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Photochemical and Substrate-Driven CO_2 Conversion

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1.1 Introduction

The use of carbon dioxide (CO_2) as a raw material in molecular science has been the subject of many investigations. Obviously, the replacement of fossil fuel-based chemistries with those primarily based on CO_2 cannot alleviate the challenges we are facing in terms of global carbon emissions and managing the carbon cycle. However, new technologies that can help to partially replace the nonsustainable feedstock into renewable and widely available ones will help to transition to a circular rather than a linear economy [1]. In this regard, technologies encompassing the use of catalysts have demonstrated that the valorization of CO_2 is feasible, offering many opportunities in the areas of organic [2–5], polymer [6–8], and fuel-based chemistries [9, 10].

The use of CO_2 as a reagent in nonreductive coupling reactions (i.e. after integrating the CO_2 molecule into an organic substrate, the oxidation state of the carbon center, +4, remains unchanged) has been prominent in the wider area of CO_2 catalysis. In this respect, the [3 + 2] cycloaddition reaction of CO_2 and epoxides [11–15], and to a minor extent oxetanes [16, 17], has been among the most widely studied transformations. Conventionally, the formation of cyclic carbonates is carried out using phosgene as a reagent (Figure 1.1a), and obviously, finding more sustainable alternative routes has been the subject of intense studies over the past 20 years. Substantial progress has been noted in the synthesis of cyclic carbonates and the required catalysts for these [3 + 2] cycloaddition reactions, and nowadays, a variety of epoxides including terminal [18–20] and the more challenging internal ones with multiple substituents can be readily utilized (Figure 1.1b) [21–28]. Notwithstanding, there are still important issues to resolve in order to further advance the sustainability of these kinds of nonreductive CO_2 conversions in terms of reaction conditions (preferably using ambient conditions) [29, 30], catalyst structures (preferably halide-free ones) [31], and expansion of

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the portfolio of cyclic carbonate compounds by using conceptually different approaches [32, 33].

Recently, various halide-free methodologies have been reported (Figure 1.1c) [31, 34–40], which are important to reduce both operational cost and corrosion issues where typical binary catalyst systems (i.e. a combination of a Lewis acidic complex and a halide additive) are used. For instance, North and coworkers used a bimetallic, O-bridged Al(III)salen complex that is able to induce insertion of CO_2 into one of the Al—O bonds, thereby forming an Al- carbonate intermediate [34]. This nucleophilic species further engages with the epoxide substrate to induce ring opening to eventually give the cyclic carbonate product essentially in the absence of any cocatalytic halide. In a more recent contribution, the same authors reported the use of a bis-phenol-type salen organocatalyst that is able to induce formation of cyclic carbonates from terminal epoxides and CO_2, albeit at rather elevated reaction temperatures [35]. This work nicely builds on previous success in this area using multiphenolic (binary) organocatalysts as effective systems for cyclic carbonates derived from internal and terminal epoxides [41, 42]. Replacing salen diphenol with other types of H-bond activators such as a combination of DBU/L-histidine (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) also enables a halide-free synthesis of these CO_2-based heterocycles [36]. The design of other halide-free systems (with this particular design characteristic although still in its early stage) clearly demonstrates a shift toward the use of more sustainable catalysts in the valorization of CO_2 into cyclic carbonates.

What should be the next step in the development of efficient catalysts for cyclic carbonate products (Figure 1.1d)? The recent literature testifies that the use of cyclic carbonates and related precursors to build more complex molecules [43–45] can only be carried out if the former can be prepared with a certain degree of substitution and functionality. Therefore, new approaches are desirable that can meet the growing need for a larger diversity in cyclic carbonate scaffolds amplifying their role as key substrates in a much wider variety of transformations compared to the recent state of the art. This chapter will thus focus on two rather new developments in the area, viz. the photochemical assisted conversion of CO_2 into cyclic carbonates/carbamates and related

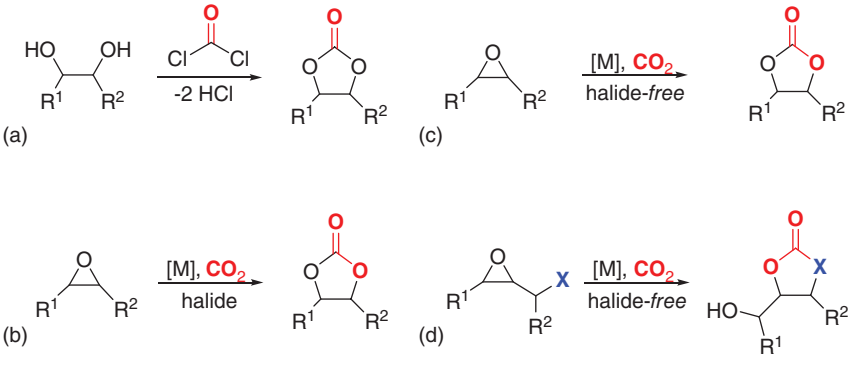


Figure 1.1 Evolution of the (catalytic) synthesis of cyclic carbonates and future perspective discussed in this chapter. (a) Conventional, (b) contemporary, (c) recent, and (d) current.

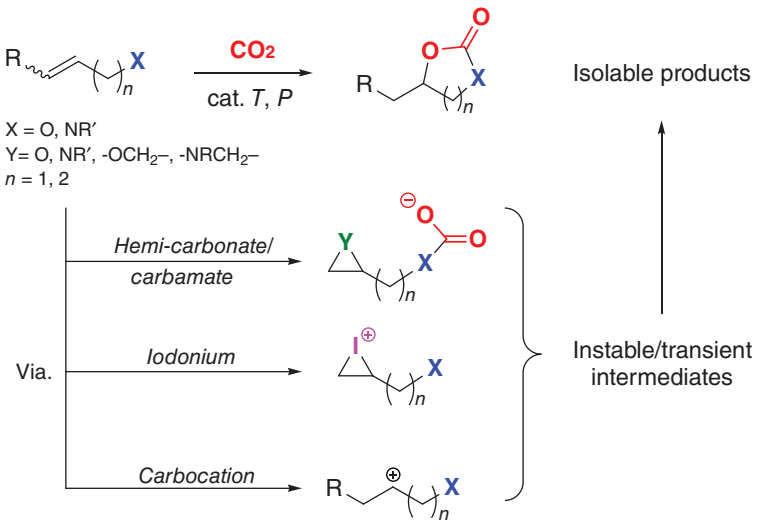


Figure 1.2 Different approaches to arrive at cyclic carbonates using functional (homo)allylic precursors and various substrate-involved activation strategies.

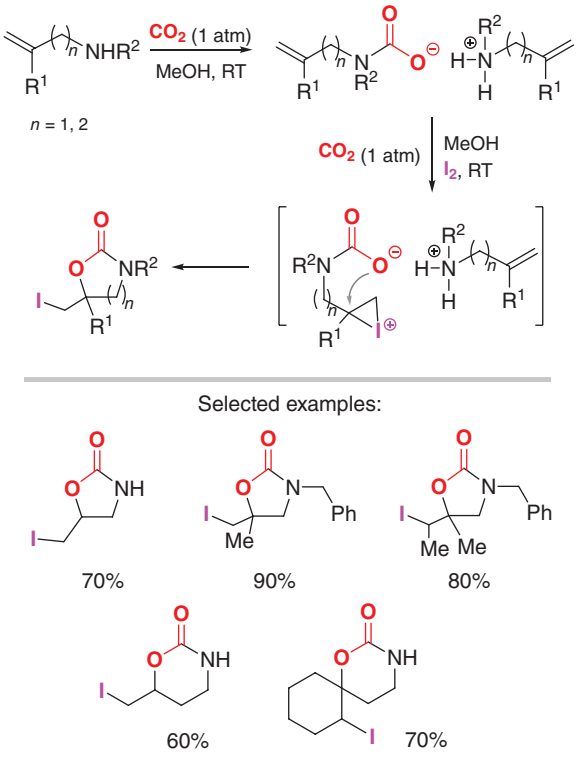
heterocycles and the use of substrate-triggered CO_2 conversion as efficient and novel strategies affording the heterocyclic targets through different manifolds and reactive intermediates (Figure 1.2). Apart from the main characteristics of the involved protocols, relevant details encompassing the key mechanistic intermediates will also be highlighted.

1.2 Iodine Activation of (Homo)Allylic Substrates

Molecular iodine (I_2) is one of the most widely used iodinating reagents and particularly readily forms reactive iodonium species with alkenes that can afford various addition products in the presence of suitable nucleophiles [46]. Recently, various research groups have used I_2 or other electrophilic I-containing reagents in reactions that utilize CO_2 and comprise of a formal addition of an activated form of CO_2 (typically being a carbonate/carbamate intermediate) to I^+-activated double bonds present within the same substrate.

