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Synthesis of Carbonates from Alcohols and CO₂

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Abstract Alcohols are ubiquitous compounds in nature that offer modular building blocks for synthetic chemistry. Here we discuss the most recent development of different classes of alcohols and their coupling chemistry with carbon dioxide as to afford linear and cyclic carbonates, the challenges associated with their formation and the potential of this chemistry to revive a waste carbon feed stock.

Keywords Carbon Dioxide • Carboxylative Cyclization • Cyclic Carbonates • Diols • Heterogeneous Catalysis • Homoallylic Alcohols • Homogeneous Catalysis • Linear Carbonates • Propargylic Alcohols

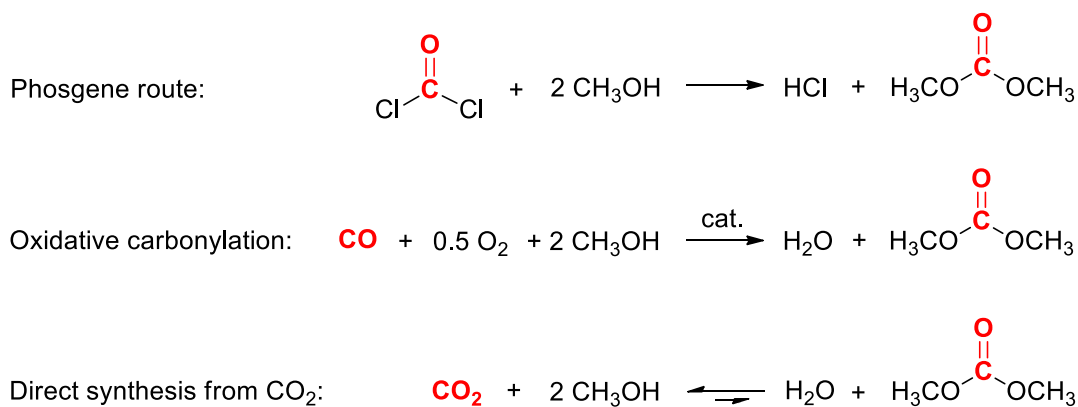
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1. Synthesis of Acyclic Organic Carbonates

1.1 The Importance of the Formation of Acyclic Carbonates from Alcohols

Among various organic molecules which can in principle be derived from CO₂ and alcohols, acyclic carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC) and diphenyl carbonate (DPC) have attracted considerable attention over the past decades [1, 2]. Especially DMC has been a focus of active recent research in the field, since it represents a multifunctional molecule that can be applied as an apolar solvent, a fuel additive, or as an organic reagent in the production of higher carbonates including polycarbonates, polyurethanes and isocyanates [3–5].

Conventionally, DMC has been produced either from oxidative carbonylation of methanol or through a reaction between methanol and phosgene (Scheme 1) [4]. Both processes cannot be regarded neither sustainable nor environmentally benign, since they use highly toxic and corrosive reagents, and require expensive catalysts in the case of the oxidative carbonylation or disposal of hydrogen chloride when using phosgene. A much more attractive way to produce DMC (and related acyclic carbonates) would be the direct reaction between CO₂ and methanol, as shown in Scheme 1. The sole byproduct of this process is water, and its atom economy is comparable to that of the oxidative carbonylation of methanol.



Scheme 1 Different routes for the synthesis of dimethyl carbonate (DMC)

One major drawback of this reaction, however, is its equilibrium limitation (thermodynamics) providing only (very) low yields in DMC. High pressures of CO₂ might help to partially overcome these limitations [6] but at the cost of a high energy demand accompanying this pressurization. Removal of the water formed in the DMC synthesis is

1 another way to shift the equilibrium towards the desired product DMC. Accordingly, the
2 development of efficient catalysts and in combination with a dehydrating agent has become one
3 major focus in the synthesis of acyclic carbonates [7]. Besides DMC, also DEC and DPC have
4 relevance in industrial processes [8, 9]. DPC has already found wide application in
5 polycarbonate synthesis being efficiently used for transesterification of Bisphenol A (BPA).
6 The derived polycarbonate is a thermoplastic polymer used on a large scale as a material for
7 numerous applications (including electrical insulation) with a production of more than a billion
8 tons per year; apart from the DPC route, the major process towards BPA based polycarbonates
9 still relies on the direct reaction of BPA with phosgene. DPC synthesis from phosgene or
10 through oxidative carbonylation, comparable to DMC synthesis, has technical and logistic
11 disadvantages. Transesterification of DMC with phenol is an attractive alternative to the
12 conventional synthesis methods, however, in order to make the overall process “greener”, DMC
13 needs to be produced in a sustainable way.

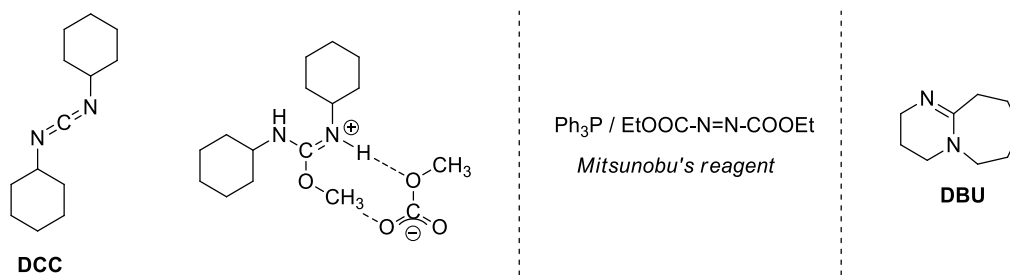
14 For the direct synthesis of DMC from methanol and CO₂, efficient removal of water – beside
15 the adequate choice of a catalyst – seems to be crucial in order to achieve an improvement of
16 this promising methodology and to increase its relevance in industrial synthesis. Thus, the
17 following sections will concentrate on organic and inorganic promoters for DMC formation,
18 and the importance of dehydrating agents.

19 **1.2 Organic Promoters**

20 One approach to address the equilibrium limitation is based on organic molecules acting as
21 promoters of DMC formation. Activation of CO₂ or water capture might both be performed by
22 the same organic molecule [10–12]. Especially in the latter scenario, a stoichiometric use of the
23 promoter is required, since water is usually bound irreversibly. For instance, Aresta and
24 coworkers established the use of dicyclohexylcarbodiimide (DCC; Scheme 2) for the direct
25 synthesis of DMC from CO₂ and methanol under mild conditions (e.g. 80 °C and 5.0 MPa of
26 CO₂). Based on the use of DCC, they reported yields of up to 62% for DMC after only 6 h, but
27 the protocol could also be successfully employed in the conversion of ethanol or allyl alcohol
28 substrates thereby giving access to other dialkyl carbonates. Mechanistic and computational
29 studies led to a putative mechanism, with an isourea/hemi-carbonate adduct as the proposed
30 key intermediate (Scheme 2).

31

1



2

3 **Scheme 2** Organic promoters for the direct formation of DMC from alcohols and CO₂

4

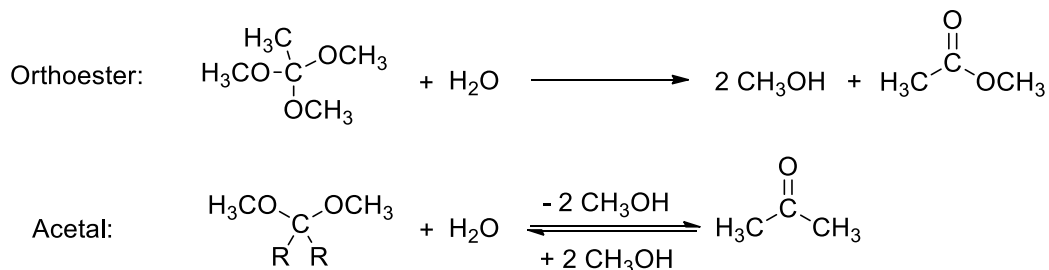
5 A different synthetic route towards DMC synthesis, which gives access to symmetric and
 6 asymmetric acyclic carbonates, is based on Mitsunobu's reagent. This methodology, developed
 7 by Chaturvedi *et al.* [11] can furthermore be successfully employed to convert primary,
 8 secondary and even tertiary alcohols in a one-pot reaction with good to high yields (70–98%)
 9 in all reported cases. Recently, the successful application of DBU for the synthesis of acyclic
 10 carbonates was demonstrated by Jang and coworkers [12]. The scope comprised the synthesis
 11 of various cyclic and acyclic organic carbonates, including DMC, which could be obtained in
 12 48% yield under comparatively mild reaction conditions (70°C, 10 bar CO₂).

13 1.3 Metal-Based Homogeneous Catalysis

14 Among the homogeneous metal catalysts considered, metal alkoxides have been intensively
 15 studied in DMC synthesis since they have been shown to absorb CO₂ to form organic carbonates
 16 [13, 14]. Besides titanium, zirconium and niobium compounds [14–18], tin(IV) complexes have
 17 been investigated in detail with respect to DMC formation from methanol and carbon dioxide.
 18 Tetraalkoxy [Sn(OR)₄] as well as dialkoxydialkyl [R¹₂Sn(OR²)₂] tin compounds are classes of
 19 organometallics both active in DMC formation, even though the efficiency of the reported
 20 systems remains rather low [18–20]. Significant improvements of the methodology were made
 21 by Sakakura *et al.* by investigating the effect of different drying agents on the DMC formation
 22 catalyzed by organometallic tin compounds. Initially starting with orthoesters, DMC yields of
 23 48% (based on the orthoester reagent) and a selectivity of 85% (DMC) were found under high
 24 pressures of CO₂ (300 atm) and reaction temperatures of 180°C, using [Bu₂Sn(OMe)₂] as
 25 catalyst [21]. Notably, a substantial enhancement of the catalyst performance by the addition
 26 of onium salts was observed. One drawback of this approach, however, was the required

1 stoichiometric use of orthoesters. As shown in Scheme 3, they can capture water under the
2 release of an alcohol and an ester, but recycling of the desiccant is not feasible.

