. The catalytic cycle of $Bu_2Sn(OMe)_2$ is shown in Scheme 3.
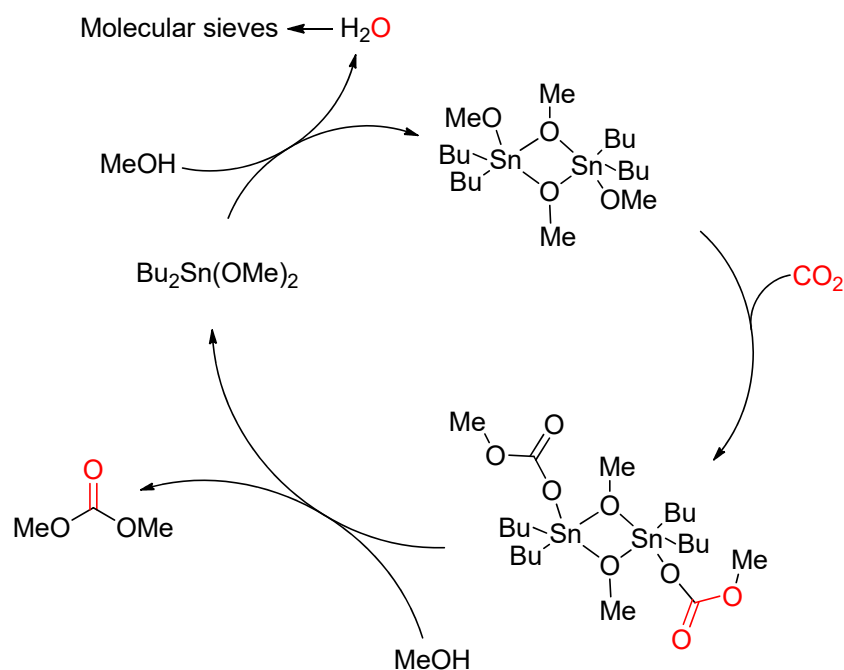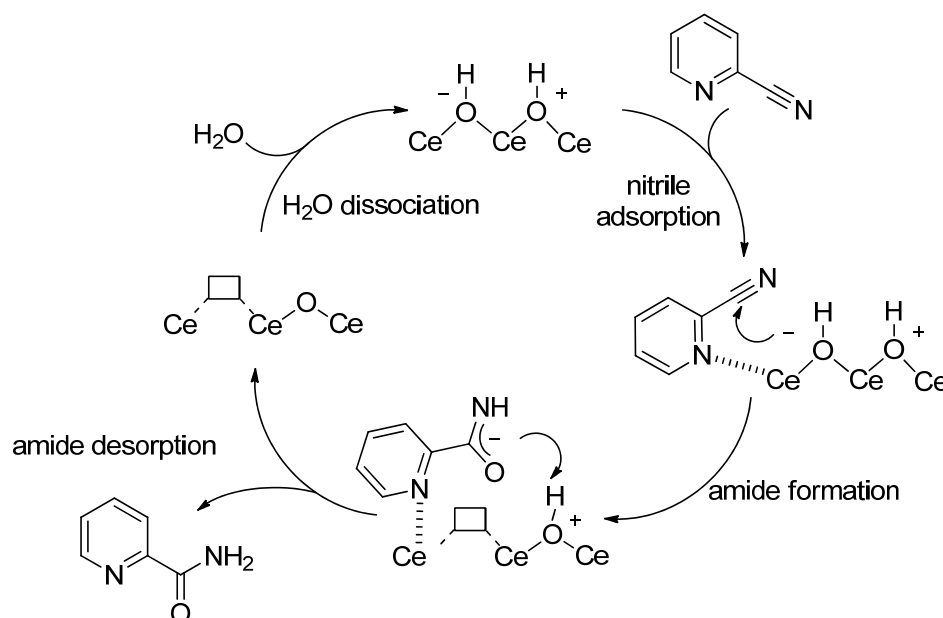
Scheme 3. Catalytic cycle for the formation of DMC using BU$_2$Sn(OMe)$_2$. Adapted from [40].
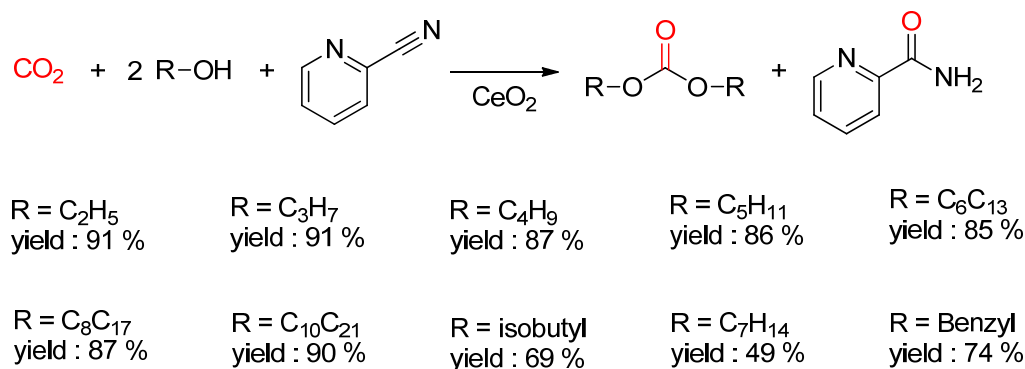
- Reactive dehydrative systems;

To tackle the water issue and push the reaction equilibrium towards DMC formation, two scenarios involving stoichiometric or excessive reactive dehydrative systems were developed. In the first one, DMC was synthesized from CO$_2$ and methanol (P$_{CO_2}$ = 15 MPa, T = 180 °C, t = 2–10 h) using (Bu)$_2$SnO in combination with CaC$_2$, which spontaneously consumed water to form acetylene as a by-product. DMC was formed with yields up to 11% with 13 mol% of CaC$_2$ [43]. In the second scenario, a single catalyst was used to simultaneously drive the alcohol carbonation and hydration of the desiccant, for example the catalytic hydration of nitriles into amides. This elegant concept was pioneered by Tomishige, who used CeO$_2$ as metal oxide catalyst and nitriles as reactive desiccants in synergy [44,45]. Zirconia-based catalysts [26,29] and amphoteric CeO$_2$ simultaneously display active acidic and basic sites that activate CO$_2$ and methanol. These acidic and basic sites were characterized by Lavalley et al., who differentiated low-coordination Ce cations resulting from oxygen defects as acid sites, and oxygen atoms adjacent to these low-coordination Ce cations as basic sites [46,47] that can properly fix alcohols and CO$_2$ [48]. Interestingly, these acid-base properties can efficiently catalyze nitrile hydration into amides. Among nitriles, acetonitrile was first considered. In situ FT-IR studies revealed the presence of CH$_3$CN adsorbed over CeO$_2$. When water is added to the system, a simultaneous decrease in CH$_3$CN species with increases in the acetamide anion CH$_3$CONH$^-$ and amide CH$_3$CONH$_2$ can be observed, meaning that CeO$_2$ successfully catalyzes this reaction [44]. Mechanistic insights revealed that water is dissociated over CeO$_2$ and the OH$^-$ species generated on the acid sites, which react with the adsorbed CH$_3$CN to form the acetamide anion. Reprotonation occurs thanks to the H$^+$ species generated on basic sites from H$_2$O dissociation over CeO$_2$.

When applied to the synthesis of acyclic alkyl carbonates from alcohol and CO$_2$, the CeO$_2$–acetonitrile system effectively increased the yield of carbonate [49,50]. DMC was obtained with a 8.9% yield and 64% selectivity and diethyl carbonate was obtained (DEC) with a 7.5% yield and 94% selectivity under relatively mild conditions (150 °C and 0.2–0.5 MPa). The low selectivity for DMC formation arose from side reactions driven by the by-produced amide. The latter can react with alcohols such as methanol to form esters with the release of ammonia. NH$_3$ further reacts with DMC to form methyl carbamate. To overcome these problems, the generated amide has to be more stable than acetamide.

Benzonitrile was then tested, since the phenolate ring would increase the stability of the benzamide and possibly prevent side reactions. At 150 °C and 1 MPa CO_2 pressure, the CeO_2–benzonitrile dual system afforded DMC in 47% yield with 78% selectivity [51]. To increase the yield, efforts were made to better understand the hydration reaction of nitriles over CeO_2. Tamura et al. successfully demonstrated that a heteroatom in the β-position of the nitrile function would considerably increase its adsorption over CeO_2 by coordinating this heteroatom, as was demonstrated for pyridine [52]. Combining all of these aspects, 2-furonitrile and 2-cyanopyridine were selected as the best candidates and showed excellent hydration yields at mild temperatures (90% at 80 °C after 7 h and 100% at 30 °C after 1 h, respectively [44]). A mechanism proposed by the authors is presented in Scheme 4. The best result was obtained with 2-cyanopyridine, whereby DMC was formed at 94% yield with 96% selectivity after 12 h at 120 °C and 5 MPa CO_2 pressure. A methanol/2-cyanopyridine ratio of 2:1 was needed, highlighting the need for a stoichiometric amount of dehydration agents. It should be noted that enhancement of the catalytic activity by increasing the amount of low-coordination Ce sites was achieved by preheating at 600 °C under air atmosphere for 3 h [53]. The protocol was extended to other alcohols and successfully demonstrated its versatility by affording a huge library of linear carbonates [54] (see Scheme 5).

Scheme 4. Catalytic cycle for the reaction of water with 2-cyanopyridine over CeO_2. Adapted from [44].

R = C_2H_5 yield : 91 %	R = C_3H_7 yield : 91 %	R = C_4H_9 yield : 87 %	R = C_5H_{11} yield : 86 %	R = C_6C_{13} yield : 85 %
R = C_8C_{17} yield : 87 %	R = $C_{10}C_{21}$ yield : 90 %	R = isobutyl yield : 69 %	R = C_7H_{14} yield : 49 %	R = Benzyl yield : 74 %

Scheme 5. Library of linear carbonates afforded via the CeO_2/2-cyanopyridine route (CeO_2 0.34 g, alcohol/2-cyanopyridine = 20 mmol:100 mmol, T = 120–150 °C, P_{CO_2} = 5 MPa, t = 16–48 h). Reprinted from [54].

2.1.2. Synthesis of Acyclic Carbonates via the Alkylation Route

Another way to promote the formation of linear carbonates from the coupling of alcohols and CO_2 is to use co-reagents in stoichiometric amounts that will bypass the formation of water. Conceptually, alcohols can be activated or even deprotonated by bases to generate a methoxy species that can bind spontaneously with CO_2 to form the corresponding $ROC(O)O^-$ hemi-carbonate. This nucleophilic anion further reacts with a halide reagent R'-X, which undergoes a nucleophilic substitution to produce the envisioned $ROC(O)OR'$ species.

Inorganic bases: Inorganic carbonates have been studied for the three-component coupling of CO_2, alcohols and alkyl or benzyl halides. Jung et al. proposed a comparative study of different inorganic carbonates with tetrabutylammonium iodide (TBAI) as an additive and n-butyl bromide as a co-reagent based on the model carbonation of 4-phenyl-1-butanol with CO_2 [55]. Interestingly, Na_2CO_3, Rb_2CO_3, K_2CO_3 and Cs_2CO_3 successfully demonstrated their activity in mild conditions (23 °C, atmospheric pressure of CO_2 bubbling). No reaction was observed with Li_2CO_3. The yield remained low for sodium- and potassium-based carbonates (2%), as well as for Rb_2CO_3 (10%). Excellent yield was displayed for Cs_2CO_3 (85%) in only 6 h. Good enhancement of the base activity was attributed to the known "cesium effect". Due to its larger ionic radius, the cesium cation weakly bonds to the methoxy species generated through alcohol deprotonation. TBAI plays its role in stabilizing the carbonate anion generated after CO_2 insertion and prevents non-desired alkylation. The scope was then extended to other alcohols and alkyl or benzyl halides were more sterically hindered, affording a wide variety of linear carbonates. By using excess base (5 eq), TBAI (5 eq) and R-X (5 eq), cheaper base K_2CO_3 could afford linear carbonates from various substrates (up to 82% with benzyl alcohol and benzyl bromide) at 60 °C [56]. The utilization of other additives such as crown ethers, KI or tetrabutylammonium bromide was found to be detrimental to the reaction yields.

Organic bases: As with inorganic bases, organic superbases drove the synthesis of acyclic carbonate from alcohols, CO_2 and alkyl halides. With KI or KI/crown ethers as additives added in a catalytic amount (10 mol% regarding the alcohol), dibenzyl carbonate was successfully synthetized in moderate yields (25% and 30% respectively), demonstrating the efficiency of DBU for CO_2 fixation onto alcohols [56]. It should be noted that in this case, benzyl chloride was used instead of benzyl bromide to prevent possible side quaternization of DBU [57]. Bicyclic guanidines were, thus, tested as bases for the coupling of alcohols and CO_2. Merging computational and experimental studies allowed the reaction mechanism to be elucidated. Computational insights (conducted at the B3LYP level using the 6–31 g(d) basis set) aided in comprehending the mechanism of the carbonate formation using DBU as a base. Wang et al. suggested the four possible mechanisms shown in Scheme 6 [58]. Considering thermodynamic and kinetic aspects ($\Delta G = -16.20$ kJ/mol and $\Delta G^{\ddagger} = 30.47$ kJ/mol, rate constant of 2.9×10^7 s^{-1}), the plausible mechanism involved a one-step trimolecular reaction between CO_2 the alcohol and DBU (mechanism 4 in Scheme 6), even though activation of CO_2 by DBU (mechanism 3 in Scheme 6) is theoretically feasible prior to formation of the acyclic carbonate via its addition onto the alkyl halide. However, it should not be generalized to other amidines and guanidines. Indeed, when using TBD, the zwitterionic adduct with CO_2 was still observed under strictly anhydrous conditions [59]. Thanks to the presence of both sp^2 amine and secondary sp^3 amine functions, the adduct was stabilized and could be isolated and well characterized by X-ray diffraction to determine the crystal structure (see Scheme 7). In this case, the adduct was more stable than in the case of DBU thanks to the hydrogen bonding between secondary amine of the N' labelled atom with the O' atom of CO_2 bound to TBD. However, when applied to the alcohol/CO_2 system, which was propanediol in this case, the synthesis of the corresponding carbonate is more likely to happen with that activation of the alcohol rather than CO_2 [60].
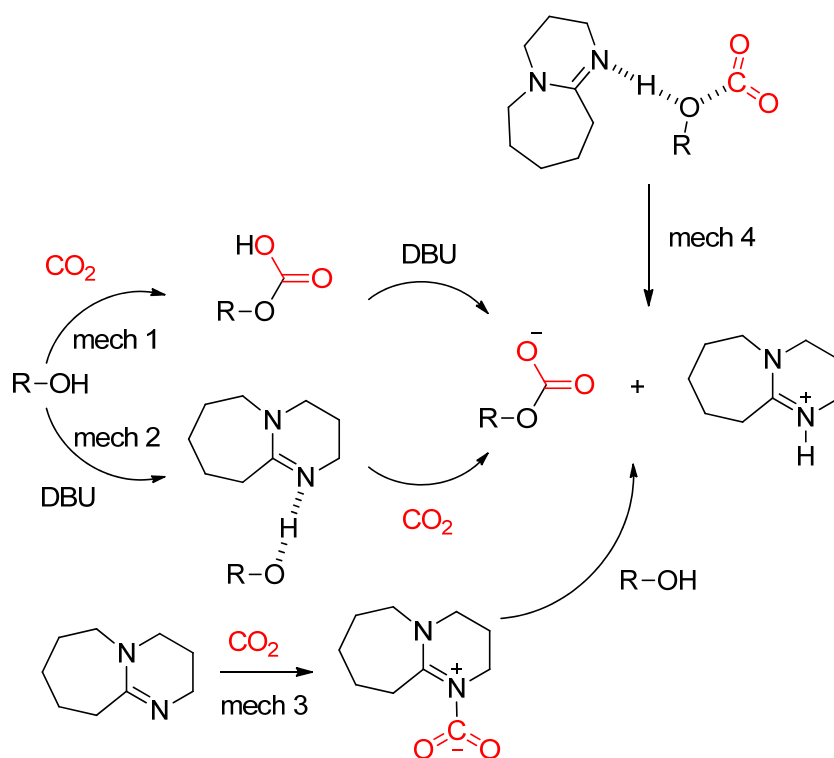
Scheme 6. Mechanisms considered for the computational studies of CO_2 fixation onto alcohols via the organic superbase DBU. Mechanism 4 displays the most favored pathway in terms of the kinetics and thermodynamics. Adapted from [58].
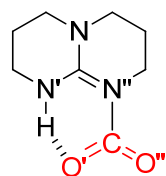
Scheme 7. TBD-CO_2 stabilized adduct isolated and characterized by X-ray diffraction. Adapted from [59].