The first synthesis to use electrophilic, I^+-directed double bond activation in the formation of either five- or six-membered cyclic carbamates (i.e. oxazolidinones and oxazinones) from CO_2 and (homo)allylic amines follows a well-known strategy that has been previously used for the synthesis of linear and cyclic carbamate derivatives by Yoshida and Saito, respectively [47, 48]. The approach reported by Toda et al. [49] starts with the *in situ* formation of ammonium carbamate salts from allylic amines and CO_2 at atmospheric pressure and temperature (Scheme 1.1). After the formation of ammonium carbamate, iodine is added to presumably form an iodonium intermediate, after which intramolecular cyclization by addition of the carbamate onto the activated allylic double bond results into an oxazolidinone product. The use of homoallylic substrates affords

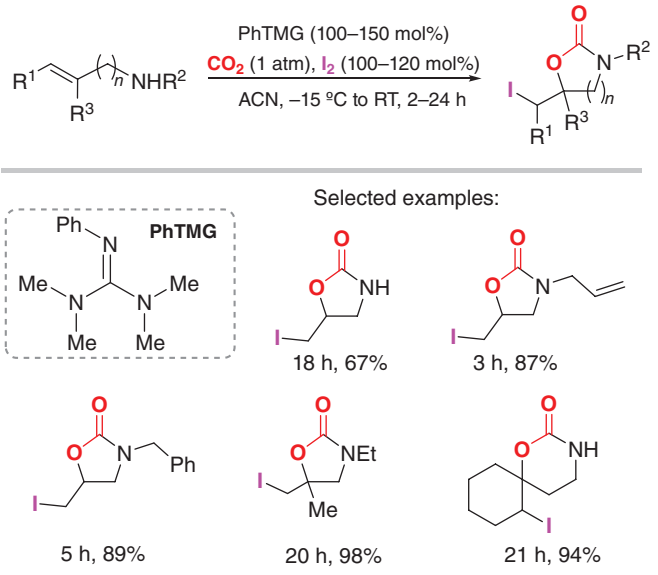
six-membered oxazinones in a similar manner (Scheme 1.1). Both primary and secondary amines were used, but the yields of the heterocyclic products were moderate. Improved yields of the products were achieved by long reaction times and a stoichiometric amount of cesium carbonate.



Scheme 1.1 Approach to five- and six-membered heterocycles using CO_2 as a reagent and I_2 as an olefin activator. Reported yields are those in the presence of Cs_2CO_3 as an additive.

Later, Muñoz and coworkers developed a similar methodology for the synthesis of five- and six-membered cyclic carbamates using (homo)allylic amines, CO_2, I_2, and a guanidine base (2-phenyl-1,1,3,3-tetramethylguanidine, PhTMG), see Scheme 1.2 [50]. The utilization of this non-nucleophilic and strong base led to higher yields and significantly shortened reaction time compared to the work by Toda. The authors propose that PhTMG does not only act as a base but also stabilizes the intermediate carbamate anions. In addition to this, and as may be expected, the regioselectivity of the carbamate attack onto the I-activated double bond follows a preference for smaller sized ring heterocycles, i.e. five-membered carbamates are produced from allylic amine precursors, whereas six-membered products are formed from homoallylic substrates. In most of the reactions studied, addition of the carbamate to the double bond takes place in an *anti*-manner, thereby locking the final stereochemistry of the heterocyclic product. This was shown by elimination reactions induced by Ag_2O and analyzing the

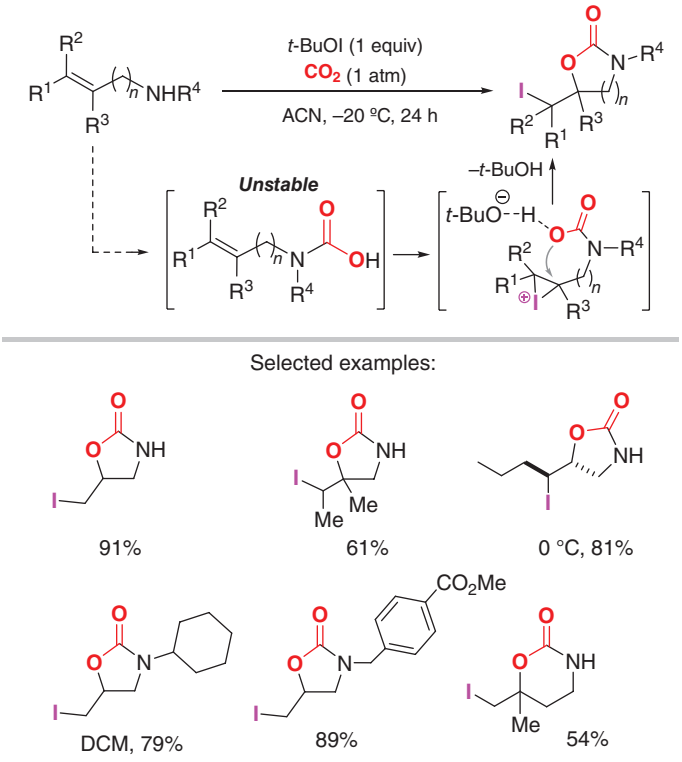
resultant alkene products by nuclear Overhauser effect (NOE) NMR spectroscopy or in some of the cases by crystallographic analysis. The same authors also included chiral substituents on the amine, in order to study if enantioenriched oxazodilinones could be prepared [51]. However, it was shown that these reactions do not undergo a stereoselective pathway thus forming two possible diastereoisomers without a significant preference for either one. Despite this, if a chiral substituent was used on the amine, the two diastereomers could be separated, resulting in the enantiopure products.



Scheme 1.2 PhTMG-mediated formation of five- and six-membered cyclic carbamates.

The methods described thus far use allylic amines for the synthesis of cyclic carbamates with I_2 being a key (stoichiometric) reagent to deliver the heterocyclic products. Minakata et al. showed that by changing the iodine source to *tert*-butyl hypoiodite (*t*-BuOI, a cheap and easily accessible compound obtained *in situ* from *t*-BuOCl and NaI) as reported by Potter and coworkers [52], the use of strong bases can be avoided, and good yields of cyclic carbamates were reported for transformations of allylic, homoallylic, and propargylic amines (Scheme 1.3) [53]. The specific advantage of using *t*-BuOI is that after the formation of the iodonium ion, the remaining $t\text{BuO}^-$ can deprotonate the acidic hemi-carbamate, thereby shifting the equilibrium from the side of the allylic amine/CO_2 toward the linear carbamate, which can subsequently cyclize to form the product. Importantly, when using *t*-BuOI, the reactions readily occur, even at –20 °C and 1 atm CO_2.

The group of Cardillo was the first to describe the use of CO_2 for the synthesis of cyclic carbonates from allylic and homoallylic alcohols [54]. They used a strong base (*n*-BuLi) to generate the corresponding lithium alkoxide, and this strong nucleophile then activates CO_2 by forming a linear carbonate anion. The addition of I_2 to this *in situ* formed Li-hemi-carbonate salt then leads to formation of

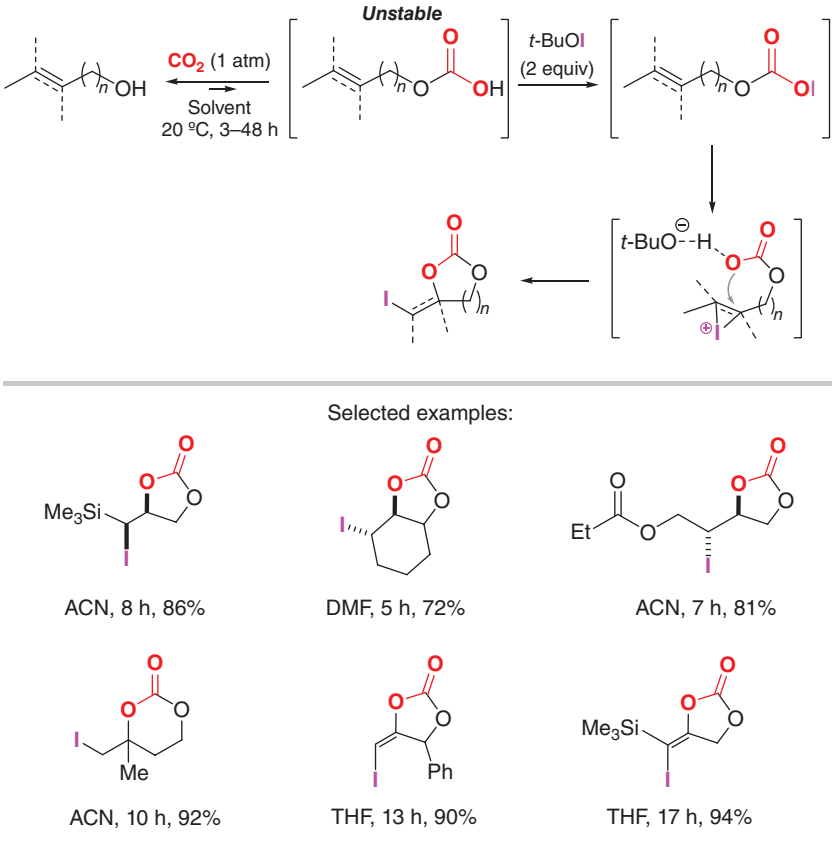


Scheme 1.3 The use of *t*-BuOI as a reagent in the preparation of cyclic carbamates. DCM = dichloromethane.

iodonium, and subsequent cyclization afforded the iodinated cyclic carbonate product. The use of a strong base such as *n*-BuLi is required to stochiometrically form the alkoxide because alcohols do not activate CO_2 with the same effectiveness as amines.