3



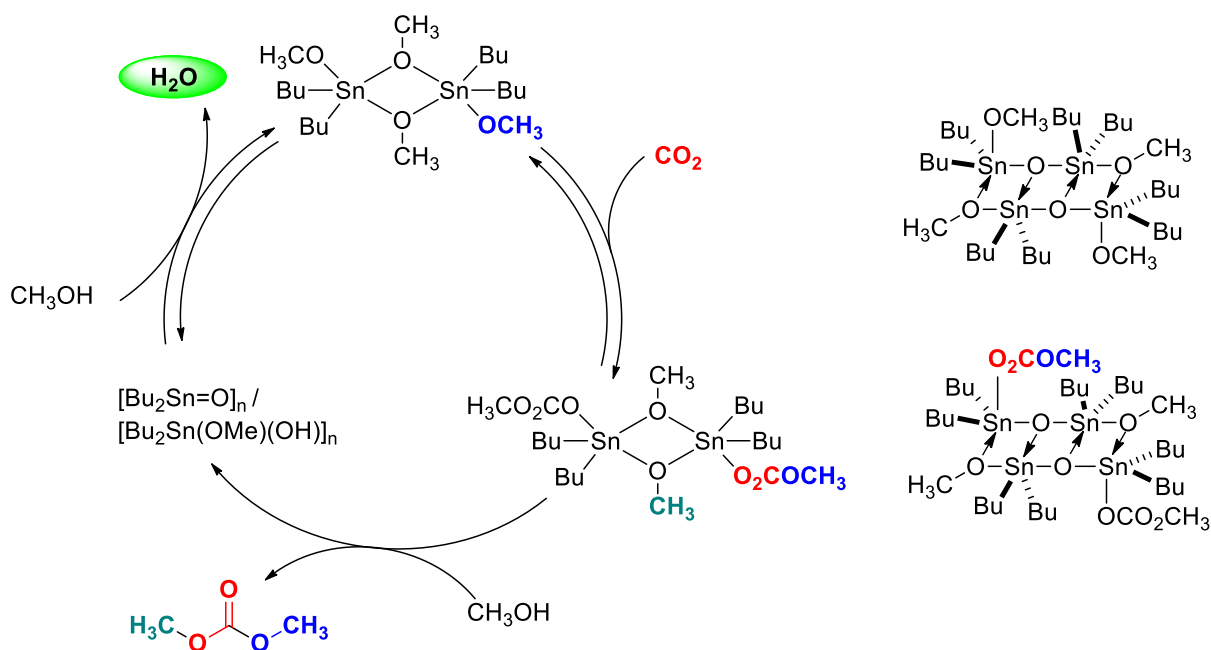
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5 **Scheme 3** Organic desiccants that have been employed as water-capturing agents

6

7 By contrast, drying agents such as acetals promised to be more sustainable, since they feature
8 recovery potential from the formed ketone that upon reaction with alcohols can regenerate the
9 acetal [22]. In comparison to the orthoester system, a combination of tin compound and acetal
10 performed slightly better with a DMC yield of 58% based on the acetal. Even though in this
11 case onium salts do not lead to improved catalyst performance, more recently it has been shown
12 that acidic co-catalysts have a pronounced influence on the efficiency in DMC formation, and
13 for instance the presence of small amounts of co-catalytic $\text{Ph}_2\text{NH}_2\text{OTf}$ accelerated the reaction
14 substantially [15].

15 Besides organic desiccants, also inorganic versions such as molecular sieves have been
16 successfully employed in the dehydration process [6]. Even though zeolites are not considered
17 to be very efficient under high reaction temperature conditions, yields up to 45% based on
18 MeOH were reported [6]. Mechanistic proposals are based on early structural findings [23], as
19 depicted in Scheme 4. After CO_2 insertion into the metal methoxide moiety, the bridging
20 alkoxide reacts with the hemi-carbonate anion with subsequent DMC release. The active
21 species can be reestablished from the corresponding oxide or hydroxide by reacting with
22 methanol under the release of water [24]. Recent reinvestigations and density functional theory
23 (DFT) calculation, though, suggest that the actual active intermediates might be stannoxane
24 dimers (Scheme 4) [25, 26].



Scheme 4 Mechanistic proposal based on structural findings (left); reactive intermediates suggested by computational and experimental studies

1.4 Metal-based Heterogeneous Catalysis

The use of heterogeneous catalysts in the synthesis of chemical compounds has several key benefits **if** compared with homogenous catalysis. Separation of the catalyst from the products is usually straightforward, e.g. by a simple filtration. At the same time, the ease of separation is advantageous when it comes to recyclability of the catalyst. This makes heterogeneous catalysts an interesting choice for industry, especially when similar selectivities and activities as in the case of homogenous catalysts can be achieved. For DMC synthesis, the use of metal oxides had a considerable impact on the field. Besides main group metal oxides such as Mg–Al hydrotalcites [27, 28], mainly transition metal oxides have been employed. Among these are vanadium oxides, doped with Brønsted acids [29] or copper/nickel [30], but the most widely studied systems consist of zirconium and cerium oxides.

Early work by Tomishige and Fujimoto revealed the great potential of the amphoteric materials ZrO_2 and CeO_2 (or solid solution mixtures) [31–35], being mainly attributed to synergistic effects between their acidic and basic sites [31]. However, for the simple metal oxides the equilibrium restriction did not allow for yields exceeding 2% [34] even under high CO_2 pressures of 6 MPa and temperatures around 127 °C. Doping of the metal oxides with

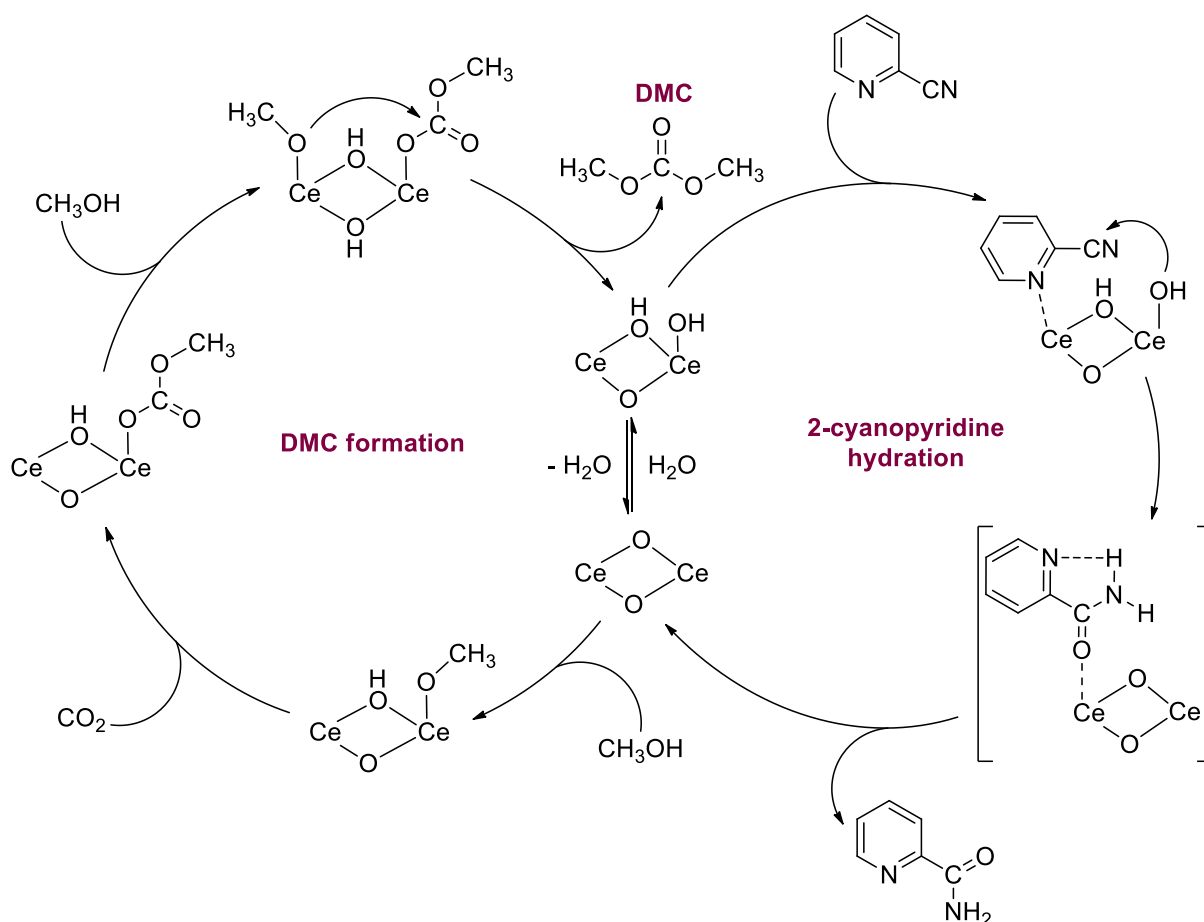
1 Brønsted acidic sites using H_3PO_4 or $\text{H}_3\text{W}_{12}\text{O}_{40}$ led to slightly improved yields or shorter
2 reaction times under comparable conditions [36–38].

3 Major breakthroughs were only achieved, though, if dehydrating agents were added. In
4 contrast to orthoesters or acetals, which were formerly used by Sakakura, Tomishige and
5 coworker suggested the use of nitriles in 2009 [39, 40]. Water capture with nitriles leads to
6 amides, which can later be converted back to the corresponding nitrile and enable the
7 regeneration of the dehydrating species. The elegance of this synthetic route is based on the
8 simultaneous conversion of CO_2 and methanol to DMC and the nitrile hydration to the
9 corresponding amide by CeO_2 . If using acetonitrile as desiccant at 0.5 MPa CO_2 pressure and
10 150 °C, the yield of DMC after 48 h reached about 9% but with only a mediocre selectivity for
11 DMC of 65%. Also the selectivity of amide formation upon water capture remained an issue,
12 especially in the light of recyclability of the dehydrating agent. Benzonitrile proved to be a
13 much better choice not only with respect to selective amide formation, but its use also increased
14 the DMC yield to a remarkable 47% (1 MPa, 150 °C, 86 h), with a significantly improved
15 chemo-selectivity of 75% [41].

16 As suggested by the authors, the reason for this improved reactivity/selectivity behavior
17 might be suppression of competitive alcoholysis of the formed amide, if compared to acetamide
18 that is *in situ* produced from acetonitrile. A systematic screening for suitable nitrile-based
19 dehydrating agents [42, 43], which are efficiently hydrated by CeO_2 , finally led to the use of 2-
20 cyanopyridine as the preferred nitrile in combination with a cerium oxide catalyst. With this
21 system (5 MPa, 120 °C, 12 h), yield of and selectivity for DMC were extraordinarily high,
22 reaching levels of 94% and 96%, respectively. The recycling of the formed amide was also
23 addressed, and the dehydration of 2-picolinamide by $\text{Na}_2\text{O}/\text{SiO}_2$ was shown to be feasible even
24 though the overall efficiency should be improved. The scope is not only limited to the formation
25 of DMC, but also ethanol or branched alcohols could be converted in a similar way albeit with
26 a drop in yield of the corresponding carbonate product.

