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Review

Versatile Use of Carbon Dioxide in the Synthesis of Carbamates

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Summary. Organic carbamates classically have been synthesized using harmful and toxic reagents like phosgene, its derivatives, and carbon monoxide. Recently, carbon dioxide was used as a cheap and harmless reagent for the synthesis of organic carbamates in the gaseous or supercritical state, or in an electrochemical process, or organic carbonates as sources of carbon dioxide as an alternative to the harmful reagents. The present review will deal with the extensive use of carbon dioxide in the synthesis of organic carbamates.

Keywords. Organic carbamates; Carbon dioxide; Organic carbonates; Carbamation.

Introduction

Carbamation of amines has frequently been utilized in the synthesis of organic carbamates [1], which hold unique applications in the field of pharmaceuticals [2] and agriculture [3]. Organic carbamates have also played an important role in the area of synthetic organic chemistry, particularly as synthesis intermediates [4], for the protection of amino groups in peptide chemistry [5], and as linkers in combinatorial chemistry [6]. Functionalization of amines as carbamates offers an attractive method for the generation of derivatives, which may have interesting medicinal and biological properties [7]. However, the scope of existing methodologies for carbamate formation is limited by the need of specialized reagents and an operational complexity due to the use of either toxic or cumbersome reagents, such as phosgene [8], its derivatives [9], and carbon monoxide [10].

Recently, carbon dioxide as the only cheap, easily available, and harmless reagent has been efficiently used as an alternative for the synthesis of carbamates in the gaseous [11] or supercritical [12] state or in an electrochemical process [13].

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Besides, it has also been used for C–C, C–N, and C–O bond forming reactions [14]. In the present review we will focus on the synthesis of organic carbamates using various conditions and forms of carbon dioxide.

Synthesis of Carbamates Using Carbon Dioxide

Gaseous Carbon Dioxide

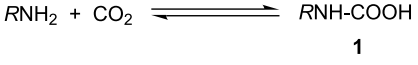
Although carbon dioxide has a low reactivity, *e.g.* with amines it forms unstable carbamic acids (**1**), which revert to their corresponding starting materials (Scheme 1).

However, *Yoshida et al.* [15] have reported the synthesis of carbamates from CO_2, amines, and unsaturated ethers (Scheme 2). But in this method only secondary aliphatic amines could be used. Moreover, it takes long reaction times (~70–80 h) and it results in low yields (3–12%).

Later on, *Yoshida et al.* [16] have also reported a carbamate ester synthesis starting from CO_2 and using two equivalents of amine and an alkyl halide in a one-pot reaction (Scheme 3). This method is also limited to primary and secondary aliphatic amines, takes long reaction times (~45 h), and the carbamates are obtained in only 6–25% yields.

Later on, *Ishii et al.* [17] have reported the synthesis of carbamates from CO_2 and ortho esters (Scheme 4). This reaction takes long reaction times, but is useful for the carbamates derived from primary and secondary amines.

Monocarbamates of 1,2-diols from the corresponding 1,2-epoxides have been prepared [18] by reaction of CO_2 and primary and secondary aliphatic amines (Scheme 5). However, about half of the epoxide is lost due to the accompanying nucleophilic ring opening by the amine.



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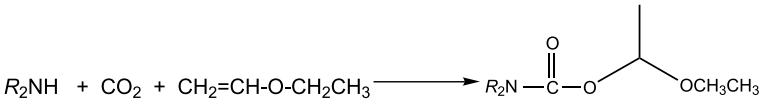
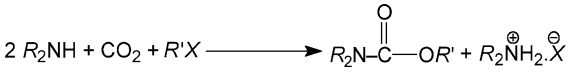
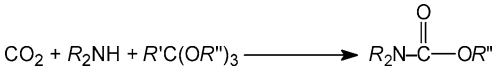
Scheme 1