Ionic liquids derived from Hünig's base-type cations were used as recyclable bases in replacement of DBU or TDB for the fixation of CO_2 onto alcohols with benzyl bromide as the co-reagent [61]. Due to their non-nucleophilic characters, no side reaction between the base and the benzyl halide was detected. The high basicity of the ionic liquids allowed the spontaneous deprotonation of the alcohol moiety. The generated methoxy species is able to attack CO_2, and SN_2 on benzyl bromide will generate the corresponding non-symmetrical linear carbonate. At 25 °C and under 1 MPa CO_2 pressure after 72 h, good yields were obtained for ethanol (82%), allyl alcohol (80%), benzyl alcohol (83%), phenol (78%), propargylic alcohol (76%) and 2-butanol (67%), with an alcohol/halide/IL molar ratio of 1:0.5:0.6. The ionic liquid was successfully recycled by distillation or extraction, with no loss of activity when reused.

2.1.3. Synthesis of Acyclic Carbonates Using the "Leaving Group" Strategy

The formation of acyclic carbonate using the leaving group strategy shares conceptual similarities with the alkylation route. The hemi-carbonate ion resulting from the trimolecular reaction between the alcohol, base and CO_2 attacks a dihalide species such as CH_2X_2 through a nucleophilic substitution to produce the corresponding acyclic carbonate. This highly reactive $ROC(O)OCH_2X$ further undergoes a transcarbonation reaction with a

second alcohol, providing the desired ROC(O)OR carbonate. This concept was applied to fabricate dibenzyl carbonate from CO_2 and benzyl alcohol using DBU with the ionic liquid bmimPF$_6$ as an additive in CH_2Br_2 at 70 °C under 1 MPa CO_2 pressure [62]. Dibenzyl carbonate was obtained in 69% yield with 2 equivalents of DBU and 0.1 mL of bmimPF$_6$ for 0.5 mmol of benzyl alcohol. Equimolar amounts of [DBUH]Br salt and BrCH$_2$OH were concomitantly generated as by-products. The authors did not mention any particular role of the ionic liquid in the mechanism itself, but rather as a promotor for CO_2 solubilization in the reaction media. When bmimPF$_6$ was not added to the system, the yield decreased from 69% to 25%. Similarly, when CH_2Cl_2 was used instead of CH_2Br_2, the yield decreased to 25%, supporting the SN_2 mechanism, which is more favorable with bromine versus chlorine in terms of its reactivity. No carbonate was produced with more reactive halides such as CH_3I, supposedly due to quaternization of DBU. The optimized protocol was applied to other benzyl alcohols derivatives and could afford the corresponding carbonates in moderate to good yields (from 47% to 73%). DMC was also synthetized with 48% yield.

2.1.4. Synthesis of Acyclic Carbonates via the Carbodiimide Route

Aresta et al. designed an elegant method for synthesizing acyclic carbonates using carbodiimides acting both as the co-reagent and base [63]. Carbodiimides react with the alcohol to produce an isolable O-alkyl isourea intermediate [64]. This reaction can be catalyzed by transition-metal-based complexes (mostly copper-based) such as CuCl, Cu$_2$I$_2$, CuO, Cu(OAc)$_2$ and ZnO$_2$; organic superbases such as TBD; or alkali–metal TBD complexes [65]. Then, the O-alkyl isourea participates in a trimolecular interaction between the alcohol and CO_2 via its remaining basic iminoether moiety, leading to an isourea–hemicarbonate adduct that allows for the carbonation of a second alcohol molecule. The latter will react with the alkyl part fixed on the O-alkyl isourea to generate the corresponding linear alkyl carbonate (see Scheme 8). Following this approach, DMC was synthetized in yields of up to 62% in 6 h at 65 °C with 5 MPa of CO_2. Allyl alcohol successfully provided the corresponding carbonates as well, with the best yield of 93% using an alcohol/DCC ratio of 15:1 and DCC/Cu$_2$I$_2$ ratio of 500 at 65 °C and 5 MPa CO_2 pressure after only 4 h.
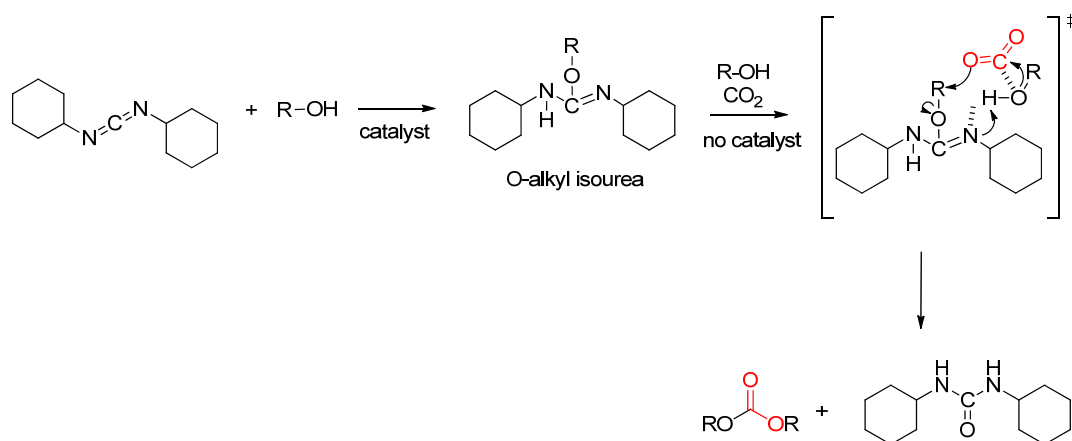
Scheme 8. Reaction mechanism proposed for the synthesis of acyclic carbonates from alcohols, CO_2 and carbodiimides. Adapted from [63].

2.1.5. Synthesis of Acyclic Carbonates from the "Protected Alcohols" Route

Ketals undergo reversible hydrolysis to form alcohols and ketones. Thus, they can be seen as the protected form of dehydrated alcohols. Upon water release, the ketal decomposes in situ into the former ketone and an alcohol that is subsequently involved in a cascade coupling reaction with CO_2 to afford the acyclic carbonate (Scheme 9). Notably, systems merging the utilization of 2,2-dimethoxypropane or 2,2-diethoxypropane with CeO$_2$ or CeO$_2$-ZrO (mixite) oxide catalysts and CO_2 [66,67] gave access to DMC with yields

of 13.8–59.3 mmol·gcat^{-1} in 2 h at 110–140 °C and 5–6 MPa of CO_2. However, the main bottleneck of these systems arose from the slow hydration rate of the 2,2-dialkoxypropane. To improve the performances, acidic co-catalysts were used as additives to boost the ketal hydration. Heterogeneous acids such as zeolites (H-FAU zeolite with SiO_2/Al_2O_3 = 5.5) used in combination with 2,2-diethoxypropane and CeO_2 catalyst remarkably increased the DEC yields up to 72% based on 2,2-diethoxypropane (T = 120 °C and 9.5 MPa of CO_2) [68].
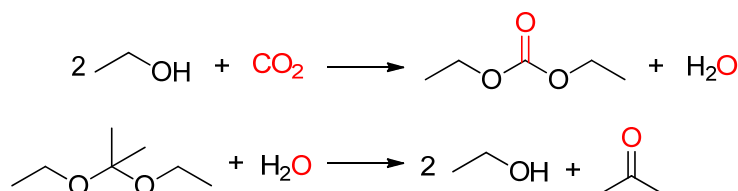
Scheme 9. Cascade reaction for the formation of DEC from 2,2-diethoxypropane, initiated by ethanol. Adapted from [68].

As with ketals, the structural features of orthoesters make them sensitive to hydrolysis and decompose into esters and alcohols. Orthoesters are good candidates for consuming water while releasing the alcohols during the fabrication of the acyclic carbonates in situ. As a representative example, DMC was synthesized by combining trimethyl orthoacetate with supercritical CO_2 using binary catalysts made of organotin complexes and ammonium, phosphonium salt additives [69] or ceria–zirconia mixte oxides catalysts [70]. The highest DMC yield of 70% was obtained after 72 h at 180 °C, under 30 MPa of CO_2 pressure using the $Bu_2Sn(OMe)_2/Bu_4PI$ catalytic system, while lower DMC yields of 1.8–10.4% were obtained at 12 MPa after 34 h when 1,1,1-trimethyl orthoformiate was combined with ceria–zirconia oxides. Recently, Fukaya revisited this conceptual route by using water-sensitive an alkoxysilane, i.e., tetraethyl orthosilicate, as the alcohol precursor and a $Zr(OEt)_4$ catalyst, which favors the ethoxylation of CO_2 [71]. The DEC yield reached 58% after 24 h at 180 °C under 5 MPa of CO_2. As with the last method, trimethylphosphate was tested as a water scavenger to synthesize DMC from in-situ-generated methanol. The transformation of CO_2 into the acyclic carbonate was performed at 180 °C for 20 h under 2.8 MPa of CO_2 using catalytic amounts of $Bu_2Sn(OBu)_2$ and provided DMC with a moderate yield of 47% [19].

2.2. Synthesis of Cyclic Organic Carbonates

Cyclic carbonates are useful chemicals deserving huge interest as green solvents, electrolyte for batteries or monomers to design polycarbonate or isocyanate-free polyurethanes. Most of them are easily produced from vicinal or 1,3-diols and highly reactive phosgene derivatives, diphenyl carbonate (DPC) or DMC [72–74], which can be CO_2-based, as demonstrated previously in this review. Finding efficient routes to convert alcohols directly into their corresponding cyclic carbonate has become a challenge in CO_2 chemistry. This section is dedicated to the various strategies that have been engineered to synthesize these heterocycles from various alcohols substrates, including vicinal and 1,3-diols, allylic and propargylic alcohols and halohydrins. One has to keep in mind that 5-membered and 6-membered cyclic carbonates will be exclusively discussed in this section, since their formation is thermodynamically and kinetically more favorable than smaller or larger rings.

2.2.1. Synthesis of Cyclic Carbonates from Diols

Diols are ubiquitous scaffolds that are readily available from biomass, making them attractive substrates for the synthesis of cyclic carbonates [75,76]. However, the direct carbonation of vicinal or 1,3-diols suffers from the same thermodynamic limitation as that observed for the synthesis of acyclic carbonates from monoalcohols, i.e., the formation of water by-products [77]. Therefore, most of the strategies proposed for the fabrication of acyclic carbonates may be transposed to diol substrates. However, the large diversity of

substrates investigated in the scientific literature to produce cyclic carbonates from diols made it difficult to summarize and rationalize the results. This may confer to the reader of the following sections the perception of a lack of coherence in the manuscript.

2.2.1.1. Dehydrative Condensation

Physical drying systems: Glycerol, a waste bio-based polyol from the production of biodiesel, was converted by Aresta et al. into glycerol carbonate with CO_2 via the dehydrative condensation approach. By using n-$Bu_2Sn(OCH_3)_2$ in combination with molecular sieves at 180 °C under 5 MPa CO_2 pressure, the cyclic carbonate was produced with a low yield of ~7% in 15 h (see Scheme 10) [78].
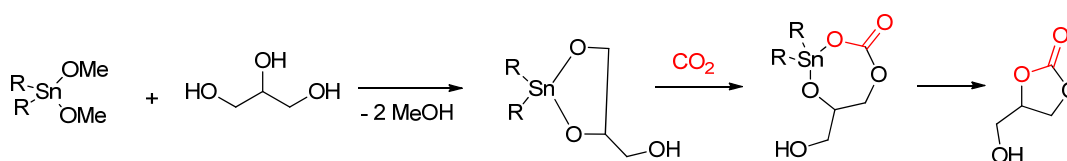
Scheme 10. Synthetic pathway for the synthesis of glycerol carbonate from glycerol catalyzed by n-$Bu_2Sn(OCH_3)_2$. Adapted from [78].