27 In order to provide a lead for further improvement of the catalytic system, mechanistic
28 insights are inevitable. Tomishige *et al.* proposed a reaction cycle based on kinetic,
29 spectroscopic and computational studies, leading to an overall mechanism as depicted in
30 Scheme 5 [44]. It resembles the mechanism suggested by Bell *et al.* for the zirconium oxide
31 catalyzed formation of DMC from methanol and CO_2 [45]. A molecule of CO_2 inserts into the
32 $\text{Ce}-\text{OCH}_3$ bond of surface bound methanol to yield a Ce–methyl carbonate species. For the
33 next step the authors suggested a nucleophilic attack of another surface bound methoxy group

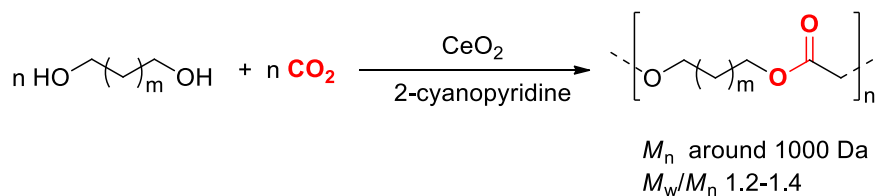
1 to give DMC. The formed hydroxide species on the cerium oxide surface can subsequently
 2 react with 2-cyanopyridine and result in the formation of 2-picolinamide [46, 47]. Other
 3 authors, however, claim the attack of gas-phase methanol [48], or the formation of a
 4 carbomethoxide intermediate on the cerium oxide surface [49]. Therefore, the exact mechanism
 5 concerning the cerium oxide mediated formation of DMC remains subject of ongoing debate in
 6 the literature.



7
 8 **Scheme 5** Mechanism of cerium oxide catalyzed simultaneous formation of DMC and 2-
 9 picolinamide formation from MeOH/CO₂ and 2-cyanopyridine, respectively

10
 11 Its superb performance regarding yield and selectivity towards DMC formation makes the
 12 combination of cerium(IV) oxide and 2-cyanopyridine a promising candidate for further
 13 commercial applications. This is reflected in the development of the first continuous flow
 14 process using fixed bed reactors [50], as well as intensified research concerning the reusability
 15 of the cerium oxide catalyst, which eventually suffers from deactivation by adsorption of the
 16 formed amide [44, 51]. Interestingly, the scope of this system is not limited to the formation of
 17 simple acyclic carbonates, but can also be employed to cyclic carbonates (see section 2 and 3

1 of this review) [52], as well as cyclic and acyclic carbamates and urea derivatives [53–55]. Very
2 recently, cerium oxide and 2-cyanopyridine was furthermore used to synthesize polymeric
3 materials from CO₂ and diols, as depicted in Scheme 6 [56]. Despite the low molecular weight
4 of the produced materials, this represents the first exciting example of a direct copolymerisation
5 between CO₂ and diols.



9 **Scheme 6** Direct polycarbonate formation from diols and carbon dioxide

10 1.5 Prospects of Acyclic Carbonate Formation

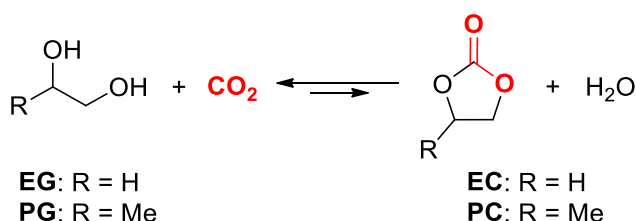
11 Over the last two decades, huge progress has been made regarding the yield and chemo-
12 selectivity in the production of DMC from methanol and carbon dioxide. Homogeneous and
13 heterogeneous catalyst systems have been improved continuously, going hand in hand with the
14 development of efficient dehydrating systems to shift the reaction equilibrium towards the
15 formation of DMC. Various studies were dedicated to homogeneous metal alkoxide
16 compounds, with tin(IV) complexes leading the way. In combination with different water-
17 removing agents, good yields and selectivities for the formation of acyclic carbonates were
18 obtained. Even better performances were achieved using heterogeneous, amphoteric metal
19 oxides such as zirconium oxide and cerium oxide, with the latter giving excellent yields and
20 selectivities towards DMC when combined with 2-cyanopyridine as desiccant. Although
21 product separation and recyclability of catalyst and dehydrating agent have been clearly
22 demonstrated, recovery of the nitrile from 2-picolinamide remains problematic for further
23 applications and is at the same time crucial to optimize the cost-benefit ratio as well as to design
24 a truly sustainable, atom-economical route for the preparation of acyclic organic carbonates.
25 New reactor technologies such as the use of flow chemistry with a clever use of recycle streams
26 may at some point in time allow to efficiently run DMC and related synthesis in continuous
27 mode at low conversion of the alcohol without the need for a dehydrating agent.

2. Cyclic Organic Carbonates from Saturated Alcohols

2.1. Synthesis of Five-membered Cyclic Carbonates

2.1.1 Metal based catalysts

From an industrial point of view, the transformation of ethylene glycol (EG) and propylene glycol (PG) is of high interest. Both EG and PG are byproducts obtained in the transesterification of ethylene carbonate (EC) and propylene carbonate (PC), respectively, using MeOH as a reagent and with the aim to produce DMC. Thus, recycling of the EG or PG by reaction with CO₂ has the potential to lift the overall sustainability of DMC synthesis from EC or PC (Scheme 7) [57].



10

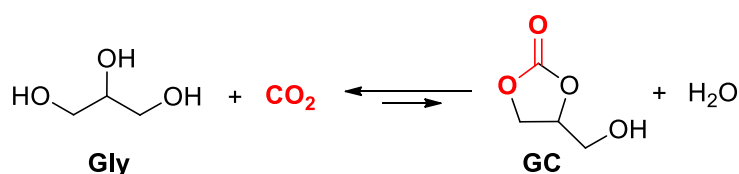
11 **Scheme 7** Synthesis of cyclic carbonates from CO₂ and the glycols EG and PG

12

13 Tomishige reported the first attempt for this transformation using a calcined CeO₂-ZrO₂
14 catalyst system in the presence of acetonitrile [58, 59]. Conversions of 0.7 and 1.6% were
15 obtained under optimal reaction conditions using 0.36 mmol (total amount of Ce and Zr) of
16 catalyst weight, 200 mmol of CO₂, 120 mmol acetonitrile, a reaction temperature of 150 °C for
17 2 h: these conditions led to the synthesis of EC and PC from EG and PG, respectively.
18 Interestingly, the EC and PC amount increased when the calcination temperature of the catalyst
19 system was increased, which resulted in lowering the amount of acid/base sites and the surface
20 area. As in the formation of linear carbonates, the reaction mediated by the CeO₂-ZrO₂ catalyst
21 system is thermodynamically limited with a maximum conversion of 2%; removal of H₂O
22 would be crucial to maximize the conversion/yield of the carbonate product.

23 Subsequently, He *et al.* reported two different catalyst systems such as dibutyltin
24 oxide/dibutyltin dimethoxide and low toxic magnesium and its oxide for the synthesis of PC
25 from PG and CO₂ under supercritical conditions using *N,N*-dimethylformamide (DMF) as
26 solvent [60, 61]. In both cases, the maximum conversion obtained for PG was <4% with 100%
27 chemo-selectivity. Also, alkali carbonates were used to catalyze the PC synthesis from PG and

1 CO₂ with a relative high yield of 10.5% under supercritical conditions in the presence of
2 ammonium carbonate and acetonitrile [62]. Acetonitrile did not only act as a solvent here but
3 also as the dehydrating agent to eliminate the water produced during the reaction thereby
4 shifting the equilibrium towards the formation of PC. However, the hydrolysis of acetonitrile
5 may generate acetamide and can subsequently react with water to form acetic acid and
6 ammonia. Acetic acid can react with PG to produce propylene glycol-2-acetate, lowering the
7 overall selectivity towards PC. Therefore, introduction of ammonium carbonate into the
8 reaction system inhibited the hydrolysis of acetamide and improved the chemo-selectivity
9 toward PC.



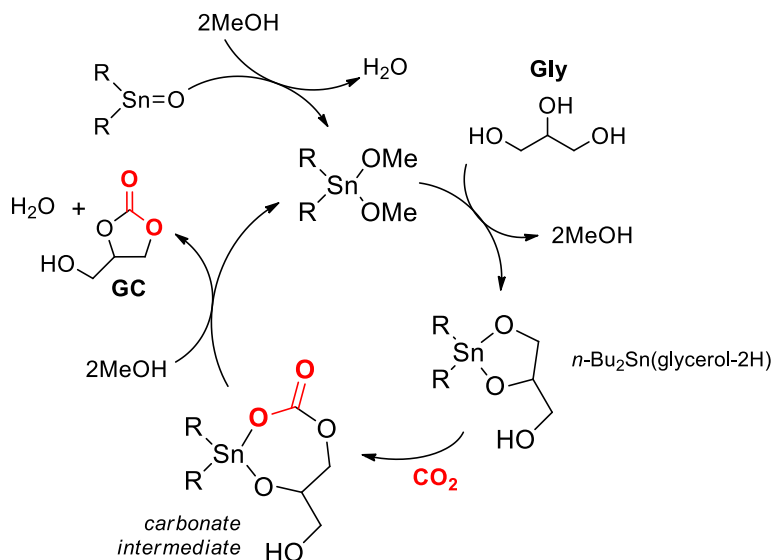
11 **Scheme 8** Synthesis of **GC** from **Gly** and CO₂

12

13 The combination of its bio-based origin and wide reactivity has made glycerol carbonate
14 (**GC**) a versatile and renewable building block for organic chemistry. The direct carboxylation
15 of glycerol (**Gly**) and CO₂ is a very interesting though challenging route that would convert two
16 waste materials from the chemical industry into a valuable product (Scheme 8). Mouloungui *et*
17 *al.* attempted to prepare **GC** under supercritical conditions but the reaction did not occur [63].
18 Later on, Dibenedetto employed tin-based catalyst systems [*n*-Bu₂Sn(OMe)₂] and [*n*-Bu₂SnO]
19 under solvent-free conditions using 6 mol% of catalyst [*n*-Bu₂Sn(OMe)₂], 5 MPa of CO₂
20 pressure, a reaction temperature of 180 °C for 15 h to obtain a maximum conversion of 6.7%
21 [64]. Molecular sieves were introduced into the reactor to reduce the water content in the
22 homogeneous phase to favor the equilibrium towards the formation of **GC**.