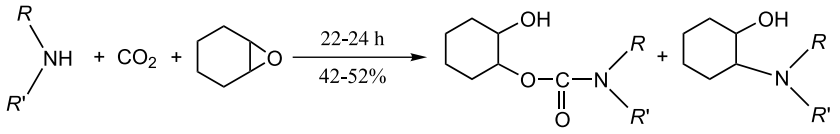
Scheme 2



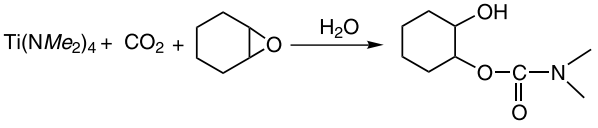
Scheme 3



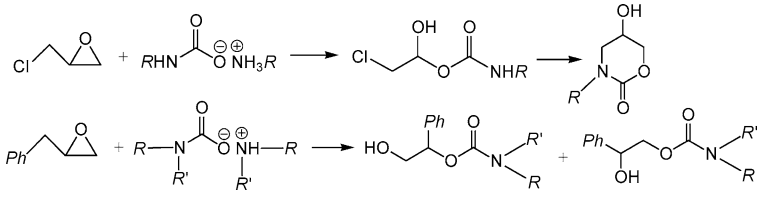
Scheme 4



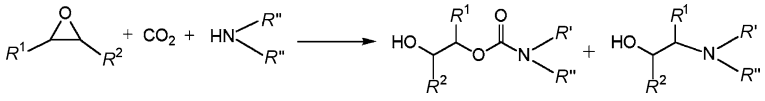
Scheme 5



Scheme 6



Scheme 7



Scheme 8

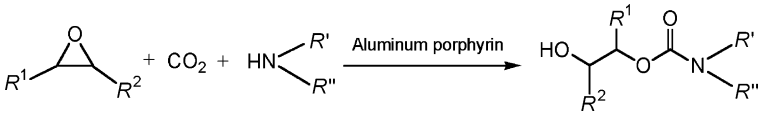
The monocarbamates could also be obtained from an epoxide using tetrakis-(dimethyl)-titanium(IV) and CO_2 (Scheme 6) [19]. But this reaction was not satisfactory due to its long reaction times (∼3–4 d) and low yields (5–20%).

Similarly, chloromethyloxirane or (phenylmethyl)oxirane on reaction with CO_2 and aliphatic amines in methanol gave carbamates (2–17%) (Scheme 7) [20].

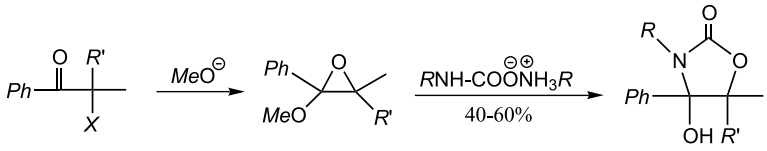
Later on, better yields have been reported by *Yoshida et al.* [21] (Scheme 8). However, the latter syntheses suffer from the formation of isomer mixtures.

Kojima et al. [22] reported a carbamate synthesis from epoxides, amines, and CO_2 where the latter was previously fixed on an aluminum porphyrin (Scheme 9).

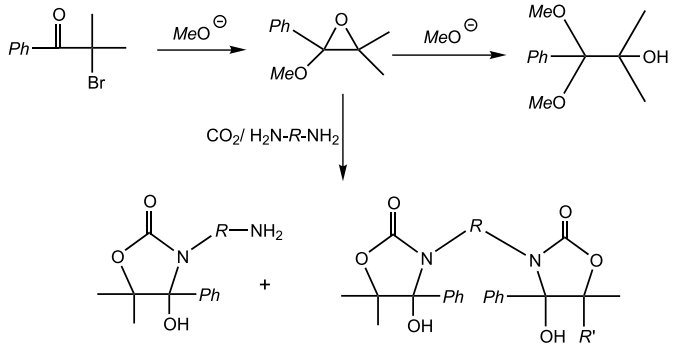
Toda et al. [23] reported the synthesis of cyclic carbamates (*i.e.* oxazolidinones). Reaction of CO_2 with α-bromoacylphenones in the presence of aliphatic primary amines in methanol afforded 3-alkyl-4-hydroxyoxazolidin-2-one derivatives under mild conditions (Scheme 10).