Switching to n-Bu_2SnO was detrimental, with glycerol carbonate yields decreasing to ~3%. The catalytic activity of n-Bu_2SnO could be enhanced via the addition of methanol [41]. Glycerol carbonate was obtained selectively with a yield of 35% in 4 h with 13X zeolite as the dehydration agent at 120 °C under 13.5 MPa CO_2. It was postulated that methanol played a dual role. It acted as a solvent, providing a homogeneous reaction mixture. Methanol also transformed Bu_2SnO in situ into the more active n-$Bu_2Sn(OCH_3)_2$ catalyst. The catalytic cycle involved is presented in Scheme 11. This protocol was extended to the selective synthesis of ethylene carbonate and propylene carbonate from ethylene glycol and propylene glycol, respectively, in good yields (61% and 42%, respectively), using zeolite as the drying system [79].
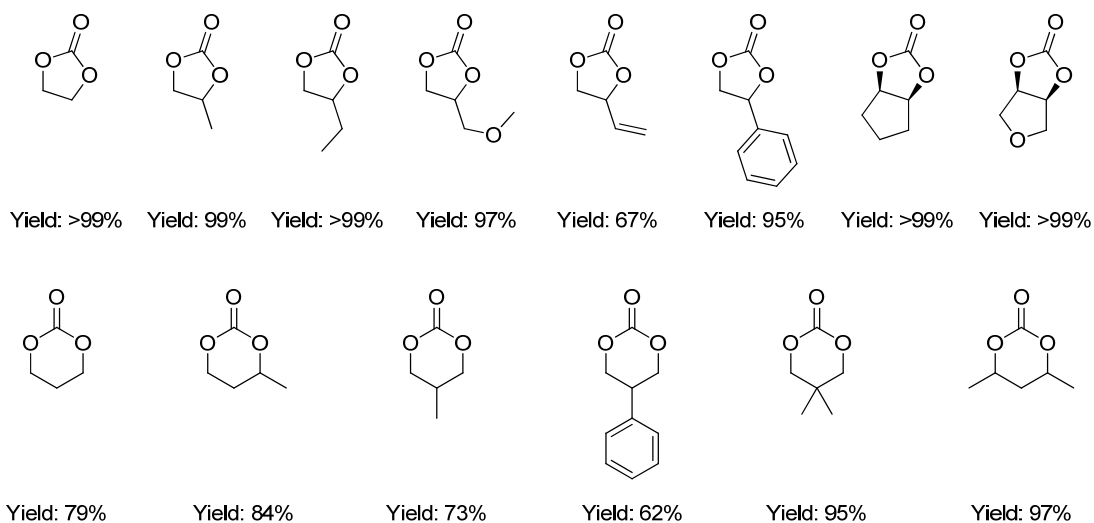
Reactive dehydrative systems: The activity of dual catalysts mixing a metal oxide (ZrO_2, Al_2O_3, TiO_2, polyhedral CeO_2 or ZnO) with 2-cyanopyridine was evaluated for the synthesis of glycerol carbonate from glycerol and CO_2 (T = 170 °C, 10 MPa of CO_2 for 12 h). The benchmarking of the glycerol carbonate yields evolving from ~10.4 to 14.2% enabled the classification of the catalysts regarding their activity in the order of $ZrO_2 \sim Al_2O_3 < TiO_2 < ZnO < CeO_2$. In the quest for the optimization of the glycerol carbonate production, the influence of the reactive desiccant on the reaction was evaluated with polyhedral CeO_2 and revealed that replacing 2-cyanopyridine by 3- or 4-cyanopyridine and acetonitrile was detrimental, with yields below ~1–5%. The crucial role of the CeO_2 crystallinity [30] in the catalytic performance was also highlighted. Mesoporous CeO_2 and nanocubes displayed the lowest efficiency, with similar glycerol carbonate yields of ~10.3%. CeO_2 nanorods and nanowires increased the cyclic carbonate yields to ~13%. CeO_2 with polyhedral crystallinity remained the most effective catalyst [80]. Tomishige et al. further extended the substrates to other mono- or disubstituted vicinal or 1,3-diols using the CeO_2/2-cyanopyridine catalytic system (T = 130–150 °C, P_{CO_2} = 5 MPa, t = 1–8 h). Remarkably, the corresponding substituted 5-membered and 6-membered cyclic carbonates were synthesized in good to excellent yields (from 62% to 99% for 14 examples) [81], demonstrating the versatility of such systems (see Scheme 12).

As 2-cyanopyridine is rather expensive and used in large excess, acetonitrile was also considered as a more affordable solvent and dehydration agent. In combination with an organic base such as TBD (2.5 mol%), propylene carbonate could be synthetized with yields up to 22.5% but with a low selectivity rate of 60.3% [82], due to the side reaction of propylene glycol with the hydrolysis product of acetonitrile, namely acetic acid (ammonia is also generated). Ammonium carbonate (NH_4)$_2CO_3$ was found to considerably increase the selectivity toward propylene carbonate by preventing the decomposition of acetamide into

ammonia and acetic acid. However, the yield was lowered to 15.6%, due to decomposition of $(NH_4)_2CO_3$ into NH_4^+, which inhibits the hydrolysis of acetonitrile.
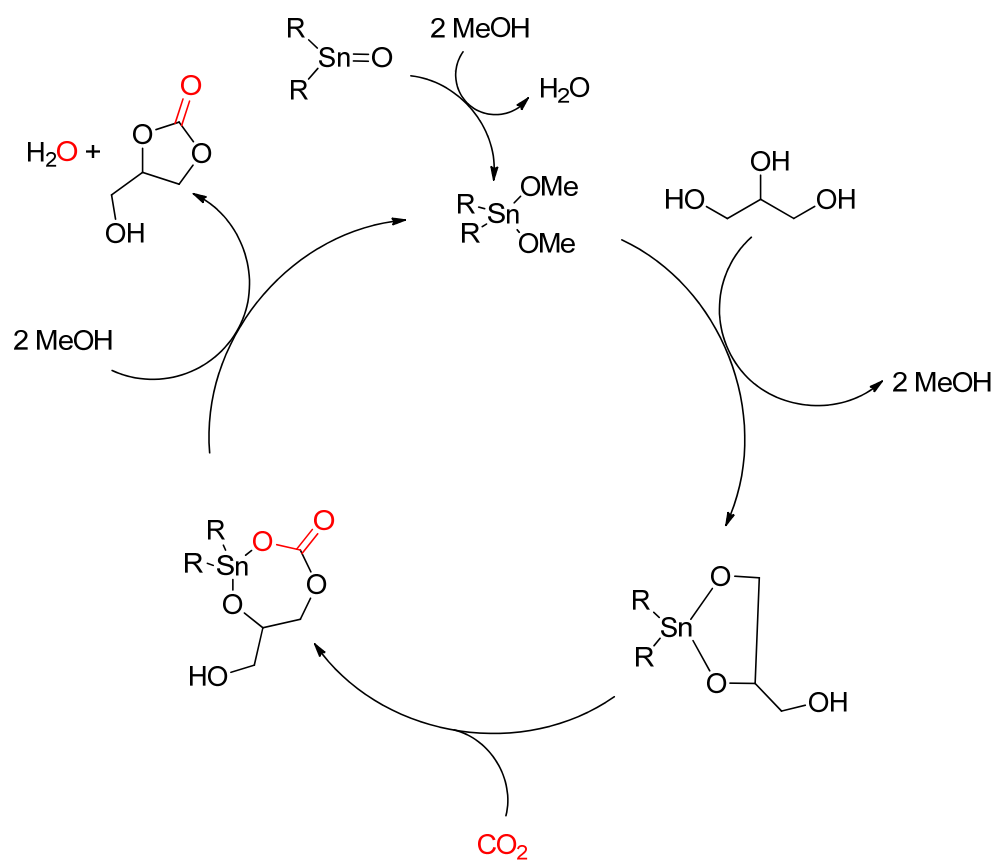
Scheme 11. Catalytic cycle for the synthesis of glycerol carbonate from glycerol and CO_2 using n-Bu$_2$Sn(OCH$_3$)$_2$ as the catalyst. Adapted from [41].

Yield: >99%   Yield: 99%   Yield: >99%   Yield: 97%   Yield: 67%   Yield: 95%   Yield: >99%   Yield: >99%

Yield: 79%   Yield: 84%   Yield: 73%   Yield: 62%   Yield: 95%   Yield: 97%

Scheme 12. Library of affordable 5- and 6-membered cyclic carbonates obtained with the a dual CeO$_2$/2-cyanopyridine system (CeO$_2$ = 2 mmol, diol/2-cyanopyridine = 10 mmol/100 mmol, T = 130–150 °C, P$_{CO_2}$ = 5 MPa, t = 1–8 h). Adapted from [81].

2.2.1.2. Cyclic Carbonates Synthesis via the Leaving Group Strategy or Alkylation Route

Alike acyclic carbonates (Sections 2.1.2 and 2.1.3), produced via strategies utilizing bases and alkyl or aryl halides R-X as co-reagents to bypass the formation of water, were used for CO_2 fixation onto vicinal or 1,3-diols. Mechanistically, the hemi-carbonate ion formed by fixation of CO_2 onto one OH moiety undergoes an alkylation by SN_2 substitution with an alkyl halide. Then, the second OH group is involved in an intramolecular transcarbonation reaction promoting the ring closure of the molecule (see Scheme 13).
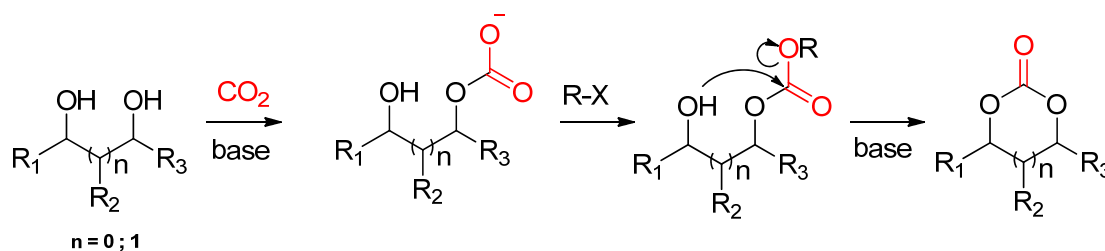
Scheme 13. General "leaving group" or "alkylation" strategy used to obtain cyclic carbonates from diols.

Organic systems combining DBU with CH_2Br_2 or BuBr as alkylation agents and ionic liquid $bmimPF_6$ or CH_2Cl_2 as solvents promoted the formation of a large diversity of (substituted) 5- or 6-membered cyclic carbonates (glycerol, styrene, propylene, *cis*-cyclohexene, trimethylene, carbonates) under mild operative conditions (T = 25–70 °C, P_{CO_2} = 0.1–1 MPa, t = 18–24 h) [62,83], with yields ranging from 60 to 90%. Unfortunately, when diols are chosen as substrates to fix CO_2, the carbonation of both alcohol moieties followed by double alkylation drives the concomitant formation of an acyclic bis-carbonate by-product. The competition between the mono- and double carbonations seems dependent on both the substrate and the nature of the base. A second challenge lies in the formation of a second type of acyclic carbonate. Upon cyclization, an alcoholate group is released in the reaction medium. This species is then capable of fixing one molecule of CO_2 and reacting via SN_2 with the alkyl halide co-reagent to form a (reactive) linear dialkyl carbonate. Inspired by these studies, Buchard et al. utilized highly reactive tosyl chloride (TsCl) as a co-reagent in combination with organic bases to promote the fixation of CO_2 onto 1,3-diols [84]. TsCl reacts easily with *O*-nucleophiles to form a tosylate known to be a very good leaving group [85]. However, TsCl is not compatible with DBU and spontaneously formed a [DBUTs]Cl, meaning that a sequential procedure was using to fabricate the 6-membered cyclic carbonates. Firstly, the carbonation of one of the two alcohol moieties by CO_2 fixation was promoted by using 1 equivalent of DBU. Once all the DBU was reacted, TsCl and TEA were introduced to perform the intramolecular cyclization. A mechanistic proposal was proposed by DFT calculations and supported by carbonation experiments of optically active diols. Similarly to what was proposed with alkyl or aryl halides, TsCl reacted more preferentially with the generated anionic carbonate than with the remaining alcohol moiety, exclusively showing stereochemistry retention (see Scheme 14). Such approach enabled the synthesis of up to ten 6-membered cyclic carbonates from substituted 1,3-diols with moderate to good isolated yields at room temperature with atmospheric pressure of CO_2 in chloroform.

Later, the same group decoupled the reaction and investigated in detail the influence of various tertiary amines and solvents on the carbonation step of neopentyl glycol [86]. With less-toxic acetonitrile instead of chloroform, 1 eq of DBU afforded 85% of CO_2 insertion with a mono/double carbonation ratio of 59:41. 2,2,6,6-Tetramethylpiperidine (TMP) and TEA showed very low CO_2 insertion rates of 2% and 4%, respectively, but with 100% selectivity toward monoinsertion. No carbonation was observed with pyridine.
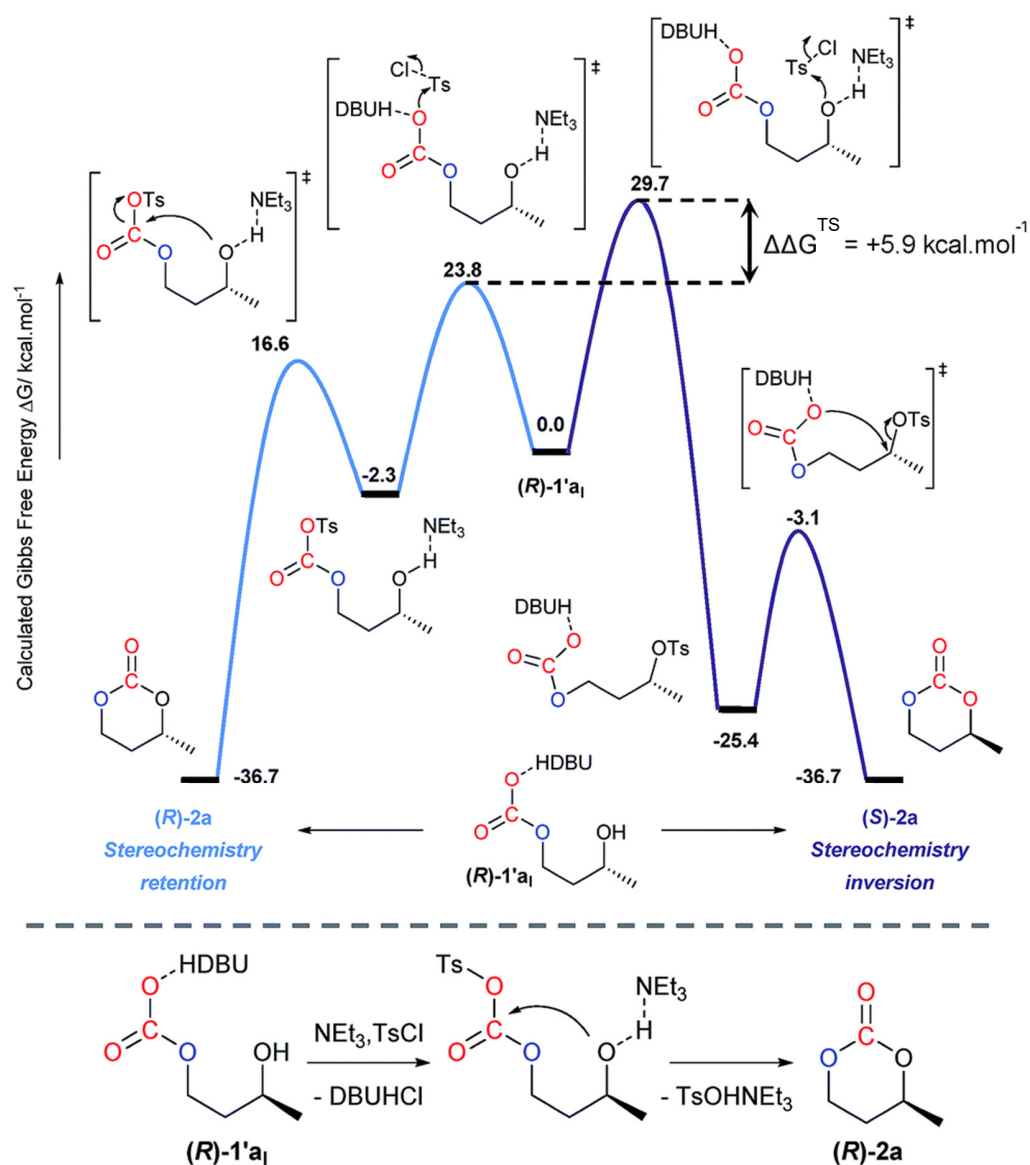
Scheme 14. Computational study of the synthesis of 6-membered cyclic carbonate from a diol using the DBU/TsCl system. G. L. Gregory, M. Ulmann and A. Buchard, *RSC Adv.*, 2015, 5, 39404; Published by The Royal Society of Chemistry [84].