A few years later, Minakata and coworkers described an improved methodology using *t*-BuOI (cf., Scheme 1.4) [55], which obviated the use of I_2/*n*-BuLi. Although the authors mentioned that the reaction mechanism is not clear, they proposed that an intermediate carbonic acid is iodinated and that it is this reactive intermediate that then forms an iodonium ion on the double bond, immediately leading to cyclic carbonate formation [56]. Allylic, homoallylic, and propargylic alcohols all performed well in this manifold and gave access to a wide variety of five- and six-membered cyclic carbonates in good yields. The synthesis of these heterocycles compared with those reported in Scheme 1.3 is more challenging as the initial equilibrium leading to the hemi-carbonate from the (homo) allylic alcohols is much more disfavored.

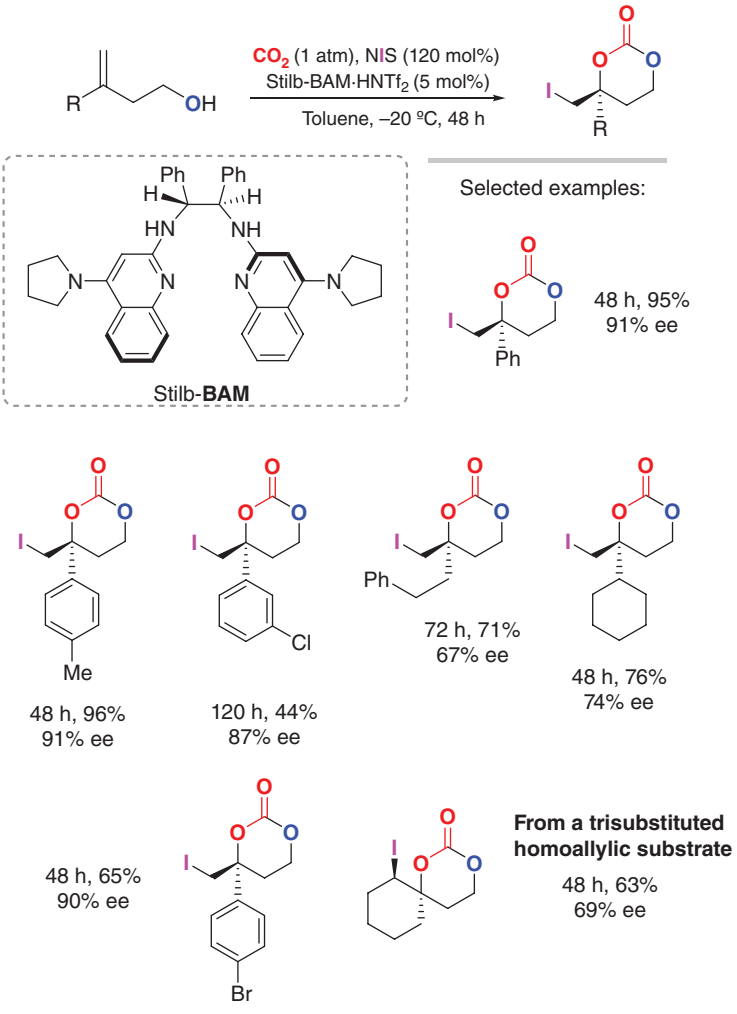
Recently, the potential of these types of transformations was further extended to the enantioselective conversion of homoallylic alcohol precursors into six-membered iodonated cyclic carbonates in high yield and under high



Scheme 1.4 Synthesis of various cyclic carbonates using *t*-BuOI as a reagent under mild reaction conditions, ACN = acetonitrile, THF = tetrahydrofuran.

enantiocontrol (Scheme 1.5) [57]. The presence of a chiral bisamidine (BAM) organocatalyst (Scheme 1.5) and *N*-iodo-succinimide (NIS) was key to provide the carbonate products under mild reaction conditions. This contribution is a rare example of a protocol that enables the asymmetric synthesis of carbonate heterocycles. The envisioned mechanism is thought to involve the BAM organocatalyst and a Brønsted acid ($HNTf_2$) that is able to orientate through H-bonding a preformed hemi-ester of the homoallylic alcohol in the presence of CO_2, which favors an asymmetric cyclization step that follows electrophilic I-mediated activation of the double bond. In the presence of water, a similar H-bonded "complex" among CO_2, H_2O, and the BAM/$HNTf_2$ is formed, which is assumed to compete with productive catalysis forming the cyclic carbonates, and the use of molecular sieves (4 Å) was thus necessary to allow for high product yields. Although most substrates afforded the cyclic carbonates with consistently high ee's, those bearing alkyl substituents (R in Scheme 1.5) gave typically inferior results with ee's around 70%. Substrates with aryl groups

having electron-withdrawing groups such as Cl provided lower yields of product (40–65%). In an attempt to use a substrate having a trisubstituted double bond, the same procedure gave access to the corresponding *spiro*-cyclic carbonate (Scheme 1.5) in 63% yield and with 69% ee.



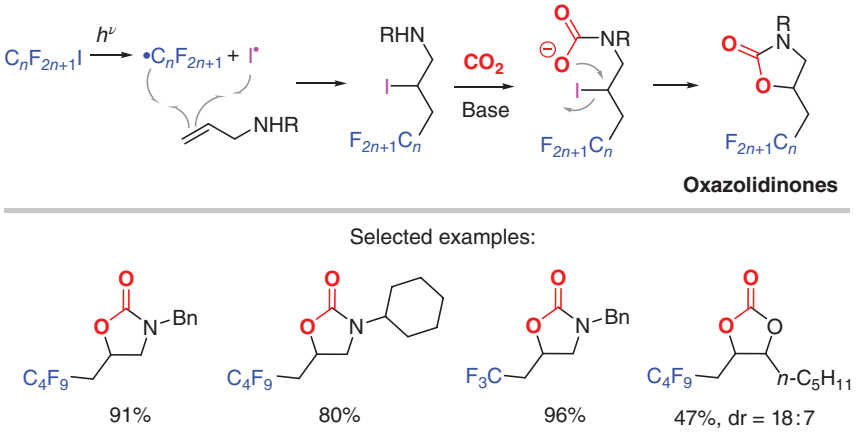
Scheme 1.5 Organocatalytic formation of chiral six-membered cyclic carbonates from homoallylic alcohol substrates.

The results discussed in this section have provided motivation for the development of other protocols that can take advantage over catalytic rather than stoichiometric procedures while contemplating on the use of functional groups within the substrate so as to allow for CO_2 activation and conversion. These approaches, based on photochemical activation and substrate-driven reactivity, will be outlined in the following sections.

1.3 Substrate Activation Via Radical Addition/ Photochemical Oxidation Processes

Analogous to the activation of (homo)allylic alcohols and amines with electrophilic iodine-containing compounds, it was recently reported that it is possible to activate (homo)allylic amines through photochemistry. Common to such reactions is the photochemical or photoredox-mediated generation of radicals that are subsequently added to the double bond of the substrate. Concomitantly, CO_2 is activated through the nucleophilic nitrogen center, followed by ring closure producing the desired heterocyclic product. In contrast to methods using "I^+," photoinduced radical addition pathways allow for the addition of a variety of functional groups affording the target products. Notably, in this manifold, direct introduction of functional fragments can be achieved without the need for an additional S_N2 substitution or a catalytic coupling reaction in order to introduce desired groups on the I-functionalized positions.