Scheme 9

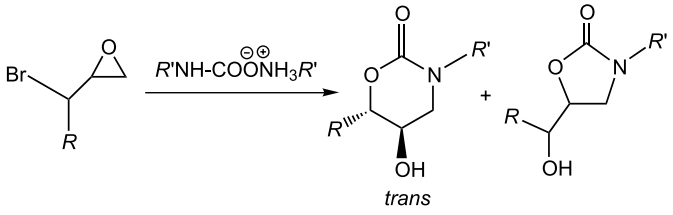


Scheme 10



$R = (CH_2)_n$, n = 1, 2, 3, 4, 5, 6, *etc.*

Scheme 11



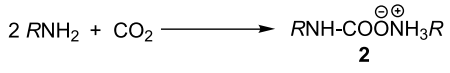
Scheme 12

This reaction led to the formation of bis(2-oxazolidinones) [24] when 2-methoxy-3,3-dimethyl-2-phenyloxirane or α-bromo-*i*-butyrophenone was reacted with CO_2 and aliphatic α,ω-diamines (Scheme 11).

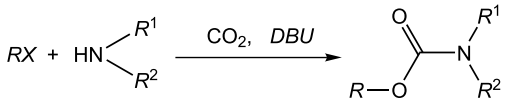
Reaction of 2-(1-haloalkyl)-oxiranes with CO_2 and aliphatic primary amines gave five- and six-membered cyclic carbamates [25] (Scheme 12).

In the above reaction it was shown that there is involved an ionic species **2**, which is formed from 2 mol amine reacting with CO_2 as shown in Scheme 13.

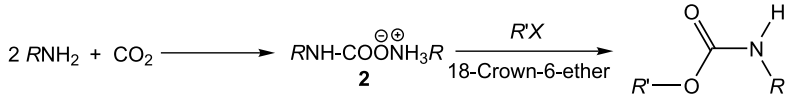
An improvement in the yields of carbamate formation has been achieved by using basic reagents, which help in the stabilization of the intermediate ionic species **2**. Thus, *Hori et al.* [26] have reported the synthesis of organic carbamates from primary and secondary amines, CO_2, and alkyl halides in the presence of *DBU* (Scheme 14).



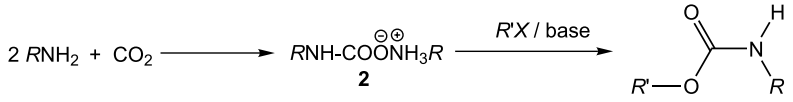
Scheme 13



Scheme 14



Scheme 15



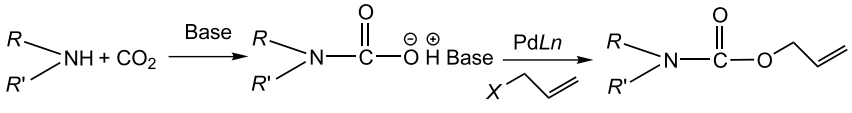
Scheme 16

Aresta et al. [27] have reported a carbamate synthesis from the ionic species **2** by alkylation with alkyl halides using 18-Crown-6-ether as a phase transfer catalyst (Scheme 15).

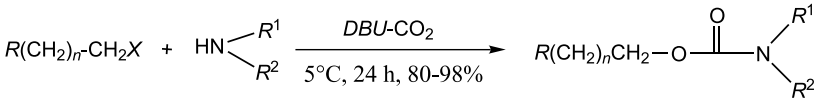
However, this method is useful only for the preparation of carbamate esters of primary and secondary aliphatic amines. Several strong bases (*CyTMG*, *TMG*, *DBU*, *MTDB*, *CyTEG*, *etc*.) have been used for providing more basic conditions to **2** by *McGhee et al.* [28]. In presence of alkylating agents this leads to the formation of carbamates (Scheme 16) in moderate to good yields (40–78%).