In accordance with these results, they adapted their synthetic procedure in a one-pot and one-step fashion by utilizing TsCl (1 eq) with TEA or TMP as the base (2 eq) for the carbonation of 1,x-diols (with x = 2–4), including challenging tri- or tetrasubstituted substrates. The non-nucleophilic character of these organic bases allowed the simultaneous addition of TsCl and the base without undesirable side quaternization of the amine. Here, 5-, 6- and even 7-membered cyclic carbonates were fabricated with excellent isolated yields using this simple approach, with similar or even better yields than those reported using the phosgene route. Nevertheless, with 1,4-diols, non-negligible amounts of oligomers were noted, possibly due to the poor stability of 7-membered cyclic carbonates in basic conditions or a competition between the cyclization and the polymerization. In the same manner, a critical study balancing two metal-free dual activating systems, namely DBU/EtBr and TEA/TsCl, was recently proposed for the coupling of CO_2 with 1,x-diols to afford (a)cyclic carbonates [87]. In situ ATR-IR monitoring correlated with DFT calculations was performed to investigate the mechanism and reaction kinetics under various experimental conditions, leading to an optimized synthetic protocol. By choosing the suitable organic dual-activation

system, it was possible to control the product selectivity to substituted ethylene- or trimethylene carbonate or acyclic compounds, providing a powerful tool to synthesize CO_2-based precursors that are highly relevant for organic and polymer chemistry from ubiquitous building blocks.

N-heterocyclic carbenes (NHC) are known to activate CO_2 under the form of imidazolium carboxylates [88,89] and can be used in combination with a base and an alkylating agent to form cyclic carbonates from diols. Dyson et al. illustrated how thiazolium carbene (20 mol%) generated in situ by Cs_2CO_3 (3 eq) promoted the formation of styrene carbonate (yield of 61%) when used in combination with 2 eq of BuBr (T = 90°C, 0.1 MPa of CO_2 in DMF) [90]. The authors suggested two competitive mechanisms leading to both cyclic carbonates. In the first one, CO_2 was activated via the formation of a thiazolium carboxylate diadduct that attacked the alkyl halide R-X through nucleophilic substitution, forming a carbonate ion. Deprotonation of an alcohol moiety by the base allows transesterification on this carboxylate with RO^- as the leaving group. The cyclization is promoted with a second equivalent of base (Scheme 15). In the second plausible mechanism, dibutyl carbonate was formed from the reaction of CO_3^{2-} with BuBr. Then, an oxidative carboxylation occurred via the reaction between the diol and dibutyl carbonate to produce the cyclic carbonate. In this case, CO_2 did not participate in the carbonation of the diol (Scheme 16). The validity of this hypothesis was supported by the formation of the cyclic carbonate, even in the absence of CO_2, as the cyclic carbonate yield considerably decreased but was still significant (25%).
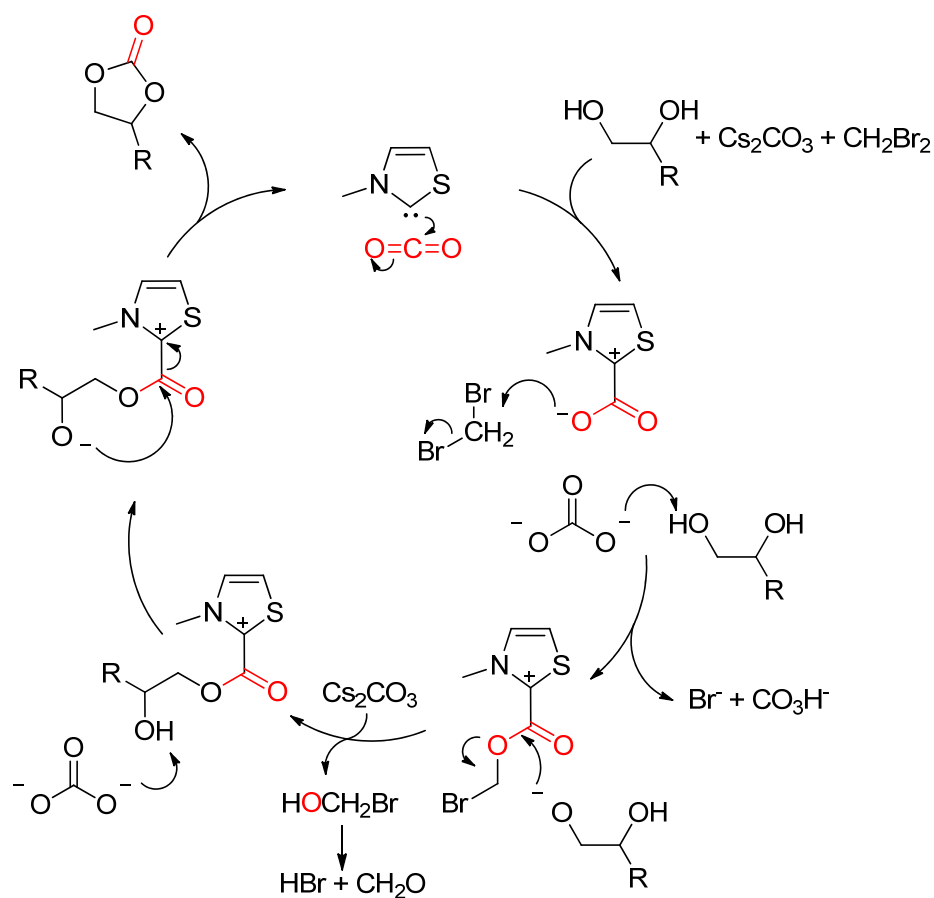
Scheme 15. Mechanism proposed for the formation of cyclic carbonates from diols catalyzed by ionic liquids and Cs_2CO_3 in the presence of alkyl halides. Adapted from [90].
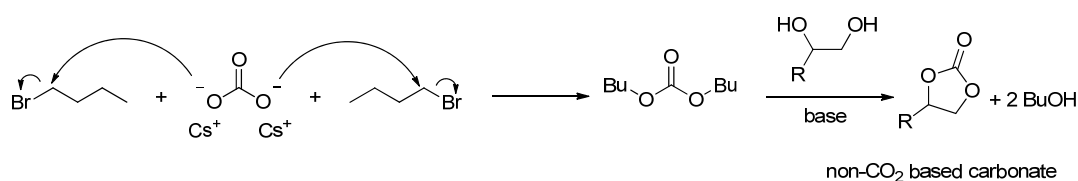
Scheme 16. Competitive pathway for the formation of carbonate linkages leading to non-CO_2-based cyclic carbonates. Adapted from [90].
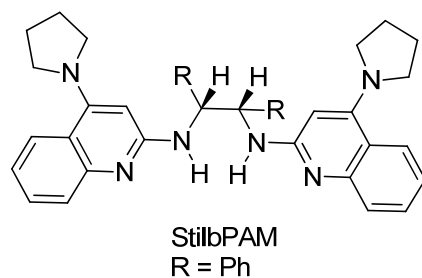
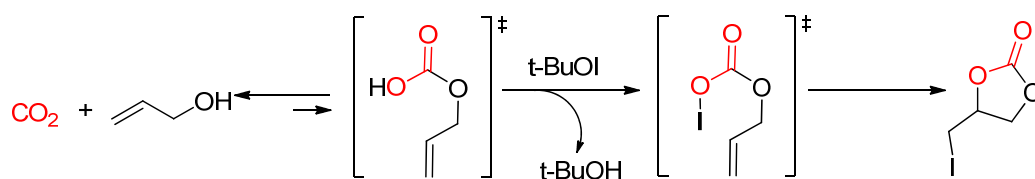### 2.2.2. Synthesis of Cyclic Carbonates from Allyl Alcohols

The pioneering study by Cardillo et al. in 1981 demonstrated the efficiency of allyl alcohols as valuable substrates for the formation of cyclic carbonates with CO_2 [91]. In their study, various 5- and 6-membered cyclic iodocarbonates were synthetized from allylic and homoallylic alcohols and CO_2, using n-butyllithium as a base and I_2 as a promotor for cyclization. Functionalization of the double bond by I_2 is highly regioselective, which allows the formation of the product in very good yields under mild conditions (CO_2 bubbling in THF; T = 25 °C, t = 12 h). With an alcohol/iodine/base molar ratio of 10:20:6.6, various 5-membered cyclic iodocarbonates were obtained from primary, secondary and even tertiary allylic alcohols in moderate to good yields (60–90%). Furthermore, 6-membered cyclic iodocarbonates were also obtained from primary and secondary homoallylic alcohols in yields ranging from 72% to 80%. The generated iodocarbonate could be converted into iodine-free carbonate via treatment with Bu_3SnH. Conversion of homoallylic alcohols into 6-membered cyclic iodocarbonates was also investigated using *N*-iodosuccinimide as the iodine agent (1.1 eq with regard to the alcohol) [92]. The catalytic system used relies on a Brønsted acid-base bifunctional salt with best results using pyrrolidine-substituted bis(amidine) incorporating *trans*-stilbene diamine (StilbPBAM, see Scheme 17) as the base and triflimidic acid $HNTf_2$ as the acid. Good to excellent yields were obtained for a large substrate range of primary homoallylic alcohols in toluene at −20 °C with CO_2 bubbling (Scheme 18). High enantiomeric excess was observed in most cases. Molecular sieves were added to prevent deactivation of the catalyst in the presence of water and CO_2. The use of an acid is assumed to stabilize the CO_2–alcohol adduct. To overcome the use of toxic or expensive iodinating agents, Minakata et al. proposed the use of ${}^tBuOI$, which can be generated in situ from ${}^tBuOCl$ and NaI, for the conversion of allylic and homoallylic alcohols into 5- and 6-membered iodocarbonates [93]. In this case, ${}^tBuOI$ abstracts the proton of a weak acid that is replaced by an iodine atom. The thermodynamically disfavored synthesis of alkylcarbonic acid from the CO_2–alcohol coupling can then be turned into a highly reactive iodinated intermediate, with which cyclization is promoted by the presence of the double bond (Scheme 19). Thus, if the alkylcarbonic acid can be trapped in some way, the equilibrium should be displaced toward the formation of cyclic iodocarbonates. This proposed mechanism should be consolidated with more theoretical and experimental studies. The substrate scope proved the efficiency of this non-catalytic method, affording cyclic carbonate scaffolds with good yields (from 57% to 93%) when 2 eq of ${}^tBuOI$ was used at −20 °C with CO_2 bubbling.

StilbPAM
R = Ph

Scheme 17. StilbPAM structure as the base for the Brønsted acid-base bifunctional salt used in the synthesis of iodocarbonates from allyl alcohols.
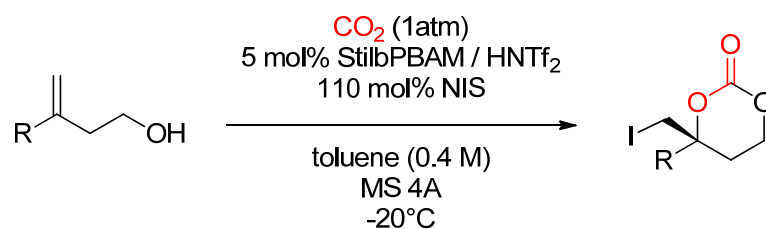
Scheme 18. Example of iodocarbonate synthesis from allyl alcohol using Brønsted acid-base bifunctional salt catalysts and *N*-iodosuccinimide as the iodinating agent. Adapted from [92].

Scheme 19. Proposed mechanism for the formation of iodocarbonate from allyl alcohol using t-BuOI as the iodinating agent. Adapted from [93].

2.2.3. Synthesis of Cyclic Carbonates from Halohydrin

A more direct route for the synthesis of 5- and 6-membered cyclic carbonates is the use of β- and γ-halohydrins in combination with a base (1.1 eq) and CO_2. Ethylene carbonate and trimethylene carbonate are examples of scaffolds obtained from 2-chloroethanol and 3-chloropropanol using this approach, providing excellent yields (>95% yield by simple bubbling of CO_2 at 40 °C) [85]. The proposed mechanism is quite simple. Cs_2CO_3 deprotonates the alcohol to form an alcoholate that fixes CO_2. Then, the ring-closure occurs via intramolecular nucleophilic substitution with Cl^- as the leaving group. Less reactive bases such as K_2CO_3 afforded lower carbonate yields (54%), as well as the more reactive KO^tBu (20%), once again highlighting the excellent properties of cesium for these reactions. Slightly lower yields were obtained when replacing 2-chloroethanol with 2-bromo or 2-iodoethanol. Interestingly, when a tosylate OT substituent was used instead of a halide, the corresponding cyclic carbonate was also obtained in very good yields for a range of substrates (from 65% to 95%). When (±)-3-chloro-1,2-propanediol was used as the substrate, exclusive formation of glycerol carbonate was observed, demonstrating the excellent selectivity of this reaction. As K_2CO_3 is a cheaper and more affordable base than Cs_2CO_3, Wang et al. investigated the effects of additives on the formation of cyclic carbonate from halohydrins and CO_2 with K_2CO_3 [94]. With Poly(ethylene glycol) of M_n = 400 g/mol (PEG-400), styrene carbonate, propylene carbonate, ethylene carbonate and chloromethyl-ethylene carbonate were formed quantitatively after 3 h at 50 °C under 2 MPa CO_2 pressure using 0.5 eq of K_2CO_3. The more challenging cyclohexene carbonate was obtained with 72% yield in the same conditions. The role of the additive was assumed to coordinate potassium cations favoring the salt dissociation in the medium, thereby increasing the basicity of K_2CO_3. Non-nucleophilic basic ionic liquids tested for the synthesis of linear carbonates by Goodrich et al. were also tested on 3-bromopropanol and 2-chloroethanol, successfully producing ethylene carbonate and trimethylene carbonate in good yields (>90%) with excellent selectivity toward cyclic products [61].