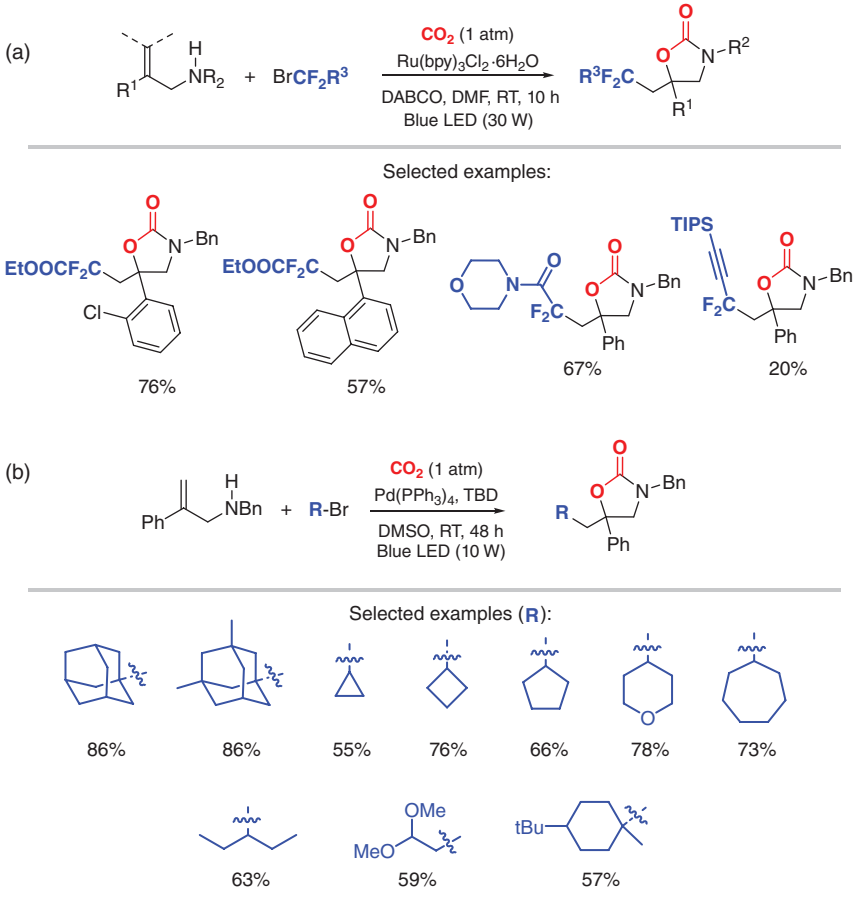
A report by He and coworkers describes the use of perfluoroiodides as a radical source that are directly activated by visible light (>420 nm). Radical addition of both the perfluoroalkyl and iodide radicals to the double bond gave a haloamine intermediate (Scheme 1.6). Subsequent carbamate formation by nucleophilic attack of the amine on CO_2 and S_N2-type cyclization releasing the iodide leads to the oxazolidinone product [58]. Various secondary amines could be transformed with alkyl or (substituted) benzyl substituents. The reaction was further shown to be feasible using different lengths of perfluoroalkyl groups (CF_3, C_3F_7, and C_6F_{13}), and it can even employ secondary and primary alcohols instead of amines to produce five-membered cyclic carbonates. Control experiments excluded a possible aziridine intermediate, as conversion of this compound under catalytic conditions does not occur. An aziridine product, however, is formed in good yield when CO_2 is omitted and the reaction is performed under inert conditions.



Scheme 1.6 Photochemical formation of perfluoroalkyl-functionalized oxazolidinones (n = 1, 3, and 6).

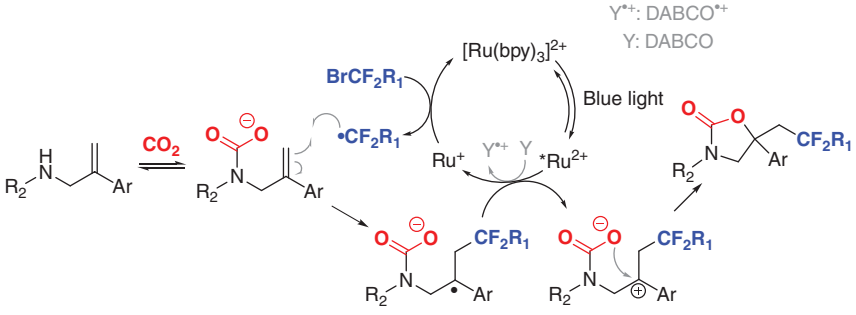
Furthermore, mechanistic studies proved the existence of the iodinated intermediate by both NMR spectroscopy and mass spectrometry [58].

Later, the first photoredox catalytic process was developed. In a report by Yu and coworkers, allylic amines were converted into difluoroalkyl-functionalized oxazolidinones by a photoinduced radical atom transfer pathway (Scheme 1.7a) [59]. The reaction was performed in the presence of the organic base DABCO (1,4-diazabicyclo[2.2.2]octane), photocatalyst $[Ru(bpy)_3]^{2+}$, and 1 atm of CO_2. Although other bases and photocatalysts also allowed for the reaction to proceed, the efficiency was optimal using the aforementioned conditions. In the investigation of the scope of this transformation, it was found that the electron-donating groups on the amine and aryl substituents on the double bond were vital for the success of the reaction, whereas both electron-donating and electron-withdrawing groups on the aryl substituents were tolerated. The reaction was further shown to occur with internal alkenes, homoallylic amines, and β-(aminomethyl)styrenes. It is worth noting that for the latter two cases,



Scheme 1.7 (a) Oxy-difluoroalkylation of allyl amines with CO_2 via Ru-based photoredox catalysis. (b) Conversion of allylic amines into their corresponding oxazolidinones through a Pd-catalyzed photoredox activation pathway reported by Yu et al. TIPS = triisopropylsilyl.

six-membered oxazinanones were produced. Furthermore, various difluoroalkylation agents could be employed, providing useful synthetic building blocks for medicinal chemistry, where difluoroalkyl substituents are used as inert substitutes for carbonyl groups. As for the previous example, control experiments showed that an aziridine intermediate is unlikely, as it does not convert to the oxazolidinone product under the optimized reaction conditions, although it is the main product when allyl amine is converted in the absence of CO_2. The reaction instead occurs through a radical addition to the double bond, subsequent oxidation to a carbocation, followed by ring closure as supported by radical trapping with TEMPO [2,2,6,6-tetramethylpiperidin-1-yl)oxyl] or BHT (2,6-di-*tert*-butyl-4-methylphenol) as well as radical clock controls (Scheme 1.8).



Scheme 1.8 Proposed mechanism for the formation of difluoroalkyl-substituted oxazolidinone . The reaction is proposed to go through a reductive quenching pathway, initially by oxidation of DABCO but later also by oxidation of the benzylic radical. R_1 = COOEt, $CONEt_2$, $P(O)(OEt)_2$, C≡CH, etc.; R_2 = Bn and *n*-Bu; and Ar = Ph, naphthyl, and substituted aryl.

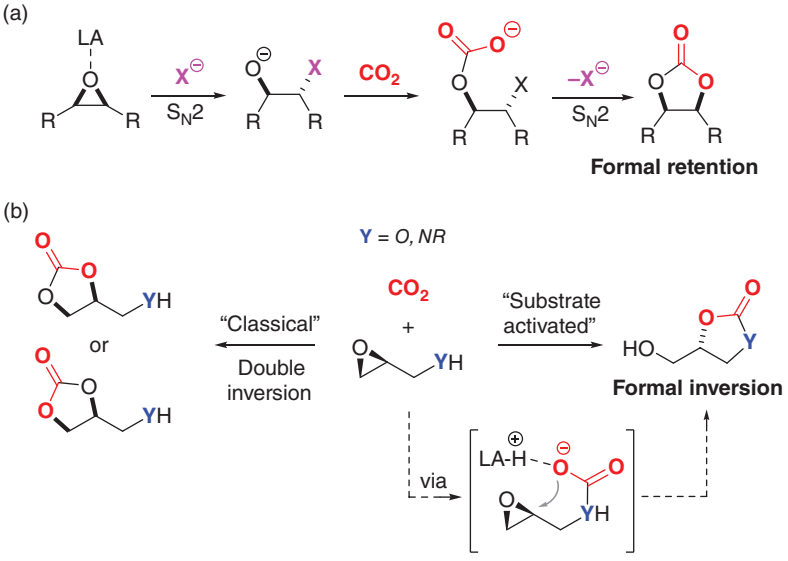
Next, the photoactivated $Pd(PPh_3)_4$ catalyst was investigated to be able to add unactivated alkyl bromides to allyl amines. In two separate reports by the groups of Yu and coworkers [60] and Cheng and coworkers [61], this strategy was used to generate alkyl-substituted five-membered and six-membered cyclic carbamates, respectively (Scheme 1.7b). The reactions worked best in polar aprotic solvents such as DMF and DMSO and required a strong organic base such as TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). Primary, secondary, and tertiary bromides could be used as radical precursors and activated only by $Pd(PPh_3)_4$ in the presence of light for the reaction leading to five- or six-membered carbamates, respectively; other photocatalysts, such as $[Ru(bpy)_3]^{2+}$ or $[Ir(ppy)_3]$, or palladium species, such as $Pd(OTf)_2$, $Pd_2(dba)_3$, or $[Pd(dppf)Cl_2]$, were ineffective.