O-Allyl carbamate [29] could be obtained by the addition of the preformed carbamate ion $RR'NH–COO^{-}H^{+}$ base generated from the addition of various primary and secondary amines and CO_2, to a THF solution of allylic chlorides under 80–100 psig CO_2 at room temperature containing a Pd-phosphine catalyst in 66–100% yields (Scheme 17).

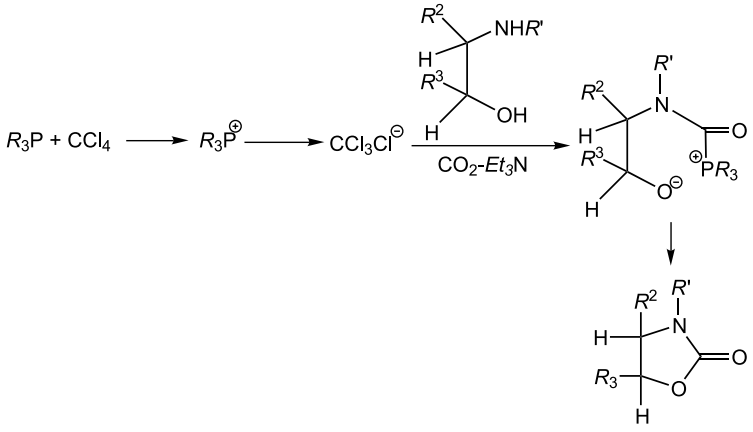
Recently, *Perez et al.* [30] have reported the synthesis of *N*-alkylcarbamates in good to excellent yields by a clean and mild transcarboxylation of several amines with the previously synthesized *DBU*-CO_2 complex and subsequent O-alkylation by different alkyl halides (Scheme 18).



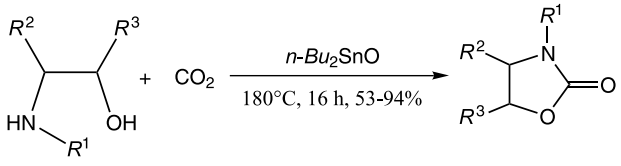
Scheme 17



Scheme 18



Scheme 19



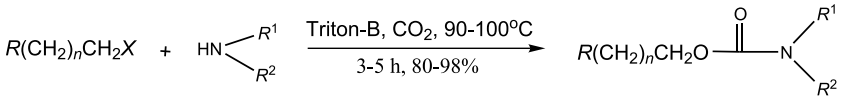
Scheme 20

Cyclic urethanes [31] could be obtained in moderate to good yields (33–93%) under mild conditions from amino alcohols and CO_2 using phosphorus(III) reagents (*i.e.* Ph_3P, $(PhO)_3P$) and haloalkanes (*i.e.* CCl_4 and Cl_3CCCl_3) (Scheme 19).

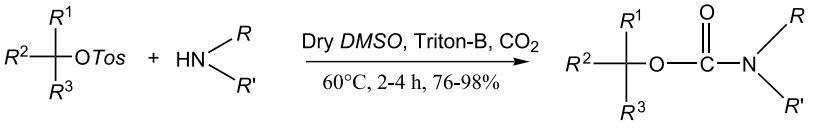
Tominaga et al. [32] have reported the synthesis of 2-oxazolidinones from CO_2 and 1,2-aminoalcohols catalyzed by *n*-Bu_2SnO (Scheme 20). The dehydrative condensation of 1,2-aminoalcohols with CO_2 was found to proceed in *NMP* as the solvent. 2-Oxazolidinones were obtained in 53–94% yields when the commercially available *n*-Bu_2SnO was used as the catalyst.

Recently, we have reported [33] an efficient one-pot, high yielding carbamate synthesis from CO_2, amines, and alkyl halides using Triton-B as the catalyst (Scheme 21).

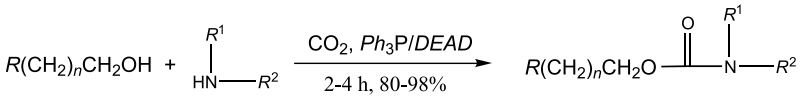
We have also reported [34] the synthesis of carbamates in high yields from a variety of alkyl tosylates and amines using the Triton-B/CO_2 system (Scheme 22).