As halohydrins are not widely available and are generally synthetized from oxidation of olefins, a one-step synthesis from terminal alkenes was proposed by Li et al. [95] (Scheme 20). This method relies on the in situ generation of bromohydrin using water as both the solvent and oxidation agent, *N*-bromosuccinimide as the bromination agent (1 eq) and DBU as the base (2 eq) for CO_2 fixation onto the generated alcohol. The 5-membered cyclic carbonates were obtained in moderate to excellent yields after several hours of reaction at 60 °C under 2 MPa CO_2 pressure. From these results, a catalytic process was then envisioned, since bromide ion can be oxidized back to bromination agents under oxida-

tive conditions, allowing a catalytic cycle for the in situ generation of bromohydrin from olefins [96]. Hydrogen peroxide was used to regenerate the bromination agent. Several bromination agents were tested, and the best results were obtained with tetrabutylammonium bromide or NaBr. Styrene carbonate could be obtained at 70% yield using an olefin/base/bromination agent molar ratio of 1.5:0.2:0.15 after 15 h at 50 °C under 2 MPa of CO_2 pressure.
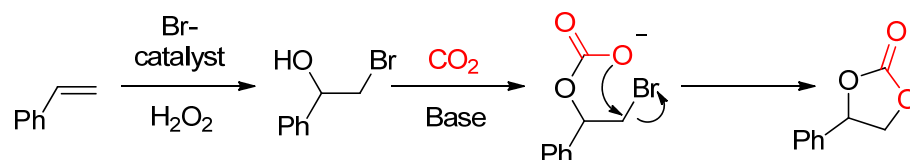
Scheme 20. Synthetic strategy used to obtain cyclic carbonates from terminal alkenes via in situ generation of halohydrin. Adapted from [97].

2.2.4. Synthesis of Cyclic Carbonates from Propargylic Alcohols

The carboxylation coupling of propargylic alcohols with CO_2 is highly attractive. This 100% atom economy synthetic pathway provides organic cyclic carbonates that slightly differ from conventional cyclocarbonate scaffolds due to the presence of an additional exovinylene moiety (Scheme 21). A large diversity of catalysts has been reported to promote this reaction. These catalysts have to fulfil a dual role: the activation of the alcohol moiety or CO_2 activation to facilitate the carbonation step, and the activation of the triple bond to drive the intramolecular cyclization and ring formation. The chemical structure of the substrate also strongly influences the formation of the cyclic scaffold. The carboxylative cyclization of tertiary propargylic alcohols is driven by the presence of 2 alkyl groups that facilitate the ring closure via the Thorpe–Ingold effect. Currently, the carbonation of secondary or primary propargylic alcohols remains very challenging.
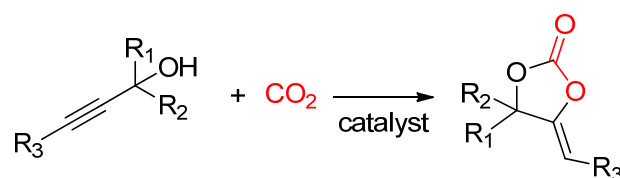
Scheme 21. Synthesis of exovinylene cyclic carbonates from the coupling of propargylic alcohols and CO_2.

Organocatalysts like organophosphorous compounds such as trialkyl- or triphenylphosphine can catalyze the carboxylation of propargylic alcohols in supercritical CO_2 (P_{CO_2} = 10 MPa and T = 100 °C). With a low (nBu)$_3$P loading rate of 5 mol%, which appears to be the most efficient phosphine, internal and terminal tertiary propargylic alcohols were converted into the corresponding exovinylene cyclic carbonate (also called α-alkylidene cyclic carbonate) in very good yields (up to 11 examples in the yield range of 64–99%) [98]. For internal propargylic alcohols, products with olefins of (Z)-configuration were exclusively observed. The plausible mechanism suggested by the authors proposed a possible phosphine–CO_2 adduct formation in supercritical conditions that would help CO_2 insertion. Attempts to obtain optically active cyclic carbonates with chiral phosphine proved its efficiency [99]. Phosphorous ylides were also investigated, as they are known to form an adduct with CO_2 thanks to the work by Matthews et al. [100]. Internal tertiary propargylic alcohols could be converted into exovinylene cyclic carbonates in good yields at 80 °C under atmospheric pressure of CO_2.

N-heterocyclic carbenes (NHC) also successfully catalyze the carboxylation of propargylic alcohols in a similar manner, with typical imidazolium-2-carboxylates acting as intermediates in the CO_2 fixation. Exovinylene cyclic carbonates were obtained under supercritical conditions and milder conditions (P_{CO_2} = 4.5 MPa, T = 60 °C) in good yields [101].

To enhance the CO_2 activation, *N*-heterocyclic olefins (NHO) such as ketene aminals are good candidates, since they display a highly polarized C=C bond that can act as a nucleophile, while stabilizing the positive charge due to electron delocalization via the heterocycle. After kinetic considerations, terminal and internal tertiary propargylic alcohols were successfully converted into the corresponding exovinylene cyclic carbonates in good yields (from 50% to 98% for 7 examples) using 5 mol% of NHO at 60 °C under 2 MPa of CO_2 pressure in neat conditions. Although NHO/CO_2 adduct generation occurs, regarding the increasing CO_2 solubility in the reaction media via its fast sequestration, computational studies suggest a mechanism based on OH activation (hemi-carbonate ion formation) rather than nucleophilic attack of the alcohol moiety on the NHO/CO_2 adduct [102,103]. In this case, the in-situ-generated $[NHOH]^+[RCO_3{}^-]$ species is more reactive compared to the analogue when NHCs are used. Moreover, NHOs are less basic than NHCs, which limits possible side reactions such as ring-opening of the exovinylene cyclic carbonate by the unreacted propargylic alcohols (see Scheme 22), which is promoted by the formation of a $[NHO]^+[RO]^-$ ionic pair [104].
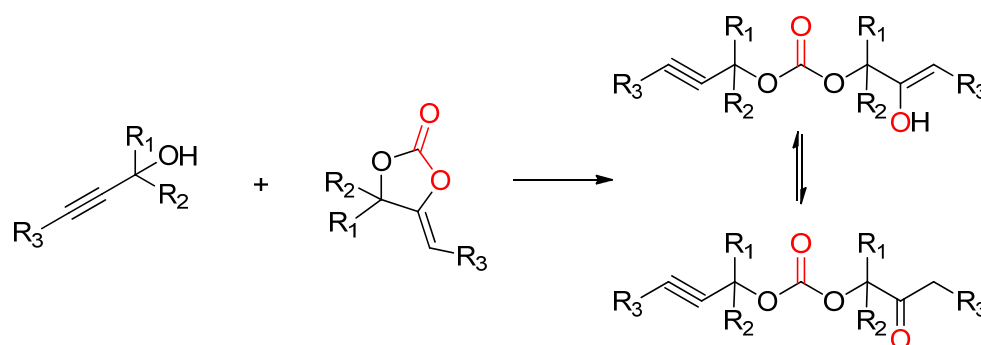
Scheme 22. Undesired side reactions of ring-opening of exovinylene cyclic carbonates by unreacted propargylic alcohols.

Amidines and guanidines are efficient promotors for the carboxylation of CO_2 onto alcohols. These organic superbases were tested with propargylic alcohols by our group [105]. Mechanistic and kinetic studies were conducted to better understand side reactions (see Scheme 22) and disparities in selectivities. Optimal conditions of 100 °C and 3 MPa CO_2 pressure in acetonitrile led to quantitative conversion of terminal tertiary propargylic alcohol with 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) as the catalyst (5 mol%). By tuning the reaction time, the best selectivity of 80% toward the exovinylene cyclic carbonate was observed. Replacing MTBD with TBD led to the formation of an oxo-alkyl carbonate (resulting from the ring-opening of the exovinylene carbonate by unreacted propargylic alcohol) with a selectivity above 85%. This arose from the capability of TBD to act both as a base and a proton donor, as proven by DFT calculations.

Basic organic salts and ionic liquids with easy tunable structures and basicity by changing both the anion and the cation structure were then investigated as cheap catalysts to selectively design exovinylene cyclic carbonates. The use of ionic liquid also offers the benefit of increasing the CO_2 solubility within the reaction medium, which is favorable for the fast and selective coupling of CO_2 with propargylic alcohols substrates. Excellent results were obtained, with alkylammonium salts displaying basic counter anions such as acetate, azide, phenolate and isocyanate, with almost quantitative formation of exovinylene cyclic carbonate after 8 h at 80 °C and 3 MPa CO_2 pressure in neat conditions [106]. Deeper investigations of the influence of the cation–anion pair of organic salts were later described by our group. Within the range of tested catalysts, the optimum activity was found for a controlled ionic separation pair made of sterically hindered cations (ideally ammonium or phosphonium cations tetrabutyl chains) and basic anions with pKa values of ~4.5–9 to promote the reaction without detrimental effects on the selectivity [107]. Several terminal tertiary propargylic alcohols were successfully converted, as well as bifunctional alkynols,

in order to quantitatively produce bis-cyclic carbonates, which are useful monomers for the fabrication of world-class polymers, i.e., poly(thio)carbonates and polyurethanes [108]. Azole–anion-based aprotic ionic liquids such as tetrabutylphosphonium/2-methyl Imidazole, tetrabutylammonium phenolate and phosphonium levulinate are just a few examples of ionic liquid that proved their efficiency to convert various terminal tertiary propargylic alcohols into their corresponding cyclic carbonate, generally under non-demanding conditions (P_{CO_2} = 0.1–5 MPa, T = 25–80 °C, t = 1 to 24 h) [109,110].

Copper-based catalysts. The synergy between a metal salt with a base or basic ionic liquid or salt represents an elegant method to boost the catalytic performance while allowing the selective formation of exovinylene cyclic carbonates. The benefits of using these binary catalysts is due to the dual activation of the alcohol substrate, i.e., the OH activation by the base, ionic liquid or organic salt, which facilitates the formation of a carbonate ion and the triple bond activation by interaction with the metal cation to favor the ring closure of the molecule. As selected examples, an ionic liquid with bio-derived levulinate anions combined with CuI provided series of exovinylene cyclic carbonates from terminal tertiary propargylic alcohols [111] with excellent yields of 80% to 99% at 25 °C and 1 MPa of CO_2 within 4 h. CuI also operate in synergy with *N,N*-diisopropylethylamine at temperatures of 80–120 °C under 4 MPa CO_2 to provide series of cyclic carbonates with internal exocyclic olefin in Z configuration, with yields from 43% to 96% [112]. Remarkably, this dual-catalyst system also enabled the conversion of a challenging terminal secondary alcohol (R_1 = H; R_2 = isopropyl) with 95% yield.

Silver-based catalysts. As with copper salts, Ag salts, which are by far the most widely used metal salts in the literature, have proven their utility in enhancing the efficiency of the catalyst. The pioneering study by Kikuchi et al. illustrated that terminal and internal tertiary propargylic alcohols were converted into cyclic carbonates in very good yields (up to 14 examples) using AgOAc as the catalyst (10 mol%) and DBU (1 eq) as the base at room temperature under 1 MPa of CO_2 [113]. A more recent study showed a different selectivity for internal secondary propargylic alcohols by tuning the amount of base [114]. In this particular case, great selectivity toward vinylene carbonate was obtained when lowering the amount of DBU (0.4 eq instead of 1 eq), while the presence of exovinylene carbonates was not observed (see Scheme 23). Other examples using silver-based catalysts such as AgI/OAc [115], silver sulfadiazine/Et$_4$NBr [116], silver oxides with KI and carbenes [117] and silver nanoparticles supported by polymers [118–120] proved their efficiency for terminal and internal tertiary propargylic alcohols. To date, only Schaub et al. have developed a remarkable dual catalyst combining a silver salt with DavePhos ligand to synthesize exovinylene cyclic carbonate from challenging primary propargylic alcohols at room temperature and 2 MPa of CO_2 in acetonitrile [121]. In this study, the use of a bulky donor ligand (phosphine) provokes an angle compression of the alcohol substrate, which mimics the Thorpe–Ingold effect [122]. The versatility of this elegant catalytic system afforded a large portfolio of exovinylene cyclic carbonates with external or internal olefin (with exclusively Z configuration) from primary, secondary and tertiary substrates in very good yields from 65% to 95%.
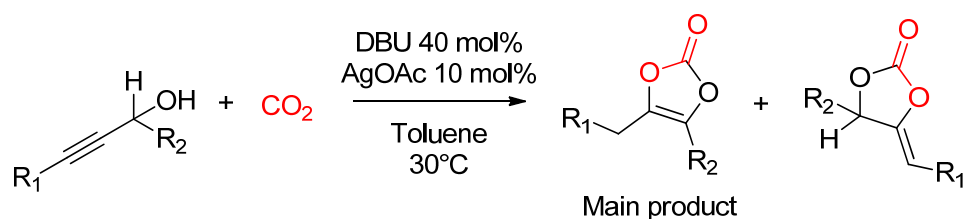
Scheme 23. Selective synthesis of vinylene carbonates rather than exovinylene cyclic carbonates using DBU/AgOAc catalytic systems on secondary propargylic alcohols.