23 Hereafter, Dibenedetto applied mixed oxide catalysts (CeO₂/Al₂O₃ and CeO₂/Nb₂O₅) under
24 the same reaction condition mentioned above in a biphasic system using tetra(ethylene glycol)
25 dimethyl ether (TEGDME) as solvent to obtain a maximum **Gly** conversion of 2.5%. The
26 catalyst was recyclable at least 3 times without any observable loss of activity [65]. Munshi *et*
27 *al.* showed that addition of methanol to the Dibenedetto's *n*-Bu₂SnO-based catalyst system
28 enhanced the catalytic activity and as a result 30% yield for **GC** in 4 h at 80 °C and 3.5 MPa
29 CO₂ pressure using 1 mol% of catalyst could be attained [66]. The reaction with diglyme, an

1 inert aprotic solvent, instead of methanol did not improve the yield of **GC** and also the use of
 2 other alcohols such as ethanol, propanol and butanol slowed down the reaction rate. These
 3 combined results indicated that the role of methanol is not just acting as a solvent but it is likely
 4 also chemically involved. The proposed mechanism presumes the activation of *n*-Bu₂SnO by
 5 methanol to give *n*-Bu₂Sn(OMe)₂ which in turn reacts with **Gly** forming *n*-Bu₂Sn(glycerol-2H)
 6 and undergoes CO₂ insertion, leading eventually to **GC** via a Sn(glycerolcarbonate) complex.
 7 The catalytic cycle is completed by ligand exchange in the presence of methanol followed by
 8 ring-closing, release of the **GC** product and the reformation of the Sn(OMe)₂ complex species
 9 as shown in Scheme 9. During the process, the monomeric species (*n*-Bu₂Sn(glycerol-2H)) can
 10 either incorporate CO₂ or oligomerize causing catalyst deactivation. The addition of methanol
 11 prevents the formation of an oligomeric species as it is actively involved in the formation of
 12 **GC** whereas the water formed during reaction is removed continuously from the system.



13

14 **Scheme 9** Proposed reaction path towards GC formation [66]

15

16 Similar to Tomishige's work [58] using acetonitrile as a medium that helps to overcome the
 17 thermodynamic limitation of the process, Sun and coworkers used acetonitrile as a sacrificial
 18 coupling in the presence of a La₂O₂CO₃-ZnO catalyst system for the transformation of CO₂
 19 and **Gly** into **GC** [67]. The highest **Gly** conversion (30.3%) with a **GC** yield of 14.3% was
 20 reported at 4 MPa of CO₂ pressure, a reaction temperature of 170 °C after 12 h when the catalyst
 21 system was calcined at 500 °C. The envisioned mechanism involves the activation of **Gly** by
 22 Lewis acidic sites (Zn²⁺) forming a glyceroxide anion, and subsequently the oxygen atom of
 23 the adjacent hydroxyl group attacks the zinc cation resulting in zinc-glycerolate species along

1 with the formation of a molecule of water which is converted to an amide reacting with
2 acetonitrile.

3 The uncalcined catalyst produces only a low yield of **GC** due to the higher content of crystal
4 lattice water, which favors the hydrolysis of acetonitrile (*cf.*, amide formation) and results in
5 more byproducts. With the introduction of $\text{La}_2\text{O}_2\text{CO}_3$, the amount of lattice oxygens (La–O
6 pairs) increases on the surface and leads to an increase of moderately basic sites, which in turn
7 enhance the activation of glycerol and CO_2 and thereby exhibit higher catalytic activity than
8 pure ZnO. Likewise, various other catalysts systems such as Cu/ La_2O_3 and Cu-supported
9 catalysts, Zn/Al/La and Zn/Al/La/M (M = Li, Mg and Zr) hydrotalcites, and Zn/Al/La/X (X =
10 F, Cl, Br) catalysts were also successfully employed for the direct carbonylation of **Gly** to
11 obtain maximum conversions of the substrate of <36% under typically harsh, supercritical
12 reaction conditions in the presence of acetonitrile [68–70].

13 Very recently, He and co-workers obtained **GC** from the carbonylation of **Gly** and CO_2 over
14 CeO_2 catalysts with the hydrolysis of 2-cyanopyridine as the sacrificial dehydrating agent [71].
15 Calcined CeO_2 with three different morphologies pertinent to nanoparticles, nano-rods and
16 sponge-like nanomaterials were prepared corresponding to three different types of methods
17 being precipitation, hydrothermal treatment and sol-gel methodology, respectively. All three
18 samples showed excellent catalytic performance obtaining **GC** yields between 20–34 % under
19 relatively mild reaction conditions (150 °C, 4 MPa, 5 h) with an activity order of nanorod
20 catalyst > catalytic nanoparticles > sponge-like catalyst. The CeO_2 nano-rod type catalyst with
21 the most abundant basic sites and oxygen vacancies gave the highest yield of **GC**, and sponge-
22 like CeO_2 with medium amount of basic sites and the least defects gave the lowest, indicating
23 that the oxygen vacancies play an important role in the catalytic system. Among various
24 dehydrating agents used, 2-cyanopyridine showed the best performance ascribed to the
25 relatively strong alkalinity and the formation of intramolecular hydrogen bonding in the
26 produced amide when the nitrile reacts with water. By optimizing the reaction conditions, the
27 **GC** yield could be increased to as high as 78.9% and the used catalyst could be easily
28 regenerated through the calcination process at 400 °C for 5 h, and was recycled five times
29 successfully.

30

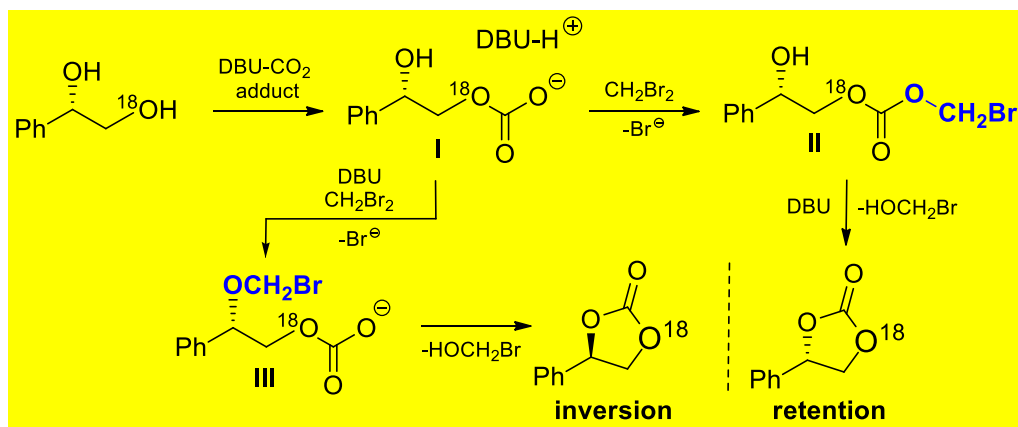
1 2.1.2 Organocatalysts

2 Jang and co-workers introduced a metal-free carbonylation reaction in which alcohols are
3 converted into corresponding cyclic carbonates in the presence of an organic base and
4 dibromomethane (CH_2Br_2) as the solvent [11]. The organic base, 1,8-
5 diazabicyclo[5.4.0]undec-7-ene (DBU), is assumed to deprotonate the OH unit of ethylene
6 glycol (**EG**), which would render it more nucleophilic. DBU is also known to form an adduct
7 with CO_2 , and can in this way increase the nucleophilic character of CO_2 favoring reaction with
8 **EG**. In the presence of 2 equivalents of DBU at 0.5 M of CH_2Br_2 and at 0.5 MPa/70 °C, **EG**
9 (0.5 mmol) was converted into **EC** (24% after 18 h). In the presence of an ionic liquid (IL:
10 bmimPF₆), the **EC**-yield was enhanced to 54% and under higher CO_2 pressure (1 MPa) it was
11 further improved to 74%.

12 ILS are well-known to increase the solubility of CO_2 in the reaction media. Under the
13 optimized reaction conditions, various other alcohols were also tested as substrates and it was
14 found that **Gly** underwent good conversion obtaining a **GC** yield of 86%. Similarly, other
15 methyl- and phenyl-substituted ethylene diols underwent smooth conversion to their cyclic
16 carbonates to afford yields of 67–79%. A cyclic diol was also tested and displayed an excellent
17 yield of 73%. A set of additional experiments was performed to understand the operating
18 mechanism in these diol/ CO_2 coupling reactions. First, an ^{18}O -labeling experiment was
19 conducted with mono- ^{18}O -labeled styrene glycol and a 70% yield of the styrene carbonate was
20 achieved, where the ^{18}O label did not exchanged with ^{16}O during the reaction, *i.e.* the cyclic
21 carbonate had the ^{18}O -labeled atom incorporated. Second, the use of optically active (*S*)-styrene
22 glycol was examined, and the resultant styrene carbonate was analyzed by HPLC showing full
23 retention of the initial configuration.

24 The mechanism of the aforementioned reaction is shown in Scheme 10 in which the primary
25 alcohol first attacks the DBU– CO_2 adduct to form the carbonate intermediate **I**, which then
26 reacts with CH_2Br_2 to form reactive carbonate **II**. Then the intermolecular attack of the (pre-
27 activated) secondary alcohol unit onto the carbonate followed by the elimination of HOCH_2Br
28 affords the styrene carbonate product. The intramolecular addition of the carbonate nucleophile
29 in intermediate **III** likely is not competitive under these conditions as supported by the
30 experimental result obtained using (*S*)-styrene glycol.

31



1
2 **Scheme 10** Plausible mechanism for cyclic carbonate formation from styrene glycol and CO₂

3
4 **3. Formation of Six-membered Cyclic Carbonates**

5
6 **3.1 Metal based catalysts**

7 The pioneering group of Tomishige has successfully performed various carboxylation reactions
8 of diols and CO₂ to afford their cyclic carbonates. Recently, they employed the privileged CeO₂
9 catalyst in combination with 2-cyanopyridine as dehydrating agent to yield various five- and
10 six-membered cyclic carbonates from CO₂ and diols [52]. From a series of different metal
11 oxides combined with 2-cyanopyridine for the synthesis of **PC** from **PG** and CO₂, CeO₂ was
12 shown to be more active by 2 orders of magnitude compared with other metal oxides. 2-
13 Cyanopyridine was preselected as nitrile for its exceptional reactivity towards hydration
14 forming 2-picolinamide. Without the addition of 2-cyanopyridine, the **PC** yield was as low as
15 0.3% due to the unfavorable thermodynamics. Addition of 100 mmol of 2-cyanopyridine
16 provided an excellent **PC** yield of >99% (chemo-selectivity >99%) in just 1 h using 20 mol%
17 catalyst (CeO₂), at 130 °C/5 MPa CO₂ and this is the highest yield of **PC** from CO₂ and **PG** to
18 date.