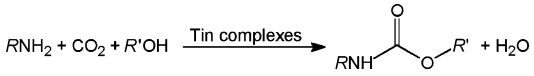
Scheme 21



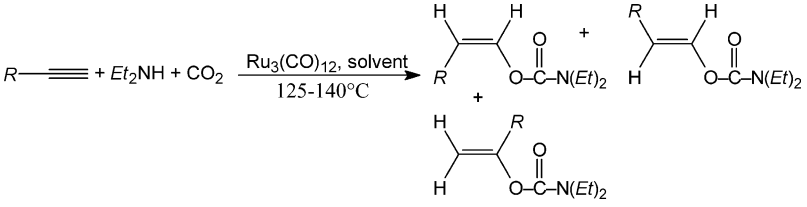
Scheme 22



Scheme 23



Scheme 24



Scheme 25

A direct synthesis in high yields of carbamates from primary alcohols and amines using the *Mitsunobu* reagent/CO_2 system was reported by our group [35] (Scheme 23).

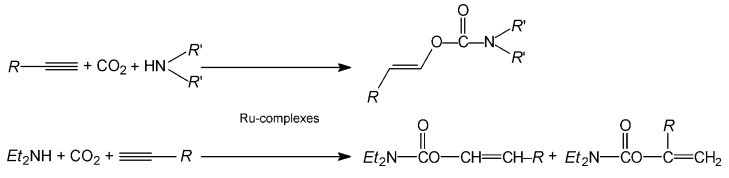
Recently, CO_2 has been converted into carbamates through reaction with amines and alcohols catalyzed by tin complexes [36]. The addition of acetals as dehydrating agents under high CO_2 pressure is the key to achieve high yields (Scheme 24).

Vinyl carbamates [37] have been synthesized from CO_2, diethylamine, and alkynes in presence of a ruthenium catalyst (Scheme 25).

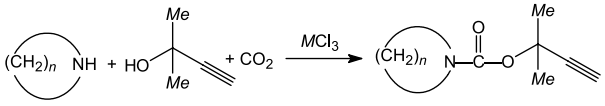
Better yields of vinyl carbamates [38] were obtained using CO_2 and ruthenium complexes (*i.e.* $RuCl_2(PR_3)$carene) and $RuCl_2$(norbornadiene)$(pyridine)_2$) (Scheme 26).

Shim et al. [39] have synthesized carbamates from amines, acetylenic alcohols, and CO_2 using a lanthanide catalyst. Thus, the reaction of perhydroazepine with 3,3-dimethylprop-1-yne-3-ol and CO_2 in presence of MCl_3 (M = Ce, Pr, Nd, Gd) gave carbamates ($n = 6$) in 20–38% yields. They have also prepared the carbamates with $n = 4$ and 5) in 31 and 21% yields (Scheme 27).

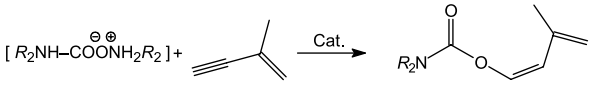
Regioselective synthesis of 1,3-dien-1-yl carbamates [40] was carried out by regioselective addition of CO_2 and secondary amines to isopropenylacetylene in the presence of $(Ph_2P(CH_2)_nPPh_2)Ru(\eta_3–CH_2–C(Me)=CH_2)_2$ as catalyst (Scheme 28).