Zinc catalyst. Ma et al. reported on the only zinc-based catalysts that provided good efficiency when associated with TEA for the carboxylative cyclization of terminal tertiary propargylic alcohols [123,124]. The ZnI_2/NEt_3 binary catalyst operated at low temperature (30 °C) and 1 MPa of CO_2 and provided the desired cyclic carbonate scaffolds. The major weakness of this system arose from the high content of the Zn salt (20 mol%) and NEt_3 (200 mol%). The mechanistic insights provided by DFT calculations suggested that the OH of the substrate was activated by the formation of a propargylic alcohol–ZnI_2–Net_3 complex, which drove the formation of a carbonate ion. The Zn salt also took part in the ring closure step by interacting with the alkyne, facilitating the formation of the envisioned cyclic carbonate [125] (see Scheme 24).
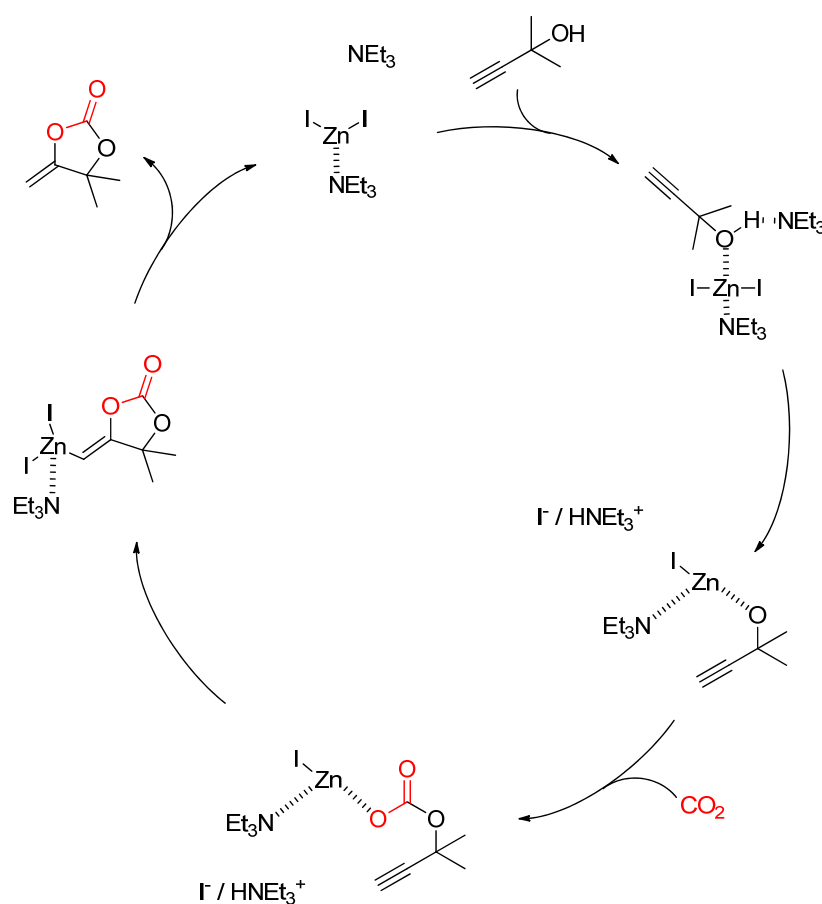
Scheme 24. Catalytic cycle of the ZnI_2/NEt_3 dual system for the carboxylation of tertiary propargylic alcohols to afford exovinylene cyclic carbonates. Adapted from [125].

3. Strategies to Afford CO_2-Based Polycarbonates

3.1. Direct Polymerization of CO_2 with Diols

The design of polycarbonates (PC) involving the direct condensation of diols with CO_2 faces the same bottlenecks as the synthesis of (a)cyclic carbonates, i.e., the formation of water as a by-product and the proper activation of the OH moieties or CO_2. A second challenge lies in the intrinsic structural features of the diols, which are involved in the polymerization manifold. Indeed, the length and nature of the spacer between the alcohol moieties are decisive: 1,2- and 1,3-diols are prone to the thermodynamically favored formation of 5- and 6-membered cyclic carbonates, whereas longer spacers or vicinal diols inducing the formation of constrained cyclic carbonate substrates would drive the formation of oligomers or even polymers.

### 3.1.1. Direct Copolymerization by Dehydrative Polycondensation

The only relevant catalytic system used to fabricate polycarbonates from the direct carboxylative coupling of diols with CO_2 was proposed by Tomishige et al. [126]. The synergistic utilization of CeO_2 with excess of 2-cyanopyridine, which was already performed well when synthesizing cyclic carbonates from 1,2- and 1,3-diols, was naturally extended to the dehydrative polycondensation of various 1,x-diol substrates (with x > 3). Aliphatic C_4–C_{10} α,ω-diols provided the corresponding polycarbonates with microstructures free of ether defects in 8 h at 130 °C and 5 MPa of CO_2. However, the polymer chains displayed low molar masses (M_n~1650 g/mol). With diols with rigid structures such as 1,4-cyclohexanedimethanol and 1,4-benzenedimethanol, oligomers with M_n of only 500–600 g/mol were obtained, while with the dimethyl-substituted 2,5-dimethyl-2,5-hexanediol, no polymer was formed. To surpass these bottlenecks, the same group evaluated the influence of other nitrile desiccants, while at the same time deepening the structural characterization of the polymers. Switching from 2-cyanopyridine to 2-furonitrile enabled the fabrication of polycarbonates with M_n values of up to 3900 g/mol from 1,6-hexane diol with a ten-fold excess of nitrile (compared to the diol) at 130 °C under 5 MPa CO_2 pressure. The fine microstructural characterization of the polymers highlighted the presence of chain end defects, causing termination reactions. The amide produced from the hydration of the cyano-derivatives was involved in a "transesterification" reaction with the hydroxyl chain ends to form a polycarbonate (PC) terminated by an unreactive ester moiety. This side reaction was accompanied by the formation of ammonia, which provoked a scission of the PC. This released short dead chains end-capped by an unreactive amide moiety and a second hydroxyl-terminated PC fragment that was capable of further growth [127]. The design of the CeO_2 catalyst plays an important role in its activity. In this case, CeO_2 nanorods enhanced the activity toward the formation of polybutylene carbonate as the capacity to uptake CO_2 was increased, along with increased oxygen vacancy sites [128].

3.1.2. Direct Copolymerization via Alkylation

The polycondensation of CO_2 with xylylene glycol using a base/CX_4/R_3P activating system was the subject of one of the pioneering studies on the synthesis of PCs from diols [129]. Polymers with M_w values up to 3800 g/mol were fabricated with CBr_4 and n-Bu_3P as polymerization promotors and *N*-cyclohexyl-N′,N′,N″,N″-tetraethylguanidine (CyTMG) as the base at room temperature in DMF. Remarkably, PCs free of ether linkages defects were synthesized. The scope of diols was further extended to di(ethylene glycol) using Ph_3P and $CBrCl_3$ to deliver the corresponding polycarbonate with M_n values of up to 6000 g/mol [130]. As with the synthesis of (a)cyclic organic carbonates, the polymerization manifold relied first on the CO_2 fixation onto the diol thanks to the OH activation by the base. The $[R_3P\text{-}CX_3]^+[X]^-$ diadduct formed in situ from the R_3P/CX_4 dual system underwent an ionic exchange with the generated RCO_3^- species, leading to the $[RCO_3\text{-}PR_3]$ intermediate. Then, the chain growth proceeded via successive transcarbonation reactions with another diol molecule thanks to the good leaving group ability of the R_3P^+-O- fragment (see Scheme 25).

In a similar concept, Du and coworkers proposed a straightforward methodology to copolymerize various diols with CO_2 using Cs_2CO_3 as the base (4 eq) and dichloromethane as the co-reagent (6.2 eq) in NMP [131]. Interestingly, the nature of the diol dictates the microstructural features of the polymer backbone toward either a polycarbonate or a poly(ether carbonate), which alternates carbonates and ether linkages. For benzylic diols such as 1,4-benzenedimethanol, a high conversion rate (>99%) was observed after 24 h at 100 °C and a polycarbonate with very few ether linkages was obtained (63.7% yield; M_n = 1800 g/mol). With the aliphatic 1,4-cyclohexanediol, the formation of a polymer (M_n = 5000 g/mol) with a pattern of alternating ether and carbonate linkages representing 93% of the structure was synthesized. The origin of the ether defects arises from side reactions on the chloromethylated intermediate. The polymerization mechanism is analogous to the one described for the cyclic carbonate formation from vicinal diols. A hemi-carbonate

anion formed by CO_2 fixation onto one alcohol moiety subsequently undergoes an alkylation reaction with dichloromethane. Then, depending on the diol, the chain growth occurs either via the carbonyl attack to provide a carbonate linkage or via the α-methylene attack forming ether linkages (see Scheme 26). By using the $DBU/CH_2Br_2/bmimPF_6$ ternary system, Jang and coworkers designed biorenewable PCs via copolymerization of a monosaccharide, i.e., α-methyl D-glucopyranoside (MDG), with CO_2 [132]. As with most sugars, this polyol possesses both primary and secondary alcohol functions. As both types of alcohols display different reactivity levels, linear polyglycocarbonates with M_n values up to 7000 g/mol were fabricated, without any protection of the hydroxyl moieties. The NMR structural characterization highlighted the absence of branching, as the carbonate linkages mostly emanated from the C-6 primary alcohol and the C-3 or C-2 secondary hydroxyls.
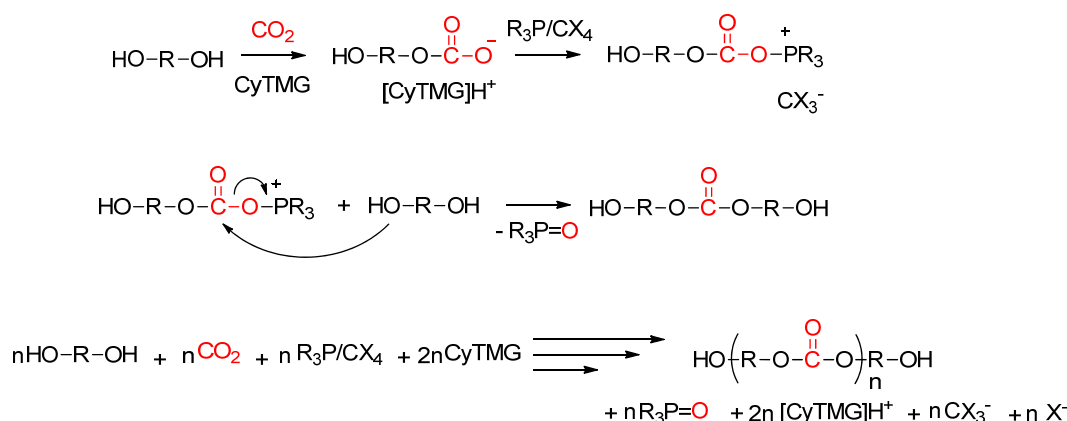
Scheme 25. Mechanism for the formation of polycarbonates from the polycondensation of diols and CO_2 promoted by the $CyTMG/R_3P/CX_4$ system.
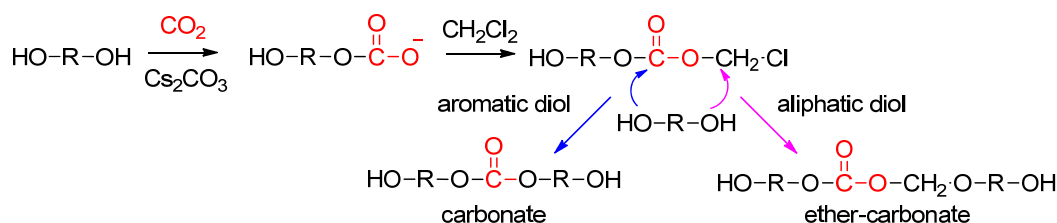
Scheme 26. Competitive pathways between carbonyl attack (blue) and methylene attack (pink) for the formation of carbonate or ether linkages. Adapted from [131].

3.1.3. Terpolymerization Methods

To overcome the limitations brought about by the formation of water for the direct diol–CO_2 coupling, the terpolymerization approach utilizing dihalides as comonomers was pioneered by Ikeda et al. More precisely, diolate potassium salts generated from diols mixed with α,ω-dibromo compounds and crown ethers led to the formation of polycarbonates under CO_2 pressure in dioxane [133,134]. The 18-crown-6-ether is believed to promote the ion separation of diolate salts by forming stable complexes with metal cations. The proposed mechanism relies on CO_2 fixation onto the diolate, followed by the nucleophilic substitution of the dihalide by the carboxylate species (see Scheme 27). After experimental investigations, it appears that crown ethers do not play a key role for CO_2 fixation onto the diolate, although they considerably increase the kinetic nucleophilic substitution on dihalides. Interestingly, this pathway provided selective polycarbonate chains free of any ether linkages.

KO−R₁-OK $\xrightarrow{\text{CO}_2}$ K⁺ ⁻O−$\overset{\text{O}}{\overset{\|}{\text{C}}}$−O−R₁−O−$\overset{\text{O}}{\overset{\|}{\text{C}}}$−O⁻ K⁺ $\xrightarrow[\text{Br}-\text{R}_2\text{-Br}]{\text{crown ether}}$ Br−R₂-O−$\overset{\text{O}}{\overset{\|}{\text{C}}}$−O−R₁−O−$\overset{\text{O}}{\overset{\|}{\text{C}}}$−O−R₂-Br
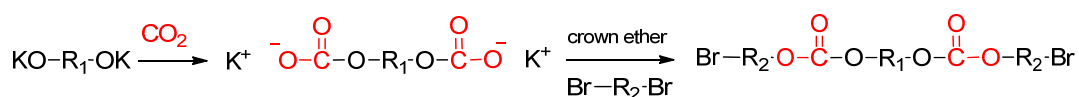
Scheme 27. Terpolymerization synthetic pathway for the formation of polycarbonates using diolates and dihalides.

Later, this terpolymerization concept was revisited by Gnanou et al. using Cs_2CO_3 as a base to generate the diolate [135]. As mentioned previously, the so-called "cesium effect" increases the nucleophilicity of the reactive diolate anions, which facilitates the fixation of CO_2 and the nucleophilic attack of the carbonate ion onto the halide. The protocol was valid for dihalides with spacers of at least 4 carbons to prevent the risk of back-biting reactions causing the formation of cyclic carbonate by-products. Other bases such as K_2CO_3, DBU and Li_2CO_3 were found to be less effective. Under the optimum parameters (T = 100 °C, P_{CO_2} = 1 MPa, t = 48 h and a diol/dihalide/Cs_2CO_3 ratio of 1:1.05:4), 97% of diols were converted into polycarbonates with M_n values up to 22,000 g/mol and a PDI of 3.6. PCs with excellent M_n values of up to 43,000 g/mol were designed, involving the proper selection of both aliphatic and aromatic diols and dihalides, as was the case for the 1,6-hexanediol–1,4-bis(chloromethyl)benzene couple. A more sterically hindered biorenewable isosorbide bearing two secondary alcohol was also successfully converted into the poly(isosorbide carbonate) (M_n = 18,000 g/mol). Similarly, the terpolymerization of α-methyl-2,3-di-*O*-methyl D-glucopyranoside (MDMG), a naturally occurring monosaccharide, with dibromobutane or 1,4-bis(chloromethyl)benzene and Cs_2CO_3 furnished PCs with M_n of 8000 g/mol and 14,000 g/mol, respectively. To obtain deeper insights into the role of the dihalide structure, Bian et al. proposed a comparative study of the use of dihalomethanes and dihaloethanes [136]. As a general result, higher monomer conversions were noted for dihaloethanes than for dihalomethanes. In the case of dihaloethane, alternating polycarbonates incorporating both the diol and dihalide structure are more likely to occur.