19 To extend the synthetic potential of this catalyst system, synthesis of six-membered ring
20 carbonates was carried out by employing various 1,3-diols with monoalkyl-, dialkyl-, and
21 phenyl-substitutions and generally the corresponding cyclic carbonates were obtained in high
22 yields of 62–97% with good to excellent chemo-selectivity (77–99%). The ester that is formed
23 by reaction of the diol starting material with 2-picolinamide *in situ* produced was spotted as the
24 major byproduct. Syntheses of six-membered ring carbonates, especially those having multiple

1 substituents, are difficult to realize using any methodology, despite the fact that they represent
2 useful chemicals and intermediates for, *inter alia*, biodegradable polymers for drug delivery
3 systems. The results obtained for this Ce-based catalyst system mediating the synthesis of
4 various six-membered carbonates are highly attractive compared to other methodologies
5 reported to date, except for the non-substituted trimethylene carbonate derived from oxetane
6 and CO₂, for which Kleij *et al.* [72] reported a very high yield (95%) using a simple though
7 highly reactive Al-catalyst based on amino-triphenolate ligands.

8 After the reaction, the CeO₂ catalyst was removed from the reaction mixture and the filtrate
9 was analyzed by coupled plasma atomic emission spectroscopy (ICP–AES), which indicated
10 that no Ce species had leached into the filtrate (<0.1 ppm). The catalyst was therefore
11 successfully reused for three times without any loss of its high selectivity and yield; the BET
12 surface area and X-ray diffraction pattern of the CeO₂ material before and after the reaction
13 remained virtually unchanged and thus indicated that the CeO₂ catalyst is highly stable under
14 the experimental conditions. The mechanistic details are similar to the ones already discussed
15 for the formation of acyclic carbonates in section 1. Overall, this catalyst system shows the best
16 yields for cyclic carbonate synthesis (five- and six-membered ones) from diols and CO₂
17 reported to date.

18

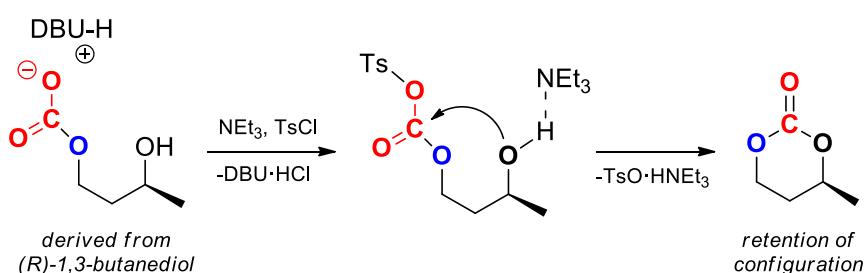
19 3.2 Organocatalysts

20 Buchard and co-workers [73] performed the synthesis of six-membered cyclic carbonates
21 directly from various 1,3-diols and CO₂ at room temperature, 0.1 MPa of CO₂ using standard
22 reagents. First, the selective mono-insertion of CO₂ into one of the O–H bonds of 1,3-butanediol
23 in various solvents was examined in the presence of DBU as catalyst. After the selective
24 formation of the mono-carbonate intermediate at low concentration, 1 equivalent of tosyl
25 chloride/triethylamine was added to the reaction mixture and stirred at room temperature. The
26 pure targeted product was isolated in an appreciable yield of 44%, which was increased to 68%
27 when a higher concentration of diol (going from 0.1 to 1.7 M) was applied. Investigation into
28 the scope of diol substrates revealed that various 1,3-diols were good reaction partners in this
29 organocatalytic approach, and the corresponding six-membered cyclic carbonates were isolated
30 in low to good yields (11–70%). After initial insertion of CO₂, into one of the O–H bonds,
31 tosylation of the carbonate species or the remaining alcohol function can be envisaged.

1 Hereafter, the cyclization proceeds *via* either an addition/elimination sequence or an S_N2
2 pathway, leading to retention or inversion of stereochemistry, respectively.

3 However, the exclusive formation and isolation of the (*R,R*)-configured cyclic carbonate
4 from (*R,R*)-2,4-pentanediol (yield: 53%) as well as the optical activities of the cyclic carbonates
5 obtained from enantiopure (*R*)- and (*S*)-1,3-butanediol, clearly indicated a preference for the
6 addition/elimination pathway (Scheme 11), with no observable racemization or inversion of
7 stereochemistry, which was further supported by DFT calculations.

8



10 **Scheme 11** Preferred pathway for the conversion of (*R*)-1,3-butanediol into its six-membered
11 carbonate [73]

12

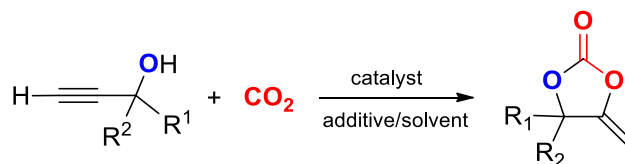
13 4. Cyclic Carbonates derived from Unsaturated Alcohols

14 4.1 Metal based catalysts

15 Reaction of CO₂ with propargylic alcohols typically affords α -alkylidene cyclic carbonates
16 through a carboxylative cyclization process (Scheme 12), which is also a promising and green
17 route to convert CO₂. Moreover, α -alkylidene cyclic carbonates possess a wide range of
18 applications in organic synthesis being for instance building blocks in the formation of α -
19 hydroxy ketones and 5-methylene-oxazolidin-2-one derivatives.

20 Inoue *et al.* [74] performed the Pd(0)-catalyzed [Pd(PPh₃)₄] carboxylative cyclization
21 reaction of CO₂ (1 MPa) with sodium 2-methyl-3-butyn-2-olate (prepared from the
22 corresponding alcohol and a slight excess of NaH) and iodobenzene in THF as solvent at 100
23 °C and obtained the cyclic vinylidene carbonate in 68% yield. Alternatively, the use of copper
24 catalysis proved to be highly beneficial to further develop this type of reaction. For instance, a
25 cationic copper complex derived from 2,5,19,22-tetraaza[6,6](1,1')ferrocenophane-1,5-diene
26 was an effective catalyst operating under 3.8 MPa of CO₂ and 100 °C affording good yields of

1 the cyclic carbonates (>90%) using various substituted propargylic alcohols under neat
2 conditions [75]. Similarly, CuCl in the presence of the IL [BMIm][PhSO₃] yielded the α -
3 alkylidene cyclic carbonate in 97% yield under a milder CO₂ pressure of 1 MPa at 120 °C [76].

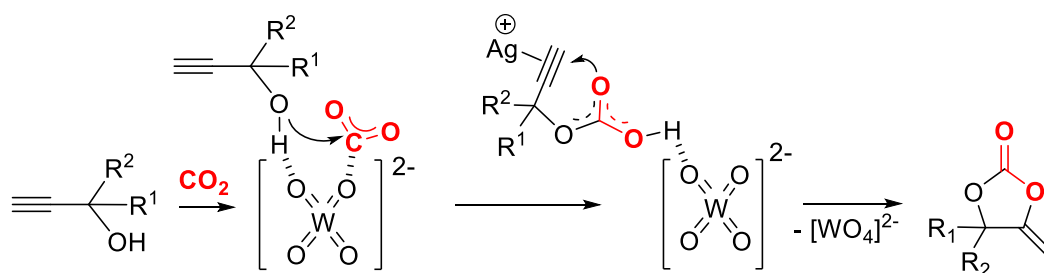


5 **Scheme 12** Conversion of CO₂ into an α -alkylidene cyclic carbonate with an *exo*-cyclic double
6 bond using propargylic alcohols

7

8 Substantial improvement in activity was reported for metal based catalyst systems when
9 Mizuno *et al.* communicated a tungstate based complex (*i.e.*, TBA₂[WO₄], TBA =
10 tetrabutylammonium) as an efficient homogeneous catalyst for conversion of CO₂ with
11 propargylic alcohols to give the corresponding cyclic carbonates under mild reaction conditions
12 [77]. DFT calculations allowed to optimize the tungstate structure and the basicities of oxygen
13 atoms in various polyoxometalates (POMs) were compared with the natural bond orbital (NBO)
14 charges; the simple [WO₄]²⁻ tungstate was found to be the most basic among the series. Under
15 only 0.1 MPa of CO₂ pressure and at a relatively low temperature of 60 °C, propargylic alcohol
16 (2-methylbut-3-yn-2-ol) was coupled with CO₂ in acetonitrile to give the corresponding
17 carbonate structure in 76% yield. Upon lowering the catalyst loading while increasing the CO₂
18 pressure (2 MPa) and reaction time, the total turnover number could be enhanced to a significant
19 473 with a yield of 95%. In a similar way, more lethargic substrates such as propargylic alcohols
20 with internal triple bonds (*cf.*, 1-ethynylcyclohexan-1-ol) were also effectively transformed to
21 their cyclic carbonates in excellent yield of up to 95%.

22 Having witnessed the enhancement in activity brought about by the [WO₄]²⁻ anion in
23 carbonate formation under much milder conditions, Song and co-workers [78] employed a
24 Ag₂WO₄/Ph₃P dual catalyst system for the conversion of CO₂ and propargylic alcohols to
25 provide the α -alkylidene carbonates under solvent-free conditions. In this dual catalyst system,
26 the [WO₄]²⁻ anion was envisioned to activate both CO₂ and the propargylic alcohol generating
27 a carboxylate intermediate which could then be intercepted by Ag-activated C≡C triple bond to
28 afford the product (Scheme 13).