The scope of alkyl bromides (Scheme 1.7b) further included substrates with synthetically useful groups such as *N*-Boc or acetals. For the amine substrate, both electron-withdrawing and electron-donating groups on the aryls were tolerated. As before, the reaction mechanism was scrutinized using several control experiments (radical trapping and aziridine intermediate exclusion) and the authors concluded a similar mechanism as postulated previously, i.e. alkyl-radical formation, subsequent addition of the radical to the double bond,

formation of the benzyl cation, and finally ring closure [60, 61]. Although it is likely that the Pd-catalyst is involved in more steps than just single-electron transfer and radical formation, it was not considered in the proposed mechanism by the authors.

1.4 Substrate-Induced Activation of Oxiranes

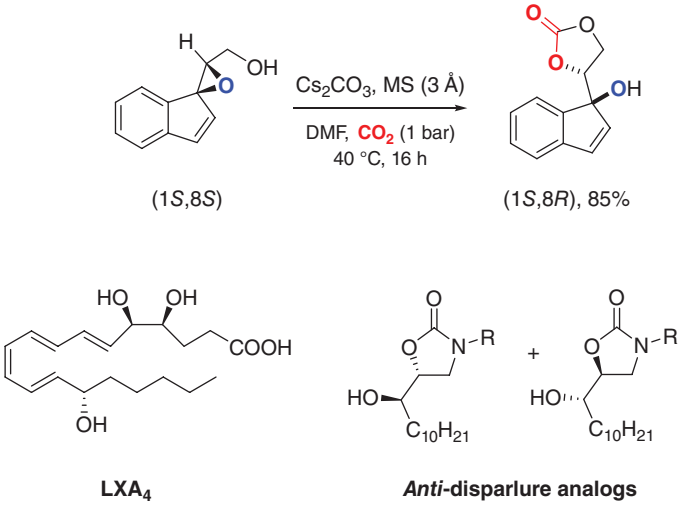
Oxiranes, or epoxides, are generally synthesized by oxidation of carbon–carbon double bonds. When such an oxidation is performed by molecular oxygen, the transformation is considered green and sustainable [62]. The [3+2] cycloaddition of CO_2 to oxiranes under the influence of Lewis acids and cocatalytic halides (also known as binary catalysts) is well known and leads to the formation of five-membered cyclic carbonates with typical retention of stereochemistry (Scheme 1.9a) [63, 64]. However, oxiranes with pending functional groups that react directly with CO_2 such as alcohols or amines can lead to a different mechanism. In such a transformation, CO_2 is activated by the pending group to give a linear hemi-carbonate species that in turn performs an intramolecular attack to open the epoxide and forming a cyclic carbonate with inversion of stereochemistry (Scheme 1.9b).



Scheme 1.9 (a) Classical mechanism for the [3+2] cycloaddition of CO_2 to epoxides catalyzed by Lewis acids (LA) and halides (X). (b) Alternative pathway of cyclic carbonate formation from epoxy alcohols through the intermediacy of a hemi-carbonate species.

The first example of such a strategy was reported in 1988 in the formation of cyclic carbonates from epoxy alcohols using (sub)stoichiometric amounts of Cs_2CO_3 as the base to deprotonate the alcohol group [65, 66]. Notably, no nucleophilic halide catalysts nor Lewis acids were needed for these reactions to occur. Later on, this method found application in the total synthesis of lipoxin

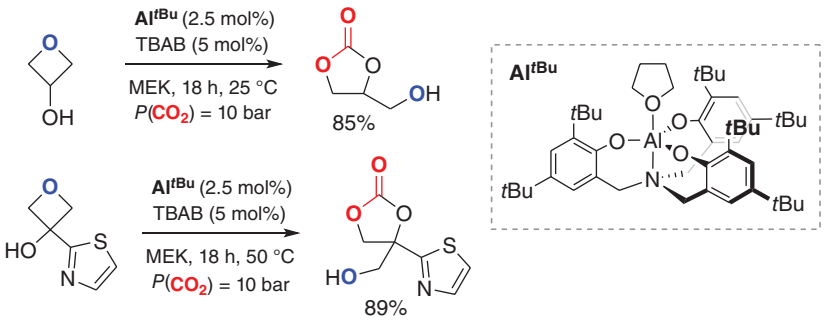
derivatives (such as **LXA_4**) where the diastereoselectivity control in these reactions was used to produce stereodefined triols (Scheme 1.10) [67]. In addition, when formaldehyde is applied instead of CO_2, 1,3-dioxolanes can be produced [68]. Similarly, epoxy amines were employed in a similar way, providing oxazolidinone rings in high yield without a base or a catalyst [69]. The synthetic usefulness of such methods was shown by using different hetero-cumulenes including CS_2, O=C=S, or isocyanates and later employed in the synthesis of disparlure analogs bearing an oxazolidinone ring (Scheme 1.10) [70]. A similar strategy can be employed with alcohol-functionalized aziridines, the nitrogen analogs of oxiranes. By base-induced CO_2 activation at the alcohol functionality, aziridine ring opening follows, giving amino-functionalized five-membered cyclic carbonates [71].



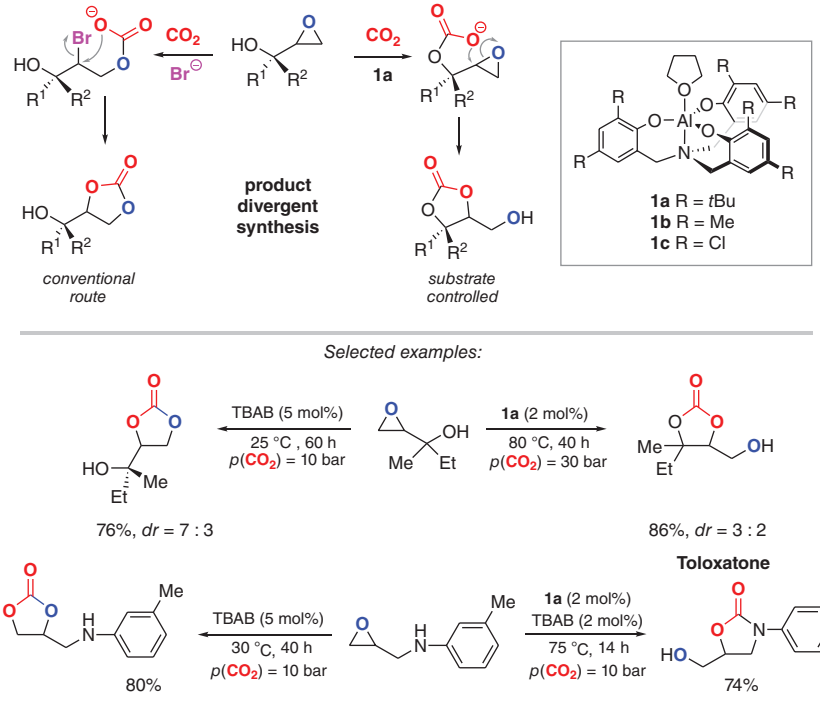
Scheme 1.10 Substrate involvement in the formation of heterocyclic compounds using CO_2 as a reagent, and application to the total synthesis of lipoxin derivatives and disparlure analogs. MS = molecular sieves.

In 2015, the Kleij group reported an unexpected low-temperature conversion of hydroxy-oxetanes into various cyclic carbonates in the presence of CO_2 and an Al(III) complex [16]. While oxetane substrates devoid of an alcohol group could only be converted at elevated temperatures (>60 °C) and in the presence of halide cocatalysts, the hydroxy-oxetanes were readily transformed into their respective cyclic carbonates at temperatures as low as 25 °C and, importantly, in the absence of halide additives. The mechanistic rationale was linked to the bifunctionality of the Al(III) complex combining both Lewis acidic (Al center) and Lewis basic (phenolate donor groups) sites. In the absence of this bifunctional catalyst, no conversion of the substrates was observed (Scheme 1.11).