3.2. Ring-Opening Polymerization of Cyclic Carbonates

As the synthesis of PCs via direct copolymerization of alcohols with CO_2 remains an elusive endeavour, one option to surpass these hurdles lies in the fixation of CO_2 into cyclic carbonate structures that undergo facile ring-opening polymerization (ROP). This technique relies on a chain-polymerization mechanism [137], which allegedly allows accurate control of the polymer molar mass, dispersity and properties. Even though most of the studies on the synthesis of polycarbonates via ROP were performed on non-CO_2 based cyclic carbonates, the general principles also apply to CO_2-based cyclic carbonates (see Section 2.2), as they present identical structural features. Among them, the polymerization enthalpy is one of the key parameters to consider, since it heavily depends on the ring size and ring constraint. The following discussion will focus on the ROP of 5- and 6-membered cyclic carbonates and exovinylene cyclic carbonates, as these substrates are well described in the literature [138].

3.2.1. 5-Membered Cyclic Carbonates

5-membered cyclic carbonates undergo ROP because of their high positive polymerization enthalpy [139,140]. However, by combining a high temperature of 170 °C with metal alkoxides catalysts such as dibutyltin dimethoxide, titanium tetrapropanolate or zirconium tetrabutanolate, polymers were obtained from ethylene carbonate with yields from 55% to 100% and M_n values ranging from 3000 to 22,000 g/mol. The structural elucidation of the polymers showed the typical features of poly(ethylene oxide-*co*-ethylene carbonate). Interestingly, the content of carbonate linkages could be controlled via the choice of the catalysts, and the incorporation of 50 mol% of ethylene carbonate units within the polymer backbone was achieved using dibutyltin dimethoxide (catalytic loading of 2 mol%). A careful investigation of the polymerization enthalpy and entropy to afford homopolycarbonates indicated

that the formation of the cyclic monomer was more favored than the polymerization itself. However, producing poly(ethylene oxide-*co*-ethylene carbonate) is slightly more favored. In fact, the polymerization mechanism involves a CO_2 loss to afford the ether repeating unit, which compensates the entropy loss and facilitates the formation of an alternating polymer. On the one hand, at 170 °C, an enthalpy of 112.5 kJ/mol was calculated for the formation of pure poly(ethylene carbonate). On the other hand, the same polymerization enthalpy dropped to -11.7 kJ/mol for a random poly(ethylene oxide-*co*-ethylene carbonate). Deeper investigations of the mechanism for the ROP of ethylene carbonate were conducted by Storey and Hoffman [141], who highlighted the role of the catalysts, namely organotin catalysts and sodium stannate trihydrate catalysts. As with the ROP of lactones [142,143], organotin complexes act both as initiators and catalysts for the ROP of ethylene carbonate. For sodium stannate trihydrate, the use of a diol as an initiator was required. In both cases, the mechanism relies on nucleophilic attack of the initiator on the carbonyl of the cyclic carbonates, generating a reactive alcoholate moiety which will further attack another carbonyl group (Scheme 28, blue pathway). Due to the high polymerization enthalpy of this reaction, a competitive pathway (Scheme 28, red pathway) is also likely to occur, leading to formation of ether linkages driven by the loss of CO_2. More insights were given by Clements [144] on the effect of the initiator's structure. As an example, aromatic alcohols involve a systematic CO_2 loss in the initiation step, whereas aliphatic alcohols preferentially favor the formation of a carbonate linkage. Lee et al. also described the several hypothetical pathways for the formation of ether linkages in the ROP of ethylene carbonate, as well as possible depolymerisation processes, using KOH as an initiator [145]. Other catalysts such as phosphazenes [146] and $ZnEt_2$ [147] were tested to design polymers via the ROP of various 5-membered cyclic carbonates. Both catalysts required high polymerization temperature (T = 180 °C) to display sufficient activity and only provided poly(ether-co-carbonates) with low carbonate contents of 21–54% and M_n values of 4300–14,000 g/mol. With ionic liquids, the ROP of ethylene carbonate proceeded at relatively low temperature (from 80 to 120 °C) but only afforded oligomers with low carbonate contents of up to 34%. Haba and Guillaume introduced an elegant concept based on the increase in ring strain of 5-membered cyclic carbonates to construct ether-free PCs by direct ROP. A known example is the ROP of ethylene carbonate fused in a trans configuration onto a cyclohexane ring, i.e., *trans*-cyclohexane carbonate [148,149], whereas its *cis*-analogue does not polymerize [150]. The Zn(diphenolate)-promoted ROP of this bicyclic monomer provided a pure isotactic poly(cyclohexene carbonate) with M_n values of up to 21,000 g/mol at 60 °C. Similarly, 4,6-*O*-benzylidene-2,3-*O*-carbonyl-r-D-glucopyranoside, i.e., ethylene carbonate fused onto a biorenewable glucopyranoside, furnished polycarbonates with M_n values of up to 16,000 g/mol at 25 °C using a superbase organocatalyst [151].

3.2.2. 6-Membered Cyclic Carbonates

The ROP of 6-membered cyclic carbonates is thermodynamically much more favored than their 5-membered analogues due to increased ring strain, yielding in most cases a negative polymerization enthalpy that compensates the positive polymerization entropy. Indeed, the carbonyl group displays a flat geometry, which increases the strain of the 6-membered cyclic compounds [152]. The ROP of 6-membered cyclic carbonates was extensively reviewed by others and will not be discussed in detail in this section. Cationic polymerization utilizes Brønsted or Lewis acids to activate the monomer and generate species capable of propagation. However, in many cases, propagation is accompanied by decarboxylation, which induces ether defects in the polymer skeleton, as well as backbiting termination reactions, as was first demonstrated by Kricheldorf et al. in their attempt to polymerize trimethylene carbonate using methyl triflate as the initiator [138,153]. Efforts to prevent such decarboxylation reactions and to obtain pure polycarbonates were successfully conducted with alkyl halides initiators (namely methyl iodide, benzyl bromide and allyl iodide) [154], methanesulfonic acids and phosphoric acids [155,156], but only afforded polymers with M_n values in the range of 3000–16,000 g/mol.
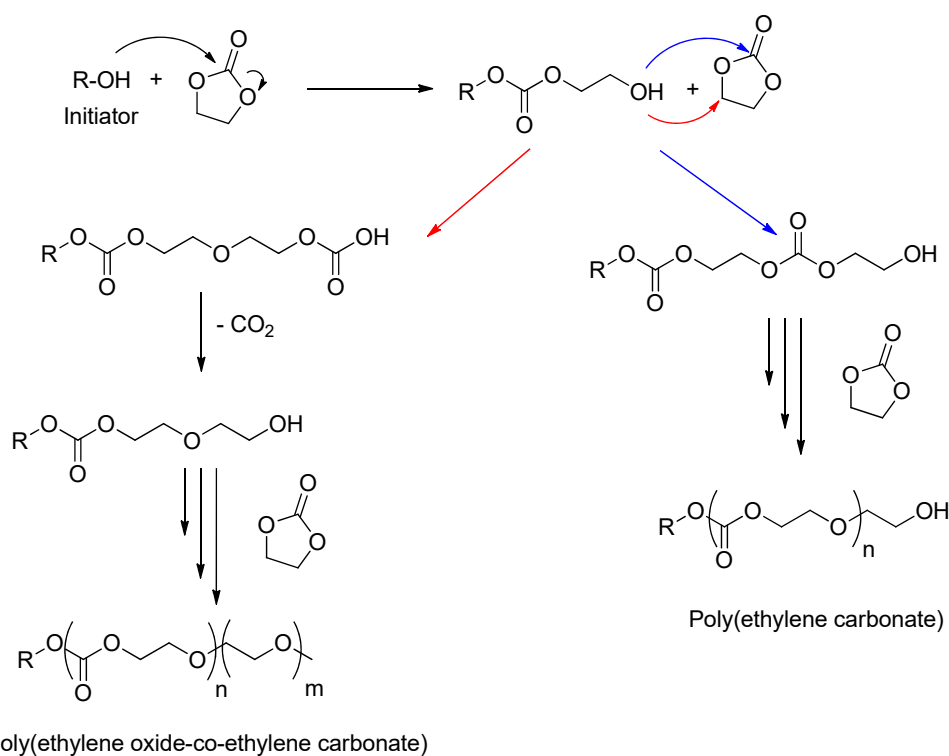
Scheme 28. Competitive pathways between methylene attack (red) and carbonyl attack (blue) to produce poly(ether-co-carbonates) or homopolycarbonates via ROP of 5-membered cyclic carbonates.

Anionic ROP provided better polymerization control and enabled the synthesis of high molar mass polycarbonates. Alkali metal alcoholates and sec-butyllithium [157] were efficient initiators, yielding ether-free polymer chains. However, backbiting termination reactions could not be supressed and oligomers with cyclic structures were concomitantly formed. Taking advantage of the facile ROP with anionic mechanisms, substituted 6-membered cyclic carbonates with pendant groups such as amino-acid (M_n values of up to 24,000 g/mol) [158], 2-ethyl-2-hydroxymethyl [159], norbornene [160], aromatic [161] and more [162,163] were polymerized efficiently.

To prevent non-desired side reactions arising from the high reactivity of the ionic active centers in anionic and cationic ROP of 6-membered cyclic carbonates, coordination–insertion mechanisms have been proposed and studied in detail by Kricheldorf et al. and Darensbourg et al. Organometallic complexes containing Al [164], Ca [165–167], Sn [168–171] or lanthanides [172] were engineered and showed great activity for the synthesis of defect-free polycarbonates. The general polymerization mechanism is based on (i) the ring-opening of the cyclic carbonate via the addition of a nucleophile initiator to the metal-activated carbonyl of the ester group, followed by the (ii) monomer insertion into the oxygen–metal bond generated after initiation, which is then (iii) prone to propagation. The authors mention that in the propagation step, the acyl–oxygen bond is broken rather than the alkyl–oxygen bond for monomer insertion [165]. These coordination–insertion ROP provide a "quasi-living" mechanism, where a linear increase in polymer M_n with the monomer conversion is observed.

Organo-ROP represents the most attractive route to design metal-free PCs with controlled molecular parameters and architectures. Systems comprising benzyl alcohol as initiators and catalysts derived from amidines, guanidines, n-heterocyclic carbenes or olefins (eventually coupled to hydrogen bond donors such as thioureas) successfully polymerize trimethylene carbonate in a very controlled manner at ambient temperatures [173–175]. In an attempt to produce CO_2-sourced polycarbonates, Buchard et al. designed 6-membered cyclic carbonates via the carbonation of polyol sugars (see Section 2.2.1.2) and further studied their organocatalytic ring-opening polymerization using TBD as the catalyst.

Promising results were obtained from D-mannose (M_n values of up to 33,000 g/mol) [176], 2-deoxy-D-ribose (M_n values of up to 42,000 g/mol) [177], thymidine (M_n values of up to 17,000 g/mol) [178] and others [179]. Similarly, Gnanou et al. also reported on the ROP of 6-membered sugar-based cyclic carbonates obtained from the coupling of glycosides and CO_2 (based on the DBU/CH_2Br_2 carbonation protocol at 70 °C). Various ROP organocatalysts were selected, i.e., TBD/4-methyl benzyl alcohol and DBU/1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea/4-methyl benzyl alcohol, yielding pure polycarbonates with M_n values of up to 4300 g/mol [180].

3.3. Polycondensation of Alcohols with (a)Cyclic Carbonates

While ROP is an appealing method to produce polycarbonates in a controlled manner, it is limited to a narrow library of aliphatic polymer microstructures, due to the thermodynamic constraints, which mostly restrict the polymerization to 6-membered cyclic carbonates. Even though substrates with a large variety of pendant groups have successfully been polymerized by ROP, the urge to develop more diversified architectural structures with cheap and easily scalable processes has brought about step-growth polymerization as a practical solution for various industries. Currently, the mass production of polycarbonates involves the polycondensation of diols with phosgene. DMC, DEC or DPC, which are easily accessible from CO_2 (see Section 2.1), are now emerging as valuable alternatives to phosgene, and their polycondensation with naturally occurring ubiquitous diols offers a route for the design of polycarbonates with reduced carbon footprints. Attempts to valorize 5-membered cyclic carbonates as useful carbonylation synthons for the production of polycarbonates were also reported but remained elusive. As highlighted for ROP, they generally face the same limitations, such as competitive methylene and carbonyl attacks, generating poly(ether-co-carbonates) [181–183].

3.3.1. DMC and DPC as Carbonylating Agents

The formation of polycarbonates from diols and DMC or DPC by polycondensation generally involves a two-step approach, usually performed in a one-pot fashion and in solvent-free conditions (see Scheme 29). First, oligocarbonates of low molar masses are fabricated via transcarbonation between the diol and the acyclic carbonate (DMC or DPC) at moderate temperatures (high enough to maintain a molten reaction media) and ambient pressure. The resulting telechelic oligomers end-capped with both alcohol and carbonate moieties are then chain-extended by applying a high vacuum shifting the reaction equilibrium (step-growth polymerization mechanism) via elimination of methanol (for DMC) or phenol (for DPC). Temperatures are progressively increased during the process to overcome mass transfer limitations, reflecting the viscosity and molar mass increases. The nature of the initial diol(s) monomer dictates the final polymer microstructure (i.e., aliphatic or non-aliphatic polycarbonates).