1

2 **Scheme 13** Chemical fixation of CO₂ through the dual activation pathway [78]

3

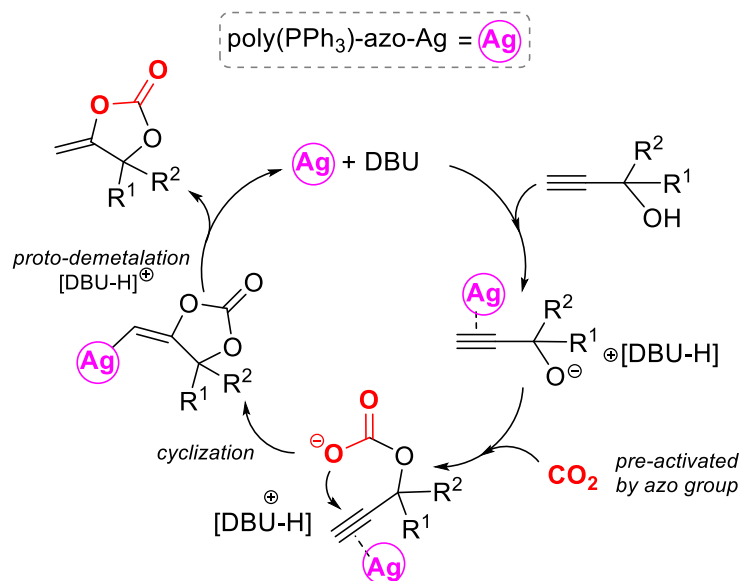
4 Using this system at 1 mol% of catalyst loading, 25 °C and 0.1 MPa of CO₂ pressure an
 5 optimum yield of 96% was obtained. Subsequently, other substrates were examined with this
 6 dual catalyst and propargylic alcohols with alkyl and aryl substituents at the propargylic
 7 position were also effective substrates to give the corresponding cyclic carbonates in good to
 8 excellent yields. The method was, however, not effective for 1-isopropyl and 1,1-
 9 cyclopentylene substituted substrates which showed (very) low conversions due to a
 10 combination of steric hindrance and ring strain. Secondary propargylic alcohols failed to form
 11 the carbonate product, while the internal propargylic substrate 2-methyl-4-phenylbut-3-yn-2-ol
 12 required both higher CO₂ pressure (1 MPa) and temperature (80 °C) to afford the corresponding
 13 cyclic carbonate in good yield (82%) using longer reaction times (36 h). This catalyst system
 14 was easily separated by extraction with hexane and after drying the catalyst could be
 15 successfully recycled four times without observable loss of activity.

16 At room temperature and CO₂ pressures <2 MPa, AgOAc/DBU [79] and F-MOP-3-Ag/
 17 DBU catalyst systems (F-MOPs = fluorinated microporous organic polymers having Ag(I) sites
 18 incorporated) [80] in toluene gave good results. Notably, both catalyst systems were successful
 19 in converting various terminal and bulky internal propargylic alcohols to their corresponding
 20 cyclic carbonates in good yields. Heterogeneous metal systems have also been reported as
 21 effective catalysts for α -alkylidene carbonate formation. Important limitations for these
 22 supported catalyst systems, though, were primarily the required supercritical conditions and
 23 high catalyst loadings and, moreover, a limited substrate scope allowing only the conversion of
 24 terminal propargylic alcohols [81, 82]. Significant improvement of activity and reusability
 25 features of heterogeneous metal catalysts was reported by Liu and co-workers [83] who used
 26 porous organic polymers (POPs) as a solid support. This material allows the introduction of
 27 various CO₂-philic functional species inside its structure to obtain a more active, functional and
 28 reusable catalyst. Specifically, the authors prepared porous poly(triphenylphosphine) with azo

1 (R–N=N–R) functionalities (*i.e.*, a poly(PPh₃)-azo material) with the Ag sites being coordinated
2 by the phosphine ligands. This system was efficiently used for CO₂ transformations taking
3 advantage of cooperative effects between the functional porous polymer and the metal species.
4 The poly(PPh₃)-azo-Ag/DBU catalyst converted at room temperature and a CO₂ pressure of 1
5 MPa the benchmark propargylic alcohol 2-methylbut-3-yn-2-ol to its corresponding cyclic
6 carbonate with a yield of 56% in 3 h; a higher yield was achieved by further increasing the
7 reaction time to 18 h (>99%) with a remarkable total TON of 1563. The presence of a high local
8 concentration of PPh₃ ligands and azo functionalities in the polymer (PPh₃/Ag = 200:1, azo/Ag
9 = 300:1) facilitated cooperative effects towards the formation of α -alkylidene compounds.
10 Moreover, the catalyst system was also shown to be recyclable at least five times without loss
11 of activity. After several uses, transmission electron microscopic (TEM) analysis of the
12 catalytic material indicated that the metallic Ag particles were still highly dispersed without
13 changes in particle size after recycling. In order to establish possible leaching, the catalyst was
14 separated through centrifugation after the reaction performed for 1 h, and the filtrate was
15 analyzed by ICP-OES which demonstrated that there was no observable leaching of Ag species
16 (<10 ppb). Then, various terminal propargylic alcohols with both alkyl and aryl substituents
17 were examined as substrates and these reacted efficiently with CO₂, though substrates
18 comprising bulky isopropyl groups or small rings required longer reaction times to obtain good
19 yields presumably due to steric effects.

20 The proposed mechanism for the formation of α -alkylidene cyclic carbonates mediated by
21 the poly(PPh₃)-azo-Ag catalyst system is shown in Scheme 14 [83]. First, the propargylic
22 alcohol, activated by DBU, reacts with pre-activated CO₂ to generate a carbonate intermediate.
23 An intramolecular ring-closing step is then followed by proto-demetalation to afford the
24 corresponding cyclic carbonate with the regeneration of the active Ag species and DBU.

25 Similarly, He *et al.* [84] used [(PPh₃)₂Ag]₂CO₃ (*in situ* formed from Ag₂CO₃ and PPh₃) as a
26 robust and highly efficient single-component bifunctional catalyst for the coupling of
27 propargylic alcohols and CO₂ at room temperature and atmospheric pressure. After only 2 h, 2-
28 methylbut-3-yn-2-ol and CO₂ were converted to the cyclic carbonate in 93% yield under



1

2 **Scheme 14** Proposed mechanism for the coupling reaction of propargylic alcohols with CO₂
 3 catalyzed by poly(PPh₃)-azo-Ag/DBU [83]

4

5 neat conditions using the *in situ* prepared catalyst. The recovered precipitate after the reaction
 6 could be reused in a subsequent carboxylative cyclization cycle.

7 Ag nanoparticles (NPs) have been immobilized to other solid supports such as sulfonated
 8 macro-reticular resins (SMRs) forming an active AgNPs/SMR catalyst [85]. Alternatively, Ag
 9 halides were supported on a porous carbon material (AgX@C, X = Cl, Br and I) [86] and the
 10 resultant catalyst was effective at room temperature and atmospheric pressure in the
 11 carboxylative cyclization of the propargylic alcohol 2-methylbut-3-yn-2-ol and CO₂ in the
 12 presence of DBU as co-promoter. The use of the AgNPs/SMR catalyst gave a 91% yield of the
 13 cyclic carbonate after 10 h in DMF, and the catalyst was shown to be recyclable at least five
 14 times. The AgI@C catalyst furnished the product in 99% yield within 4 h in acetonitrile, and
 15 was used in a total of 10 cycles without any significant loss in activity.

16 Interestingly, a zinc salt (ZnI₂) in combination with triethylamine (NEt₃) was recently
 17 proposed as a catalyst system in this area and showed excellent synergistic effects to promote
 18 the solvent-free reaction of CO₂ and 2-methylbut-3-yn-2-ol under a CO₂ pressure of 1 MPa and
 19 at 30 °C to obtain 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one in 95% yield after 10 h [87].
 20 These results are promising to devise new catalyst systems based on earth-abundant and cheap
 21 metals such as Zn.

22

1 4.2 Organocatalysts

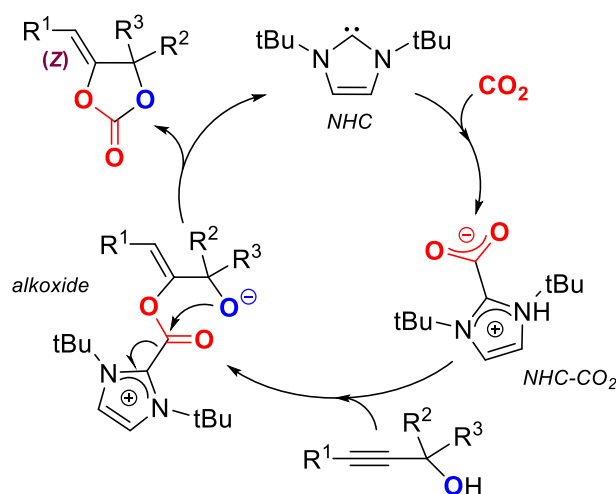
2 As CO₂ prevalently behaves as an electrophile, strong Lewis bases based on nitrogen
3 heterocycles have the potential to activate CO₂ affording zwitterionic adducts. Thus, such
4 organocatalytic promoters can be utilized as convenient and cheap CO₂ transformers to
5 accomplish its conversion by increasing its nucleophilic character. **N-Heterocyclic** carbenes
6 (NHCs) incorporating electron-donating heteroatoms have a strong basic character and this
7 enables strong σ -donor ability of the NHC useful for CO₂ activation. Imidazolium-2-
8 carboxylates (with the integrated CO₂ molecule in an activated state) have been
9 spectroscopically and structurally identified as NHC–CO₂ adducts. Ikariya and co-workers [88]
10 prepared NHCs (1,3-dialkylidazol-2-ylidenes) and their corresponding CO₂ adducts (1,3-
11 dialkylimidazolium-2-carboxylates), and employed them as efficient catalysts for cyclic
12 carbonate synthesis using propargylic alcohols and CO₂.

13 **The NHC–CO₂ adducts showed comparatively** superior activity under milder conditions
14 than the NHCs themselves, which required supercritical conditions to obtain good results for
15 the conversion of 2-methyl-3-propyn-2-ol in the carboxylative cyclization with CO₂ to form the
16 corresponding cyclic carbonate. Under solvent-free conditions at 4.5 MPa CO₂ and 60 °C,
17 various NHC–CO₂ adducts, prepared by variation of the N–substituents (di-isopropyl, di-tert-
18 butyl, diaryl) were tested for their catalytic activity. The NHC–CO₂ adduct 1,3-di-tert-
19 butylimidazolium-2-carboxylate gave the best yield (99%) for the cyclic carbonate product
20 among the adducts tested. **If** the catalyst loading, CO₂ pressure and/or temperature were
21 lowered, a significant amount of an acyclic product (1,1-dimethyl-2-oxo-propyl-1',1'-
22 dimethyl-2'-propynyl carbonate) was obtained along with the desired cyclic carbonate. The
23 carboxylative cyclization affording the cyclic carbonate and the subsequent addition of another
24 propargylic alcohol to the product is thought to lead to this 2:1 coupling product of both
25 substrates.