Further studying this type of reactivity, the same group reported a catalytic version of the conversion of a wide range of epoxy alcohol substrates using similar Al(III) catalysts (**1a–1c**, Scheme 1.12), affording various cyclic carbonates in high selectivity and yields [72]. They further demonstrated that the presence of a (co)catalytic amount of tetrabutylammonium bromide (TBAB) or other



Scheme 1.11 Al(III)-catalyzed conversion of hydroxy-oxetanes into five-membered cyclic carbonates under mild temperature conditions. MEK, methyl ethyl ketone.

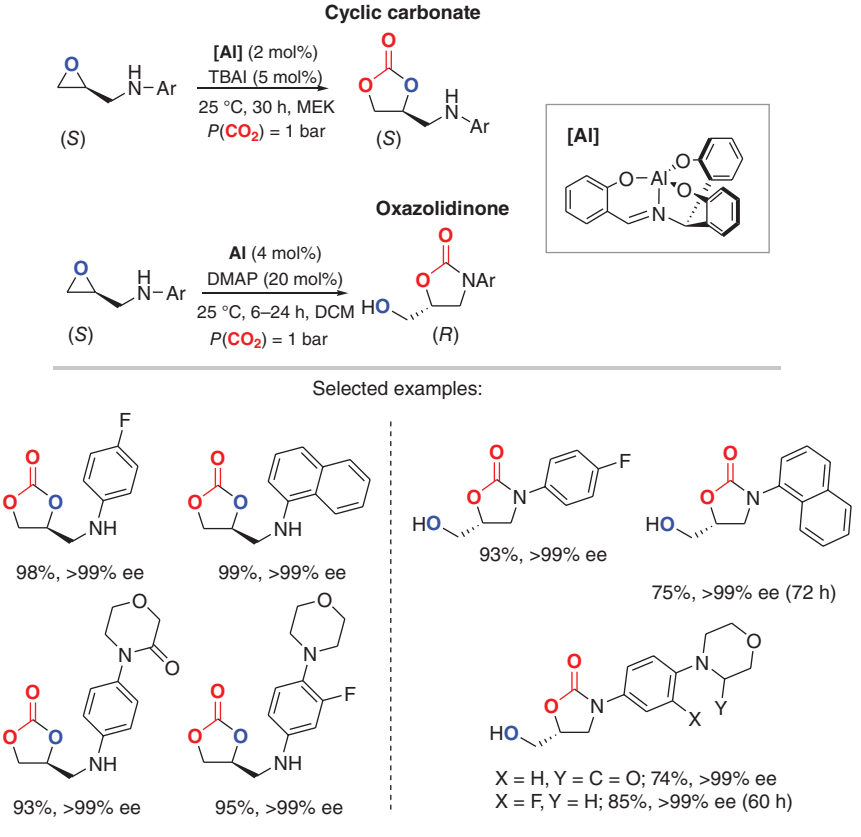


Scheme 1.12 Product divergence through conventional and substrate-directed cycloaddition of CO_2 to epoxy alcohols catalyzed by Al(III) catalysts **1a–c**.

types of additives such as diisopropyl ethylamine (DIPEA) can steer the product selectivity toward the more conventional cyclic carbonate. Thus, product diversity could be accomplished using two different sets of reaction conditions and catalyst components, selectively giving rise to the formation of two different cyclic carbonates. Notably, both epoxy alcohols and epoxy amines were productive substrates with the epoxy amines allowing, in some cases, for ambient reaction temperature to be employed. In addition to this, by having the epoxy amine

precursor equipped with appropriate N-substituents, an easy access to the pharmaceutically relevant Toloxatone was enabled. Therefore, this conceptually new substrate-induced route toward heterocyclic products derived from epoxy amines and CO_2 allows for simple variations of the oxazolidinone scaffold with the potential for new drug discovery. Another noteworthy aspect of the new manifold is that it allowed for the first time to prepare trisubstituted cyclic carbonates using an epoxide/CO_2 coupling strategy.

This divergent synthesis concept was later applied by Kim and coworkers on enantiopure epoxy amines. By using a related Al(III) iminotriphenolate catalyst, divergent synthesis was demonstrated, yielding either a cyclic carbonate or an oxazolidinone using cocatalytic tetrabutylammonium iodide (TBAI) or DMAP, respectively (Scheme 1.13) [73]. Full retention of stereochemistry was shown in the case of cyclic carbonate synthesis in line with a double inversion mechanism, whereas inversion of stereochemistry in the case of preparation of oxazolidinones evidenced the substrate-activated mechanism. Importantly, the substrate-controlled pathway could be triggered by a basic additive (DMAP), and both the Al complex and additive were needed in both transformations for



Scheme 1.13 Al(III)-mediated enantioretentive synthesis of chiral cyclic carbonates and enantioinvertive chiral oxazolidinone synthesis using a common epoxy amine substrate.

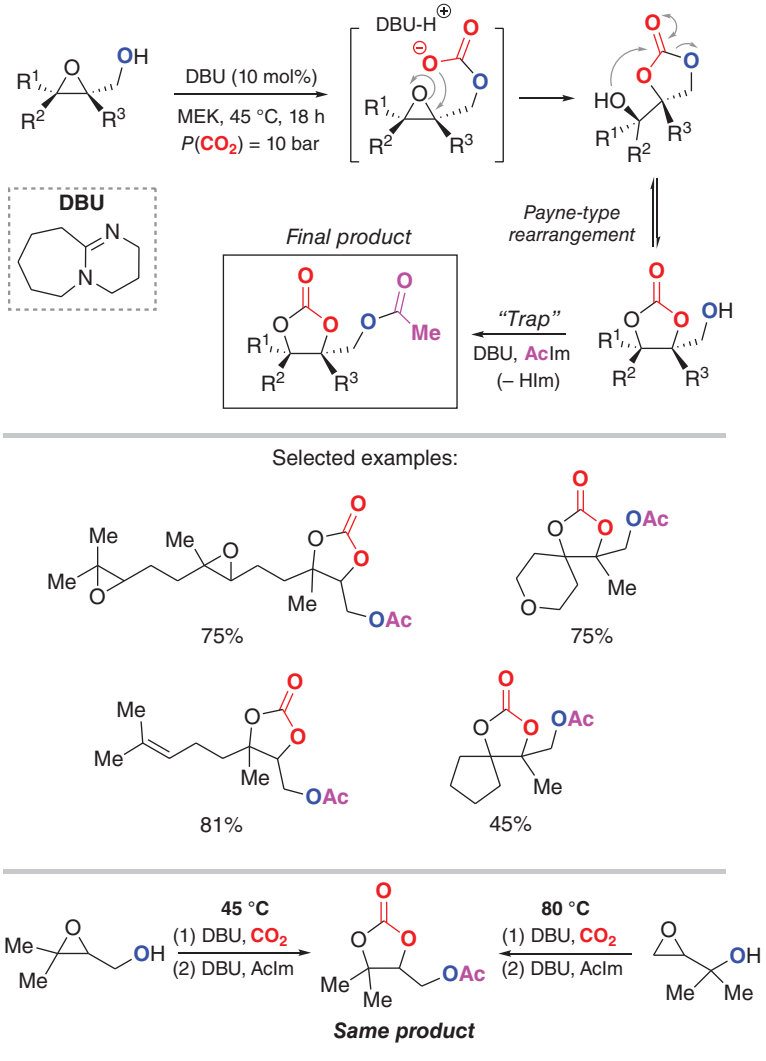
effective turnover. The presence of the base additive did not lead to any significant epimerization of the epoxy amine substrate.

Substrate-directed conversion of oxiranes and CO_2 can also be used to devise new conceptual approaches to highly challenging, multisubstituted, and functional cyclic carbonates. Recently, the classical Payne rearrangement of epoxy alcohols [74] was considered as a design element to achieve this elusive objective. Sopeña and coworkers envisioned that a similar rearrangement of hydroxymethyl-substituted cyclic carbonates would be feasible under basic conditions (i.e. using DBU), allowing equilibration between the initially formed, less substituted, and a more substituted cyclic carbonate product. Because both cyclic carbonate products contain an alcohol group with distinct reactivity (primary versus tertiary -OH), selective trapping of the primary alcohol was easily accomplished (Scheme 1.14) [75].

In this base-mediated "Payne-type" carbonate-to-carbonate rearrangement reaction, the free alcohol in the initially formed product attacks the carbonate carbon center and then releases the more-substituted product. Although the process is an equilibrium between two carbonate products, it is possible to trap the more substituted species by protecting the alcohol using *N*-acetyl imidazole that selectively reacts with primary OH groups [76, 77] leading to high yield formation of the most substituted cyclic carbonate. By using this strategy, access to a wide range of (functional) trisubstituted and even tetrasubstituted cyclic carbonates was established for the first time from epoxide substrates using organocatalysis under mild temperature conditions (45 °C).