Aliphatic PC

Aliphatic PCs have recently gained huge interest in research thanks to their biodegradability and biocompatibility, making these materials suitable for the biomedical field [184]. Depending on the structure of the aliphatic diols, the occurrence of side reactions was highlighted by Xie and coworkers when dialkylcarbonate was used as the carbonylating agent [185], limiting the access to high molar mass aliphatic PCs. However, side alkylation reactions of the alcohol chain end either via the methylene attacks of DEC or via backbiting side reactions furnished polycarbonates with unreactive ether chain ends or cyclic by-products, causing the death of the chain growth. These side reactions were especially highlighted for poly(ethylene carbonate) and poly(propylene carbonate) made from ethylene glycol and 1,3-propanediol, but were considerably limited or even totally supressed when diols with spacers larger than 3 carbon units were used as monomers. Following this approach, aliphatic PCs with moderate to high molar masses were successfully synthetized from a diverse library of linear alkyl diols with DMC when suitable

catalysts were used. For example, the utilization of a binary DMAP/thioureas organocatalyst provided poly(butylene carbonate) with M_n values of up to 52,000 g/mol [186,187], while imidazolium or TBD furnished poly(hexamethylene-co-trimethylene carbonate) with M_n values of up to 7400 g/mol [188] and poly(hexamethylene carbonate) with M_n up 33,000 g/mol [189].
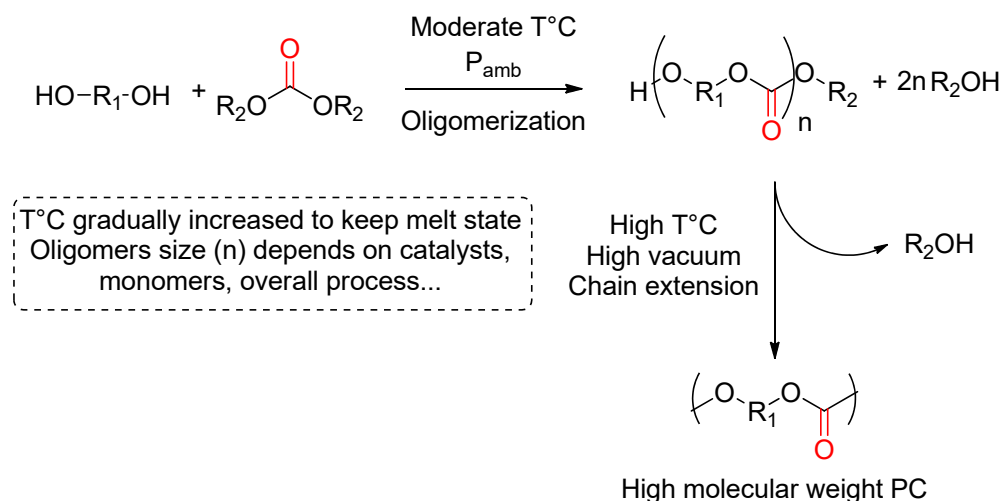

Scheme 29. Schematic representation of polycarbonate synthesis via melt polycondensation of diols with DPC or DMC ($R_2 = CH_3$ or C_6H_5).

Metal-based catalysts such as sodium alkoxide Li(Acac), Na(Acac) and K(Acac) were also reported as efficient systems for constructing polycarbonates, with diversified microstructures and M_w values of up to 200,000 g/mol [190,191], while TiO_2/SiO_2-based catalysts provided poly(hexamethylene carbonate) with M_w of 160,000 g/mol and terpolymers with M_w values of up to 87,000 g/mol [192,193]. Interestingly, this concept was extended to the fabrication of hyperbranched PCs when blends of diols and triols were condensed with DMC using DMAP or Li(Acac) as catalysts [194].

Unlike DMC and DEC, the utilization of DPC enabled suppression of the side alkylations of the hydroxyl chain ends of growing PCs. Moreover, phenol may be viewed as a better leaving group than methanol for DMC, which should facilitate the construction of high molar mass polymers. However, phenol displays a high boiling point so that the polycondensation was generally performed at temperatures over 200 °C. As selected examples, poly(butylene carbonate)s with M_w values of up to 156,000 g/mol or 202,000 g/mol were synthesized using Zn(OAc)$_2$ or basic solid MgO as catalysts, respectively, at temperatures of 200–210 °C [195,196].

A different approach was proposed by Miller and Vanderhenst, who first synthetized decane-1,10-diyl dimethyl dicarbonate from 1,10-decanediol with an excess of DMC, catalyzed by Na$_2$CO$_3$ at 85 °C. The bifunctional carbonate was then subjected to self-polycondensation and aliphatic polycarbonates were obtained via carbonate metathesis polymerization after isolation of these bis-carbonates. M_w values of up to 88,000 g/mol were observed with Zn(OAc)$_2$ as the catalyst and a reaction temperature of 150 °C for the oligomerization step (12 h) and 175 °C for the chain extension (1.5 h). The mechanism proposed by the authors is presented in Scheme 30 with K$_2$CO$_3$ as the catalyst. A one-pot process with the diol and an excess of DMC as the starting reagent was proposed to afford aliphatic PC with M_w values of up to 56,000 g/mol [197].
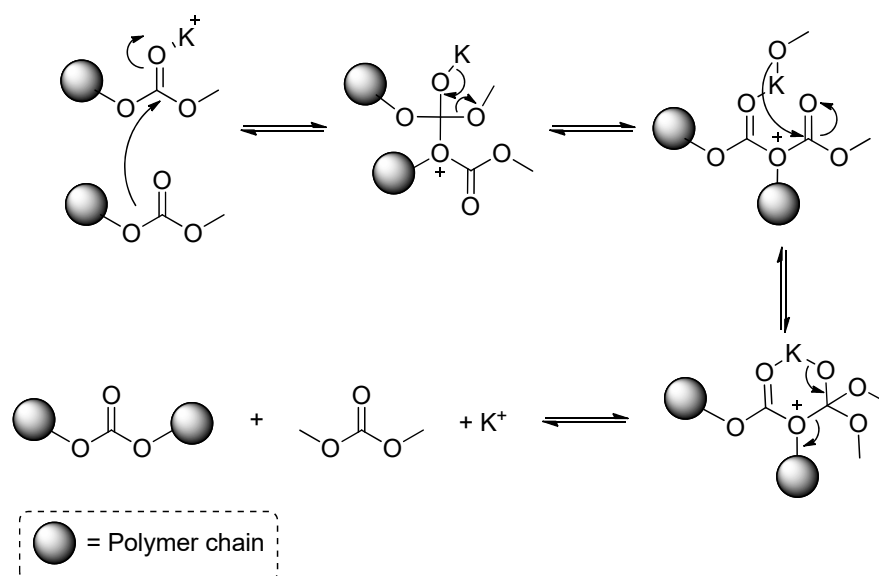
Scheme 30. Carbonate metathesis polymerization principle catalyzed by K_2CO_3. DMC is removed under vacuum to displace the equilibrium toward PC formation. Adapted from [197].

Aromatic and Cycloaliphatic PCs

Aromatic PC displays remarkable thermo-mechanical and optic properties useful for plethora of applications within the construction, automotive, electronics and other sectors. Historically, high molar mass polycarbonates were firstly industrialized via the phosgenation of bisphenol A (BPA). The toxicity and safety issues linked to the utilization of phosgene pushed scientists to evaluate the potential of DMC and DPC for constructing aromatic PCs from BPA. In combination with molecular sieves, a dual DMAP/$(Bu_2SnCl)_2O$ catalytic system afforded PC with a high-molecular weight (M_w values of up to 75,000 g/mol) using BPA and DMC, but a very high temperature of 320 °C was needed to maintain the molten reaction medium, leading to poor control of the dispersity (Đ = 3.8) [198]. Lithium- and lanthanum-based catalysts were also reported and proved their efficiency in accessing to aromatic polycarbonates from BPA [199,200]. The utilization of DPC as a carbonylation agent is now emerging at the industrial level (also known as the Asahi–Kasei process) to construct PCs derived from BPA [201]. Briefly, a carbonate source is brought about by the coupling reaction between CO_2 and ethylene oxide, affording ethylene carbonate, which further undergoes methanolysis to produce DMC. The latter is converted into DPC using phenol. The melt polycondensation responds to a two-step procedure with a first oligomerization phase between DPC and BPA at 230 °C, followed by a chain extension at 265 °C to design aromatic PCs with molar mass values of up to 117,000 g/mol.

In the quest for sustainable and less toxic alternatives to BPA-based PC, emerging research studies are now focusing on the utilization of sugar-based bicyclic diols, i.e., 1,4:3,6-dianhydro-D-sorbitol, also known as isosorbide, to construct the new generation of PCs with thermomechanical properties competing with those of aromatic PC.

Due to the bicyclic structure (two fused tetrahydrofuran rings) of isosorbide, the two alcohol functions are not equivalent. The so-called "endo" OH displays intramolecular H-bonding with the O atom of a tetrahydrofuran ring, inducing disparity in the two OH reactivities (see Scheme 31). In this regard, a large range of catalysts was tested to selectively activate the endo or exo alcohol moieties and to prevent reactivity disparities that would considerably limit the molar mass of the PC. Among them, metal salts [202], metal alkoxides [203,204], inorganic carbonates [205], ionic liquids [206–213], organic bases [214] and others [215–218] enabled the facile construction of defect-free PCs derived from isosorbide with M_n values in the range of 14,000 to 55,000 g/mol.
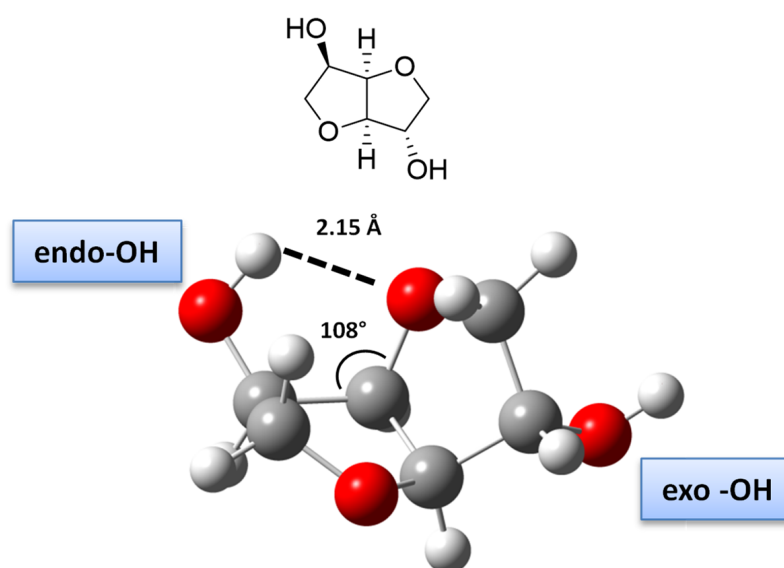
Scheme 31. The 3D structure of isosorbide with explicit intramolecular H-bonds for endo-OH.

3.3.2. Polycondensation between Bis(α-Alkylidene Cyclic Carbonates) and Diols

Unlike conventional 5-membered cyclic carbonates that poorly react with alcohol in "soft" experimental conditions, CO_2-based exovinylene cyclic carbonates (see Section 2.2.4) undergo facile and regioselective alcoholysis, even at room temperature. The thermodynamic driving force of the ring-opening lies in the formation of a keto-enol equilibrium (see Scheme 32).
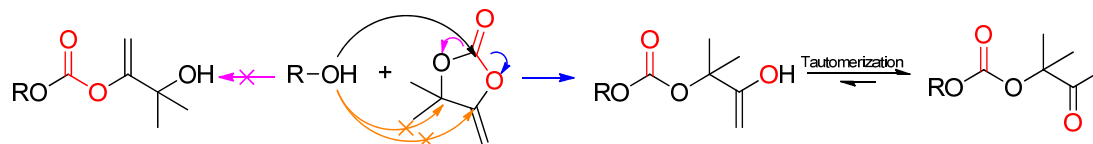
Scheme 32. Regioselective alcoholysis of exovinylene cyclic carbonates.

Taking advantage of this concept, new CO_2-based bis(α-alkylidene cyclic carbonates) were designed by our group. Bis(α-alkylidene cyclic carbonates) were either prepared by direct coupling of bis-propagylic alcohols with CO_2 (aliphatic spacer R_2, see Scheme 33) or by heck coupling of two CO_2-based exovinylene cyclic carbonates with 1,4-diiodobenzene (aromatic spacer R_2, see Scheme 33). These new monomers were further copolymerized via step growth with diols to obtain regioregular PCs with microstructures free of any defects [108,219–221]. Indeed, unlike conventional 5-membered cyclic carbonates, the formation of ether linkages (via decarboxylation) was not observed. New poly(β-oxo carbonates) with M_n values ranging from 5500 to 25,000 g/mol were fabricated using DBU as the catalyst in DMF or chloroform (see Scheme 33). This concept was extended to the formation of poly(oxo-urethanes) and poly(hydroxyl-oxazolidone) [108]. Aliphatic poly(oxo-carbonates) synthetized with OH-terminated poly(ethylene glycol) and bis(α-alkylidene cyclic carbonates) with M_n values of up to 60,000 g/mol showed great properties for potential applications as solid electrolytes for solid Li-ion batteries [219]. An attempt to synthesize poly(β-oxo carbonates) in a one-step or one-pot strategy directly from the terpolymerization of diols, bis-propargylic alcohols and CO_2 was recently reported. The key to the success lies in the utilization of a single dual system, i.e., tetrabutylammonium phenolate/AgI, capable of catalyzing two different reactions, i.e., the carboxylative cyclization of CO_2 with the bispropargylic alcohol to deliver the bis(α-alkylidene cyclic carbonates) in situ, followed by its polymerization in cascade with a primary diol. Even though the

results were promising, only oligomers with M_n values in the range of 1000 to 2700 g/mol were obtained due to the occurrence of side reactions [220].
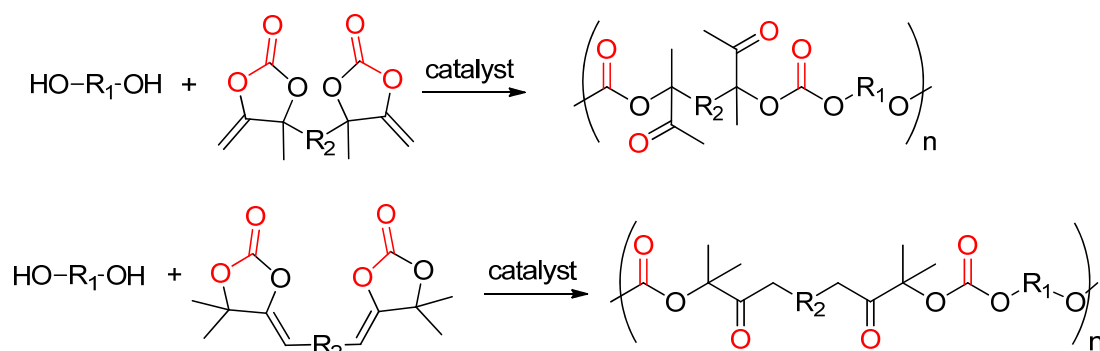
Scheme 33. Synthetic procedure used to access regioregular poly(β-oxo carbonates). Adapted from [108].

4. Conclusions

This paper reviews the main strategies to afford (a)cyclic carbonates and polycarbonates from the coupling of alcohols and CO_2 or CO_2-based synthons. Compared to the well-known coupling of CO_2 with epoxides, these systems suffer from limitations in terms of the yields and demanding experimental conditions, due to the formation of water as a by-product, which considerably affects the formation of carbonates. However, the challenging coupling of alcohols and CO_2 is still very interesting, as it provides a large manifold of accessible and easy-to-handle substrates, opening the possibility for the formation of carbonates that are hardly affordable with epoxide–CO_2 coupling. Many routes have been proposed to overcome the formation of water, combining dehydration agents with catalysts or co-reagents with excess base to trap the water formation. In all cases, the synthesis of (a)cyclic carbonates or polycarbonates could not be achieved without the use of stoichiometric or excess amounts of additives, as the quantitative removal of water is needed to achieve satisfying yields.

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