26 Various five-membered cyclic carbonates were prepared in good yields from different
27 propargylic substrates having disubstituted alkyne groups using the NHC–CO₂ catalyst. The
28 presence of electron-withdrawing groups conjugated to the triple bond in the substrate led to
29 the targeted products in faster rates and at lower reaction temperatures. The NHC–based catalyst
30 also tolerates propargylic substrates equipped with heterocycles such as pyridine and thiophene,
31 whereas *allylic* compounds such as 2-methyl-3-buten-2-ol and 2-methyl-4-phenyl-3-buten-2-ol
32 did not **give** any cyclization product. In each product, the C=C double bond was found to have
33 a (Z)-configuration, indicating that the addition of the NHC–carboxylate to the alkyne fragment

1 proceeded predominantly in an *anti* fashion. The postulated mechanism for the NHC–CO₂
 2 mediated carboxylative cyclization of propargylic alcohols and CO₂ involves the nucleophilic
 3 addition of the imidazolium-2-carboxylate to the C≡C triple bond and subsequent
 4 intramolecular cyclization of the alkoxide intermediate (Scheme 15). A significant positive
 5 effect of electron-donating *N*-alkyl substituents present in the NHC structure implies that the
 6 intramolecular nucleophilic attack of the CO₂ moiety, once bound to the NHC, onto the
 7 substrates may be rate-limiting step in this catalytic cycle.

8



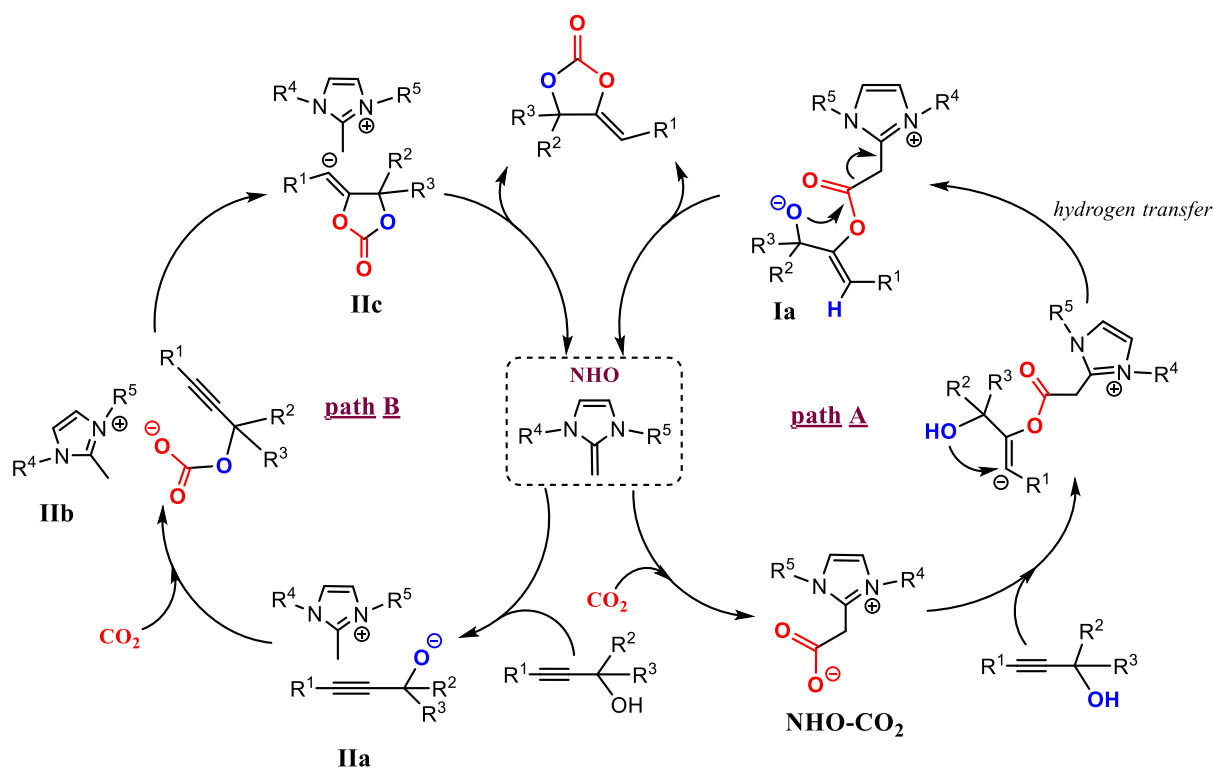
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10 **Scheme 15** Mechanism of the carboxylative cyclization catalyzed by a NHC–CO₂ adduct [88]

11

12 **N-Heterocyclic olefins** (NHOs) are compounds that are capable of further stabilizing the
 13 positive charge that arises upon activation of CO₂ due to aromatization of the heterocyclic ring
 14 thereby making the terminal carbon atom of the initial olefin group more electronegative and
 15 susceptible towards the activation of electrophilic reaction partners. Recently, Lu *et al.* [89]
 16 prepared various NHO–CO₂ adducts and employed them as catalysts for coupling of
 17 propargylic alcohols and CO₂ to yield α -alkylidene carbonates. For comparative reasons, NHC–
 18 CO₂ adducts were also prepared and *in situ* decarboxylation experiments monitored by IR
 19 spectroscopy in CH₂Cl₂ at 40 °C revealed that decarboxylation of the NHO systems occurred
 20 within 2 h, whereas only small amounts of NHC adducts decomposed under similar conditions.
 21 This demonstrates that the decarboxylation of NHO–CO₂ adducts is relatively easy and
 22 therefore of more practical use for cyclic carbonate synthesis. The relatively poor thermal
 23 stability of NHO–CO₂ adducts therefore offers an opportunity to use these compounds as active
 24 catalysts for CO₂ transformations at low temperature. In the catalyst activity screening phase,

1 2-methyl-4-phenylbut-3-yn-2-ol was chosen as a model substrate and reacted with CO₂ at 2
 2 MPa pressure and 60 °C for 12 h. Among the various NHO-CO₂ adducts, the isopropyl-
 3 substituted NHO-CO₂ adduct showed the best results leading to a 93% isolated yield of the
 4 cyclic carbonate. The difference in catalytic activity observed for the NHO-CO₂ adduct in
 5 comparison with its corresponding NHC-CO₂ was established for various propargylic
 6 substrates, and typically the NHO adducts are about 10–100 times more active than their NHC
 7 analogues. Various terminal and internal propargylic alcohols smoothly underwent the
 8 carboxylative cyclization reaction and were converted into their corresponding α -alkylidene
 9 cyclic carbonates in moderate to excellent yields. Apparently only a slight structural difference
 10 exists between the NHO and NHC adducts; the much higher reactivity for the NHO-CO₂
 11 adducts was tentatively ascribed to the lower stability of the C_{carboxylate} – C_{NHO} bond.



12
 13 **Scheme 16** Proposed mechanism of the carboxylation reaction catalyzed by the NHO-CO₂
 14 adduct [89]

15
 16 The proposed mechanistic manifold begins with the zwitterionic compound NHO-CO₂ that
 17 adds to the triple bond of propargylic substrate through nucleophilic attack. Meanwhile,
 18 hydrogen transfer of alcohol generates the new zwitterion **Ia** (Scheme 16, path A), and then the
 19 alkoxide anion attacks the carboxylate carbon to release the desired product and regenerating

1 the NHO, which rapidly captures free CO₂ to form the NHO–CO₂ adduct to induce further
2 turnover. The higher thermal instability of the NHO–CO₂ adducts favorably adds to the overall
3 kinetics of the reaction, thus creating higher turnover at lower temperatures as compared with
4 the reactivity of analogous NHC–CO₂ adducts. The NHO with increased electronegativity at
5 the terminal carbon atom can also act as a Brønsted base able to abstract a proton from the
6 propargylic alcohol to form the intermediate **IIa** (path B) which subsequently reacts with CO₂
7 to give intermediate **IIb** (Scheme 16, path B). Subsequently, the intermediate **IIc** is obtained
8 by intramolecular ring-closure within intermediate **IIb**, which abstracts a proton from the 2-
9 methyl imidazolium cation to release the desired product. The obvious difference between both
10 pathways A and B is that the hydrogen at the alkenyl position of cyclic carbonate originates
11 exclusively from the propargylic substrate (path A) or both substrate and catalyst (path B): this
12 aspect may be elucidated by a proper labeling of the NHO and/or propargylic substrate.

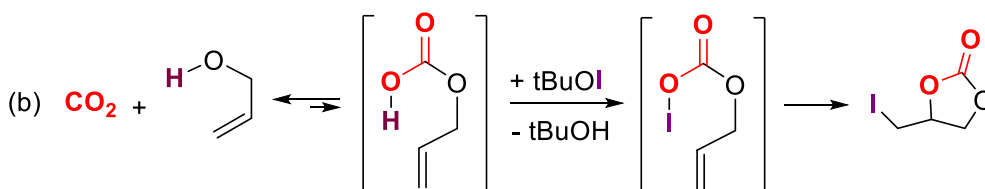
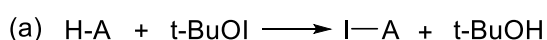
13 The same group also prepared various CO₂ adducts of alkoxide-functionalized imidazolium
14 betaines (abbreviated as AFIBs) and explored the AFIB–CO₂ adducts as effective
15 organocatalysts within the context of carboxylative cyclization of propargylic alcohols with
16 CO₂ [90]. The best result (97% yield) for the AFIB–CO₂ mediated formation of the cyclic
17 carbonate product was obtained under 2 MPa pressure at 60 °C using 2-methylbut-3-yn-2-ol as
18 substrate. The catalyst system proved to be more effective for the carboxylative cyclization of
19 terminal rather than internal propargylic substrates.

20 Minakata *et al.* [91] treated various allylic alcohols with stoichiometric *t*BuOI under 0.1 MPa
21 of CO₂ pressure and low reaction temperature resulting in the synthesis of five-membered cyclic
22 carbonates containing a potentially useful alkyl iodide group. The reagent, *t*BuOI, can be readily
23 prepared *in situ* from commercially available *tert*-butyl hypochlorite (*t*BuOCl) and sodium
24 iodide (NaI), and serves to iodinate an elusive and rather unstable alkyl carbonic acid that is
25 first generated from CO₂ and an unsaturated alcohol. The introduction of the iodine atom
26 radically changes the position of the equilibrium of the initial CO₂-trapping reaction (Scheme
27 17). The use of tetrahydrofuran (THF) as solvent and a reaction temperature of –20 °C resulted
28 in the conversion of prop-2-en-1-ol into the corresponding cyclic carbonate in 92% yield. To
29 further investigate the efficacy of *t*BuOI, other iodinating reagents such as bis(pyridine)iodine
30 tetrafluoroborate (IPy₂BF₄), *N*-iodosuccinimide (NIS), I₂ and a combination of I₂ and
31 triethylamine were tested, but all these reagents failed to provide the desired product.