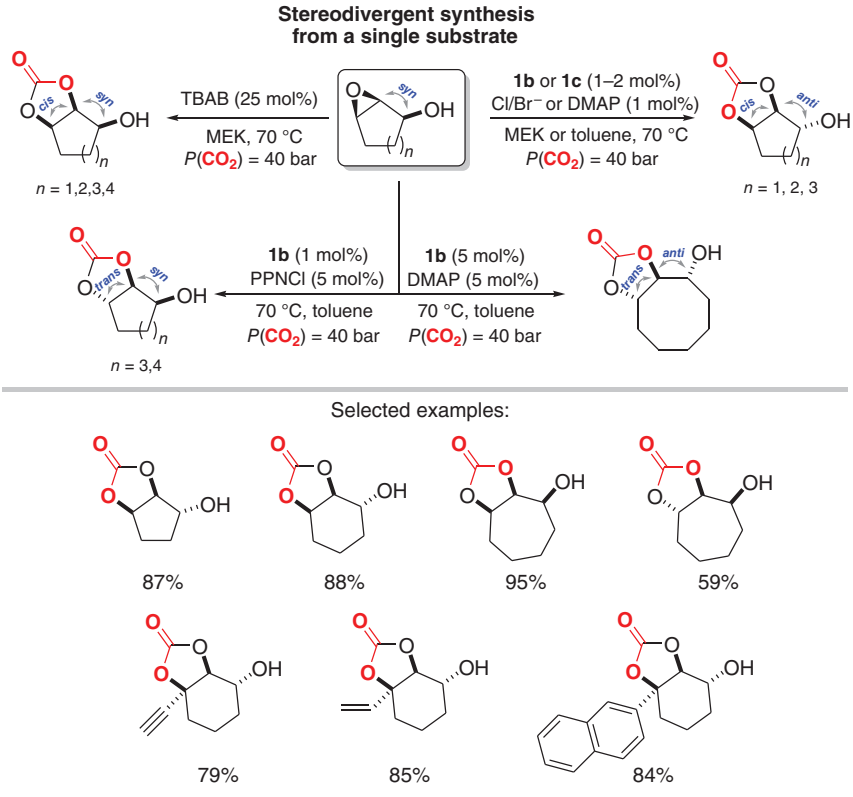
Interestingly, the tetrasubstituted carbonate structures originate from tetrasubstituted alkenes featuring a β-alcohol group, as the process involves a double-isomerization pathway ultimately leading to the cyclic carbonate one would expect from a classical epoxide/CO_2 coupling [75]. This strategy is therefore complementary to that using tertiary alcohols as starting materials to obtain trisubstituted cyclic carbonates [72]. Both strategies have in common that the chemoselectivity is exclusive in allowing to form cyclic carbonate groups at the epoxy alcohol positions, while leaving other epoxide fragments unaffected. Mechanistic support was provided by several control experiments. Classical Payne rearrangement of the epoxy alcohol substrates followed by coupling with CO_2 could be excluded as no isomerization was noted when the substrate was mixed with DBU only. In addition to this, the same carbonate product was obtained when using either a mono-substituted or trisubstituted epoxy alcohol precursor (see the bottom part of Scheme 1.14), in line with the existence of a cyclic carbonate equilibrium.

In addition to control the type of cyclic carbonate (cf. product divergence), the stereoselectivity of these kinds of transformations can also be regulated offering stereodivergent synthesis of cyclic organic carbonates (COCs). Cyclic epoxy alcohols can be employed to probe the formation of different diastereoisomers that form under different (catalytic) conditions (Scheme 1.15). By using distinct catalytic conditions, several diastereoisomers could be synthesized from a single *syn*-epoxy alcohol substrate [78]. Because of the cyclic nature of the epoxy alcohol, the observation and distinction between possible regioisomers is not feasible but simplifies the overall analysis.



Scheme 1.14 Organocatalyzed route toward trisubstituted and tetrasubstituted cyclic carbonates from epoxy alcohols using a Payne-like isomerization pathway.

For all the cyclic epoxy alcohol ring sizes studied (n = 1–4), the *syn–cis* configured cyclic carbonates were obtained under simple TBAB catalysis. Here, the term *syn* denotes the relative position of the alcohol group with respect to the carbonate ring and *cis* corresponds to the relative position of the carbonate ring substituents. The presence of TBAB ensures the occurrence of a well-established double-inversion pathway (as indicated in Scheme 1.9). However, differences in the product distribution can be observed when using Al(III) catalysis (**1b** or **1c**) combined with halide or base additives. For epoxy alcohols with n = 3 or 4, unexpected *anti–cis* configured cyclic carbonate products were observed. Such

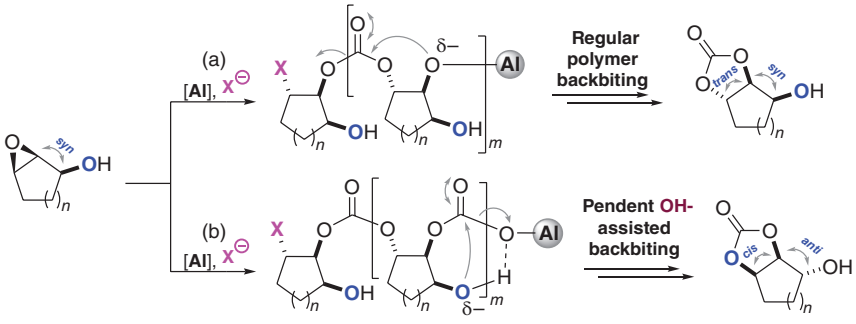


Scheme 1.15 Stereodivergent transformations of cyclic epoxy alcohols using Al(III) catalysts **1b** and **1c** (see Scheme 1.7) and halide or base additives. PPNCl = bis(triphenylphosphine) iminium chloride.

isomers cannot be explained from the substrate activation mechanism described above. For larger ring-size cyclic epoxy alcohols (n = 3 and 4), unusual *syn–trans* configured carbonates were formed using Al(III)-complex **1b** and a chloride-based nucleophile. Remarkably, an *anti–cis* configured cyclic carbonate product could be accessed from a seven-membered cyclic epoxy alcohol using **1b** together with DMAP, whereas under the same conditions, an *anti–trans* isomer was preferentially formed from an eight-membered epoxy alcohol substrate.

Although the synthesis of the *syn–cis* and *anti–trans* configured cyclic carbonates can be explained by a double inversion pathway or substrate-controlled CO_2 activation, respectively, the formation of the *anti–cis* and *syn–trans* products indicates a more complex mechanism for their formation. Therefore, it was postulated that under the reaction conditions (particularly considering the potential of the Al complex to be involved in the copolymerization of epoxides and CO_2 [79, 80] and the low nucleophile-to-Al ratio), an oligomeric linear carbonate forms first that is subsequently broken down to give rise to various cyclic carbonate products. The *syn–trans* products can then be explained by a typical and well-known alkoxide backbiting (Scheme 1.16, path a). This type of process has

previously been shown to be useful in the synthesis of linear carbamates from CO_2, epoxides, and amines on similar substrates [81, 82].

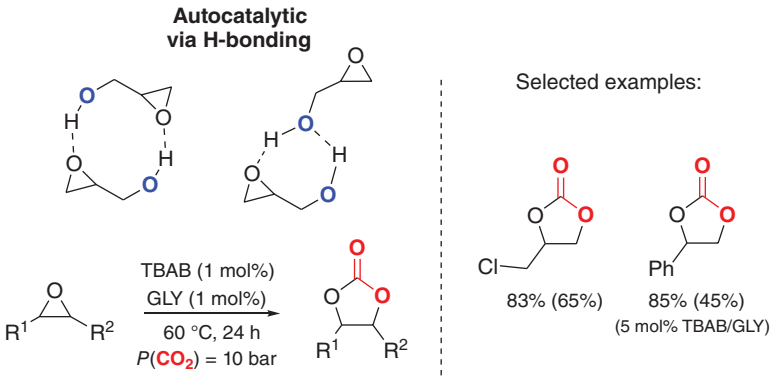


Scheme 1.16 Postulated mechanisms leading to different diastereoisomeric products through (a) regular polymer backbiting (depolymerization) or (b) pendent OH-group-assisted backbiting. $\mathbf{X}^-$ is the nucleophilic additive (bromide or chloride) and [**Al**] is an aminotriphenolate Al(III) complex.

The *anti–cis* carbonate product, however, cannot be formed by a regular backbiting process [83–85] and instead requires depolymerization initiated by the pendent OH group (Scheme 1.16, path b). Such a process seems to be disfavored for larger ring-size substrates for which depolymerization instead occurs through alkoxide backbiting. Although for epoxy alcohols with $n = 3$ it is possible to obtain the *anti–cis* product by using base catalysis, the product does not form for substrates with $n = 4$ under any of the investigated conditions [78]. The pendent OH group therefore provides orthogonal reactivity, leading to different stereoisomers, which are produced without the involvement of the OH group in the initial formation of the oligomer.