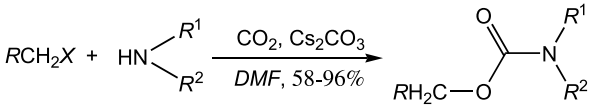
Scheme 26



Scheme 27



Scheme 28



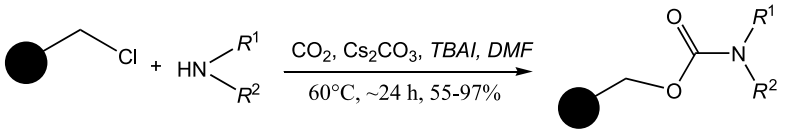
Scheme 29

Carbon dioxide providing the carbonyl functionality for the carbamates is not sufficient itself for the excellent production of carbamates. The basicity of the ionic species **2** is increased by adding basic reagents. Furthermore, it has been proposed that metal carbonates, like Na_2CO_3, K_2CO_3, Cs_2CO_3, *etc*. are suited basic reagents, which could provide carbonyl functionality in addition to their basic properties. Based on this concept there are many reports on the use of metal carbonates for carbamate synthesis. Thus, *Butcher* [41] has reported a carbamate synthesis in good to excellent yields (58–96%) from alkyl halides using the Cs_2CO_3/CO_2 system (Scheme 29).

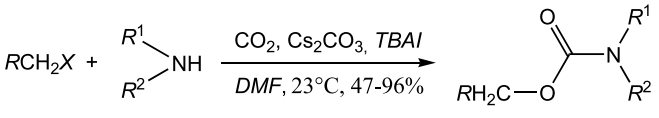
Later on, *Salvatore et al.* [42] have reported a carbamate synthesis on a solid phase *Merrifield* resin in good to excellent yields using Cs_2CO_3/CO_2 and *TBAI* as phase transfer catalyst (Scheme 30).

Carbamate synthesis was also carried out in solution [43] using aliphatic, aromatic, and heterocyclic amines in the Cs_2CO_3/CO_2 system in presence of a catalytic amount of *TBAI* (Scheme 31).

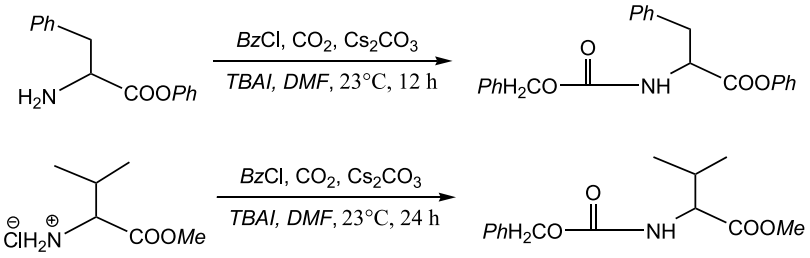
Besides using different amines they have also used the same technique in peptidomimetic synthesis as shown in Scheme 32.



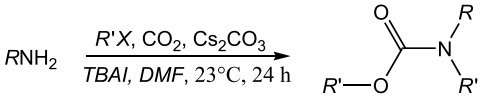
Scheme 30



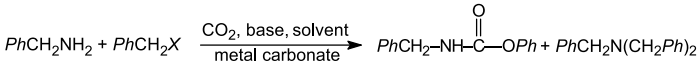
Scheme 31



Scheme 32



Scheme 33



Scheme 34

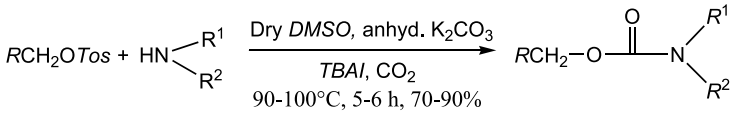
A direct synthesis of *N*-alkylcarbamates from primary amines and alkyl halides using the Cs_2CO_3/CO_2 system has been reported [44] by *Salvatore et al.* (Scheme 33).

A study of comparative yields by using different metal carbonates and bases of *O*- as well as *N*-alkylated products in the synthesis of carbamates using CO_2 and different metal carbonates and bases have been reported by *Shi et al.* [45] (Scheme 34).

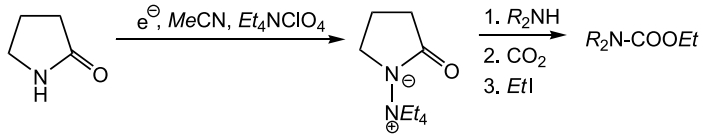
We have reported [46] a convenient, one-pot synthesis of carbamate esters in very good yields (70–90%) from alkyl tosylates and amines using the K_2CO_3/CO_2 system in presence of a catalytic amount of tetra-*n*-butylammonium iodide (Scheme 35). This method has been used for carbamate esters starting from aliphatic primary and secondary, and aromatic amines.