32 The main reason for *t*BuOI being the most appropriate iodinating reagent is related to the
33 liberation of a relatively weak acid (*i.e.*, *t*BuOH) during the reaction of allyl-carbonic acid and

1 *t*BuOI. β -Branched allylic alcohols also could be smoothly transformed into their corresponding
 2 cyclic carbonates in good yields. Both (*E*)- and (*Z*)-allylic alcohols were transformed into their
 3 corresponding cyclic carbonates. Allyl alcohols containing rigid cyclic olefins, hydroxyl, ester
 4 or silyl groups, and homo-allylic alcohols allowing the formation of six-membered cyclic
 5 carbonates were also compatible with this CO₂ conversion reaction. Similarly, various internal
 6 propargylic alcohols reacted with CO₂ under similar conditions and permitted the synthesis of
 7 the corresponding iodoalkyl derived carbonates in good yields.

8



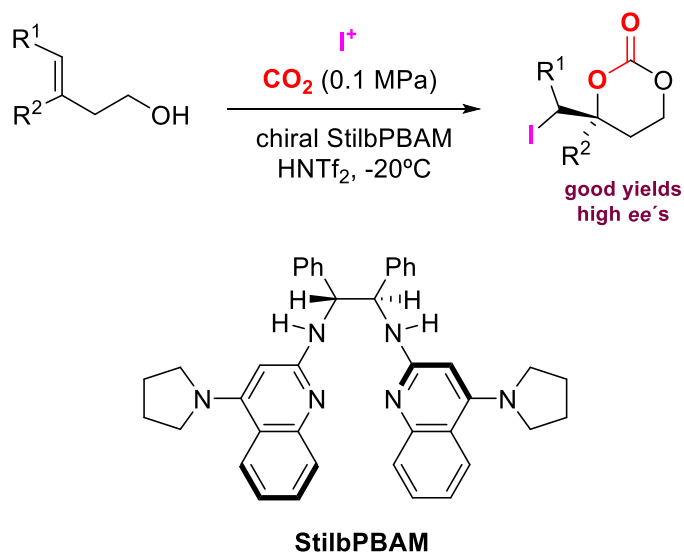
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10 **Scheme 17** (a) Reaction of tert-butyl hypoiodite with weak acids. (b) Strategy for trapping
 11 carbonic acids with tert-butyl hypoiodite [91]

12

13 Recently, an efficient carboxylation/alkene functionalization reaction of homoallylic alcohols
 14 was reported by Johnston *et al.* to produce chiral cyclic carbonates (Scheme 18) [92] using an
 15 approach similar to the one reported by Minakata (*vide supra*). At low temperatures and
 16 ambient pressure, a toluene solution of 3-phenylbut-3-en-1-ol was treated with CO₂/*N*-
 17 iodosuccinimide in the presence of various bases including NaH, DBU, TBD, DMAP as well
 18 as hydrogen bond donors such as TFA and thiourea but these conditions failed to deliver the
 19 desired carbonate product or gave only rise to low yields. A Brønsted acid/base combination
 20 was then explored to promote the reaction and the use of a chiral pyrrolidine-substituted
 21 bis(amidine) gave a promising 18% yield of the iodinated cyclic carbonate in 39% *ee*. An
 22 analogous catalyst incorporating *trans*-stilbene diamine (StilbPBAM; Scheme 18) instead of
 23 *trans*-cyclohexane diamine provided the product in 33% yield and 36% *ee*. Exploration of
 24 strong Brønsted acid additives (HNTf₂) (1 equiv) combined with the StilbPBAM organocatalyst
 25 enhanced the activity to provide a 95% yield (91% *ee*) in the presence of molecular sieves (4
 26 Å). Combined, the results suggest an important role for hydrogen-bonding in the key
 27 selectivity-determining step, and a unique reactivity associated with the proper mutual
 28 positioning of the Brønsted acid and base in the relevant transition state that controls the

1 asymmetric induction. Various other substituted styrene homoallylic alcohols were also tested:
2 β -naphthyl substituted anisole derivatives (*meta*- and *para*-substituted), and halogen substituted
3 substrates were all converted into their six-membered carbonates with excellent
4 enantioselectivity and in good yields, whereas substitution near the alkene moiety was not
5 tolerated and no conversion was noted in these cases.



6

7 **Scheme 18** An enantioselective method for the synthesis of cyclic carbonates from homoallylic
8 alcohols and CO₂ using a chiral StilbPBAM organocatalyst [92]

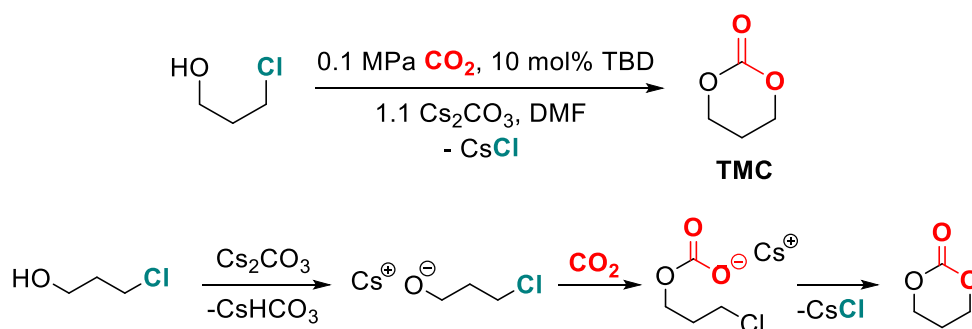
9

10 5. Cyclic Carbonates from Halo-Alcohols

11 Another approach for the preparation of cyclic carbonates from CO₂ could be the use of
12 halohydrins (haloalcohols) as potential starting substrate in presence of a base. The obvious
13 drawback of this approach is the stoichiometric amount of halide waste that is produced
14 alongside, but in certain cases it may provide an alternative if other methods fail to deliver the
15 desired organic carbonate structure.

16 Using PEG-400 as an environmentally friendly solvent and K₂CO₃ as an easily accessible
17 base, various cyclic carbonates (yield 72-100%) were prepared by the group of Wu starting
18 from vicinal halohydrins such as chlorohydrin, bromohydrin, and phenyl and alkyl-substituted
19 halohydrins at low CO₂ pressure (2 MPa) and temperature (50 °C) [93]. The choice of PEG-
20 400 as a reaction medium is beneficial in terms of solvation of the potassium cation to increase
21 the basicity of K₂CO₃, an increase in CO₂ concentration in this specific medium accelerating
22 the reaction, and the ease of product separation. Similarly, Zhang and co-workers [94] reported

1 on the utilization of 1.1 equiv. of Cs₂CO₃ as base, obtaining both five- and six-membered cyclic
 2 carbonates in good to excellent yield under relatively mild conditions (40 °C under 0.1 MPa
 3 CO₂, Scheme 19). By variation of different solvents and bases, the optimal conditions were
 4 determined (Cs₂CO₃, DMF) and the haloalcohol substrate 3-chloro-1-propanol reacted
 5 efficiently with CO₂ giving 95% yield of trimethylene carbonate (TMC). One advantage of this
 6 method, which seems a general approach if the haloalcohol is readily available, is the easy
 7 formation of larger-ring size cyclic carbonates which remains a synthetic challenge in the area
 8 of organic carbonates. The mechanism of this reaction is pretty straightforward with the Cs₂CO₃
 9 first deprotonating the alcohol resulting in the formation of a cesium alkoxide. The latter in turn
 10 reacts with CO₂ to form a carbonate intermediate which in the final step undergoes an
 11 intramolecular ring closing reaction affording CsCl as a byproduct and TMC.



14 **Scheme 19** Reaction manifold for the formation of TMC using 3-chloro-1-propanol as the
 15 starting material and Cs₂CO₃ as base [94]

16

17 Even more recently, Buchard and coworkers developed a related protocol for the formation
 18 of six-membered cyclic carbonates starting from 1,3-diols at low (0.1 MPa) CO₂ pressure and
 19 using DBU [95]. The procedure involves the activation of both the alcohol functions of the
 20 substrate by tosyl chloride and DBU allowing the *in situ* formation of a *pseudo* haloalcohol.
 21 This intermediate is then easily converted in the presence of NEt₃ to the desired cyclic
 22 carbonate. DFT analysis revealed that the mechanism most likely goes through an
 23 addition/elimination sequence with intermediate formation of a tosylated carbonate species, and
 24 subsequent attack of the other activated alcohol (by NEt₃) onto this carbonate fragment
 25 releasing the product with retention of configuration as was indeed experimentally observed for
 26 various chiral substrates. As for the aforementioned methodologies, stoichiometric amounts of

1 DBU-HCl and TsOHNEt₃ are produced, and some optimization regarding the atom-economy
2 will still be required.

3

4 **6. Conclusions and Outlook**

5 This overview of the latest developments in the area of cyclic carbonate synthesis from alcohol
6 substrates and CO₂ shows several advances made over the last 5–10 years with a major focus
7 on the more recent achievements. Since the direct conversion of alcohols in the presence of CO₂
8 is thermodynamically limited and only low equilibrium yields can be attained, several catalytic
9 processes have been developed to circumvent this issue by using dehydrating agents. This
10 approach has resulted in the high yield synthesis of both cyclic as well as acyclic carbonates in
11 good yields, though a crucial feature to optimize remains the regeneration of the dehydrating
12 species. If this agent can be efficiently recycled then such a process would be extremely useful
13 for larger scale preparation of carbonates, and commercial exploitation. Apart from bypassing
14 the thermodynamic limitations, other approaches that use more functional substrates such as
15 propargylic alcohols have also been proven to be effective, and the carboxylative cyclization
16 reaction is now a valuable tool in organic synthesis. Similar types of activation protocols where
17 the initial alcohol function can first react with CO₂ to form a linear carbonate followed by
18 intramolecular attack onto a pre-activated alkyne fragment would be welcome in order to design
19 new conversions and amplify the role of mono- and polyalcohols as suitable platform molecules
20 in organic synthesis. Several useful protocols towards five- and six-membered carbonate
21 synthesis in the presence of stoichiometric amounts of often simple and cheap reagents have
22 already been developed. However, to answer to ever-growing need for more sustainable
23 manufacturing of bulk and fine chemicals, new catalysis protocols are warranted to address this
24 feature more effectively. Thus it seems that the combination of (poly)alcohols and CO₂ as
25 reaction partners will continue to inspire scientists to work on greener and more sustainable
26 catalytic methods for the production of carbonated compounds that will find use in areas diverse
27 as bulk, polymer and pharmaceutical chemistry.

28

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