The above mentioned results show that the mechanism of epoxy alcohol conversions can be rather complex. Indeed, besides possible activation of CO_2 through linear carbonate formation via the pendent alcohol group, hydrogen bonding of the alcohol group to the epoxide may also play an important role for these substrates. Such hydrogen bonding has recently been shown to be essential in the conversion of the simplest epoxy alcohol, i.e. glycidol (Scheme 1.17). In this latter case, intermolecular hydrogen bonding leads to autocatalytic conversion of the substrate into glycidol carbonate in the presence of CO_2 [86]. Furthermore, glycidol could be used as a cocatalyst for the conversion of other epoxides into their respective cyclic carbonates.

This prompted a more thorough investigation into the mechanism of the conversion of glycidol by the Al(III) catalyst **1a** in the absence of an external nucleophile. In a combined experimental and theoretical study, the groups of Kleij, Urakawa, and Bo uncovered several intermediate species, while portraying the importance of the Al(III) catalyst in the activation of the substrate [87]. In a first step, the alcohol group of glycidol coordinates to the Al catalyst (proven by X-ray crystallography, see Figure 1.3) and a proton transfer to one of the phenolate O-atoms of the catalyst occurs. This alcohol coordination is somewhat unexpected as typically epoxide coordination takes places through the oxirane unit.



Scheme 1.17 The use of glycidol (GLY) as a cocatalyst in the TBAB-mediated conversion of epoxides and CO_2 into COCs. The reported yields are based on NMR analyses using mesitylene as an internal standard; the yields of the cyclic carbonates in the absence of GLY are presented in parenthesis.

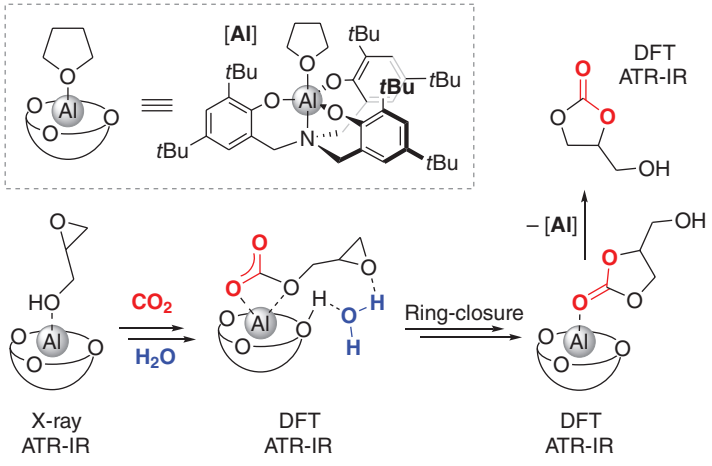


Figure 1.3 Intermediates observed in the Al-mediated substrate-activated conversion of glycidol to glycidyl carbonate.

Subsequent nucleophilic attack of the glycidol alkoxide on CO_2 gives a linear carbonate species that is stabilized by coordination to the Al center. Interestingly, the ATR-IR (ATR = attenuated total reflection) frequency of the carbonate unit of this intermediate was predicted at 1835 cm^{-1}, whereas *operando* IR spectroscopic conditions allowed to observe this intermediate at 1837 cm^{-1}. Notably, detection of the Al complex coordinated by the cyclic carbonate product (1740 cm^{-1}) and dissociation of the product (1790 cm^{-1}) were further shown to occur through *operando* high-pressure IR.

The activation energy predicted by computational analysis initially proved to be very high ($\Delta G^{\ddagger}$ = 46.2 kcal/mol) and did not match the experimental results ($\Delta G^{\ddagger}$ = 23.3 kcal/mol). It was further proven by DFT studies linked with experimental

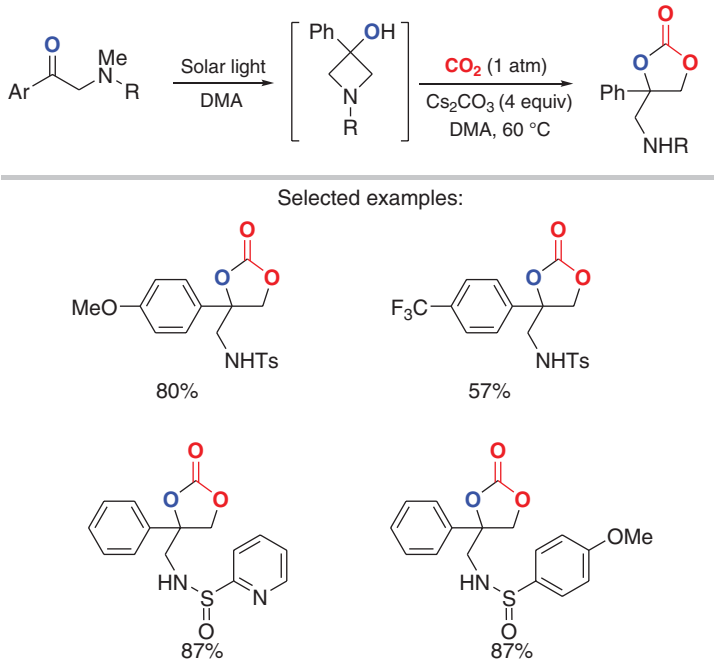
operando IR spectroscopy and kinetic studies that trace amounts of water were required to bring down the activation energy barrier to $\Delta G^{\ddagger} = 24.6$ kcal/mol, and the reaction performed under anhydrous conditions indeed proved to be more sluggish. It was found that such epoxy alcohol–water–catalyst clusters are key to the high reactivity of these types of substrates. These results further highlight the importance of the previously mentioned hydrogen bonding and proton transfer in the activation of such substrates and their subsequent reaction with CO_2.

1.5 Substrate-Involved Activation of Oxetanes and Azetidines

Although less common, oxetanes, the four-membered analogs of oxiranes, can be synthesized from alkenes by the Paterno–Büchi reaction, i.e. [2 + 2] photocycloaddition of carbonyl compounds to alkenes [88]. Oxetanes have been employed as precursors for the preparation of high-value six-membered cyclic carbonates through reaction with CO_2 and mediated by binary Lewis acid/nucleophile catalysis similar to oxiranes [16, 89–91]. Such cyclic carbonates are especially useful for the synthesis of 1,3-diols [92] or polycarbonates through ring-opening polymerization (ROP) [93]. However, when functionalized with alcohols or amines, such molecules can undergo substrate-activated pathways instead, leading to cyclic carbonates and oxazolidinones, respectively, incorporating the pending nucleophilic group [16]. When an external amine is used to activate CO_2, an intermolecular opening of the oxetane yields linear carbamates [94]. A similar reactivity can also be obtained from azetidines (which can be synthesized from alkenes through an aza-Paterno–Büchi reaction, although various other methods are known) [95, 96], the nitrogen analogs of oxetanes (Scheme 1.18). Hydroxy-substituted azetidines can be prepared under solar light-driven cyclization of α-amino ketones. These alcohol-based substrates can then be converted in the presence of CO_2 into amino-functionalized five-membered cyclic carbonates under mild reaction conditions using stoichiometric amounts of base [97].

1.6 Concluding Remarks

The preactivation of readily available (homo)allylic and epoxy-containing alcohols or amines are increasingly investigated and have provided new manifolds for the efficient conversion of carbon dioxide into various heterocyclic products such as cyclic carbonates and carbamates. The recent literature illustrates great advances in the design of catalytic versions of these promising transformations, with both bifunctional, metal-based catalysts and simple organocatalysts playing an important role. Apart from simple conversions, product/stereodivergent and enantioselective processes have also been introduced, showing that rather complex organic molecules may be constructed from CO_2, thereby amplifying the impact of this renewable carbon feedstock in organic synthesis. Several fundamental and practical future challenges are still to be resolved, among which are



Scheme 1.18 Solar-driven formation of hydroxy-azetidines and their subsequent conversion into cyclic carbonates under basic conditions. DMA = *N,N*-dimethylacetamide, Ts = tosyl, NHTs = (NH)-Ts.

the development of a wider variety of substrates that are actively involved in CO_2 conversion, the implementation of multiple CO_2 molecules within a substrate via (for instance) cascade processes, and expanding the asymmetric synthesis opportunities with CO_2 [98, 99]. In order to enable to meet these challenges, it will be vital to mature the portfolio of accessible, cheap, and modular catalyst systems that can allow for easy scale-up and optimization of the CO_2 conversion process.

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