Electrochemical Synthesis Using Carbon Dioxide

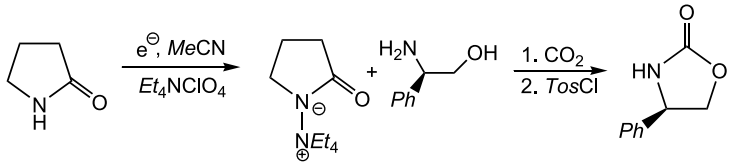
Inesi et al. [47] have reported carbamate synthesis by using CO_2 in an electrochemical process (Scheme 36). This synthesis is based on the reaction of amines and anilines with the base electrochemically generated from 2-pyrrolidone (associated with the Et_4N^+ cation) followed by sequential addition of CO_2 and ethyl iodide.



Scheme 35



Scheme 36



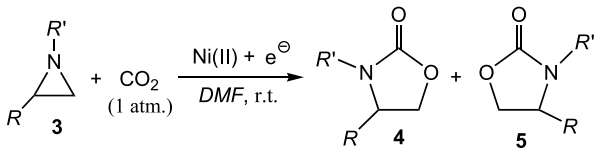
Scheme 37

Recently *Inesi et al.* [48] have reported an improved electrochemical synthesis of chiral oxazolidin-2-ones from chiral 1,2-amino alcohols. These are obtained by direct electrolysis of a solution of *Me*CN-*TEAP* containing the amino alcohol with subsequent CO_2 bubbling and addition of *Tos*Cl. This synthesis avoids any addition of bases or probases and oxazolidinones are obtained in high yields (Scheme 37).

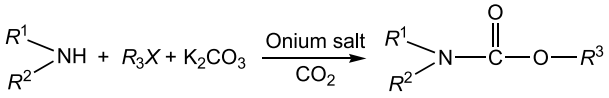
A new and selective method of 2-oxazolidinone synthesis using a simple electrochemical procedure by which the cyclic carbamates **4** and **5** can be obtained in good yields from the direct reaction of substituted aziridines **3** with CO_2 has been recently reported [49]. CO_2 insertion into the C–N bond takes place under very mild conditions at room temperature and with atmospheric CO_2 pressure. The reaction was catalyzed by a Ni(II) complex (10 mol%) and was carried out in a single compartment cell fitted with a consumable Mg anode and an inert cathode (Scheme 38). This electrochemical decarboxylation of *N-Boc* protected aziridines leads to the cyclic carbamates as a 60:40 mixture of two regioisomers in 83 and 60% aziridine conversion. The major isomer corresponds to the incorporation of CO_2 at the less hindered side of the monosubstituted aziridine. No reaction has occurred in the absence of current, and in absence of the Ni catalyst only a very low yield of cyclic carbamates was obtained (<10%).

Supercritical Carbon Dioxide

Yoshida et al. [50] have reported the synthesis of carbamates in good yields from amines and alkyl halides using supercritical CO_2 and K_2CO_3, and tetra-*n*-alkylammonium halides acting as phase transfer catalysts (Scheme 39). They have also demonstrated the effect of different catalysts on carbamates synthesis.



Scheme 38

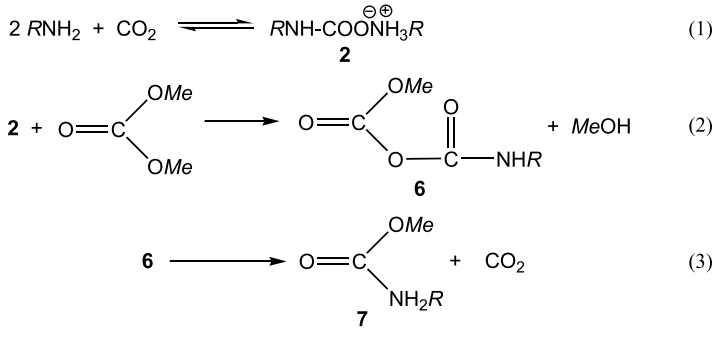


Scheme 39

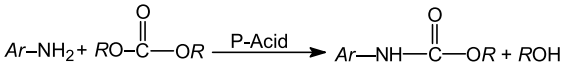
Organic Carbonates and Carbon Dioxide

Organic carbonates constitute an important source for carbonyl functionality during the synthesis of carbamates. Their reaction with amines [51] represents an alternative synthesis route to carbamates that has gained growing attention in the last few years as a non-phosgene route to organic carbamates. Nowadays, dimethyl carbonate (*DMC*) can be produced on a large scale by oxidative carbonylation of methanol [52] and thus constitutes a convenient source of CO_2. Other organic carbonates can be easily obtained by transestrification of *DMC* with phenols [53] and long chain high boiling alcohols [54]. The reaction between primary and secondary amines and dialkyl carbonates needs a suitable catalyst in order to obtain satisfactory conversion rates and high selectivities. Strong bases [55], such as alkali metal alkoxides, Zn, Co, Sn, Al, and tin compounds [56] have been widely employed as catalysts in the carboalkoxylation of anilines and more generally of aromatic amines. Moreover, *Lewis* acids, such as $AlCl_3$, $SnCl_2$, $ZnCl_2$, $Zn(OAc)_2 \cdot 2H_2O$, $FeCl_3$, or metal complexes (Rh, Ru) have proved to be effective in promoting the conversion of *n*-propylamine and diethyl carbonate selectively to ethyl *n*-propylcarbamate [53].

Primary and secondary aliphatic amines can equilibrate with CO_2 to give the monoalkylammoniumalkylcarbamate ion (**2**) (Eq. (1) of Scheme 40) [56] that serves as a convenient source of carbamate moiety in carbamate ester synthesis [57] using *DMC*. *O*-Carbomethoxylation of the carbamate anion is the first step (Eq. (2) of Scheme 40), to give a mixed carbamic-carbonic anhydride, *R*NH–COOCO*Me* (**6**). This step could be catalyzed by acidic species, such as RNH_3^+ and *R*NH–COOH, present at equilibrium. Selective decarboxylation of **6** by expulsion of CO_2 from its carbamic moiety leads to the formation of **7**. Molecular models of mixed anhydrides **6** (*R* = benzyl, cyclohexyl, allyl) show that there exist conditions for an intramolecular transfer of the NH*R* group to the carbonylic carbon of the methyl carbonic moiety to give **7** (Eq. (3) of Scheme 40).

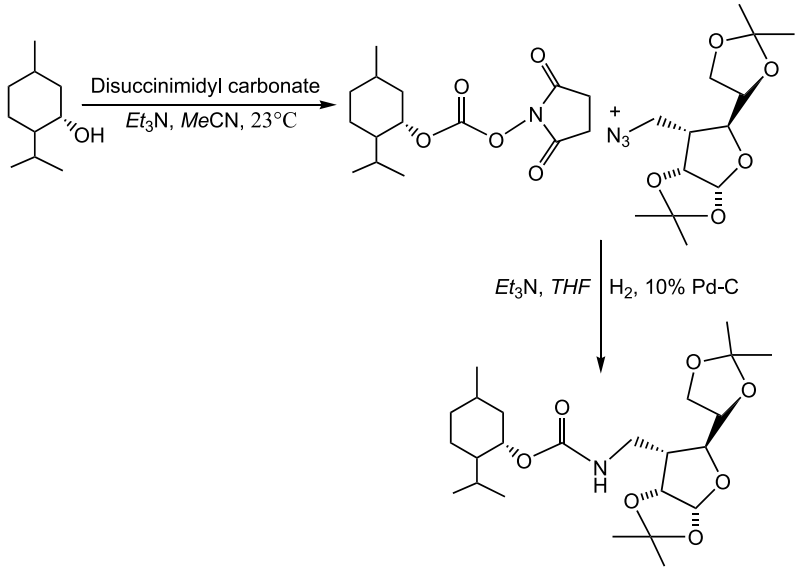


Scheme 40

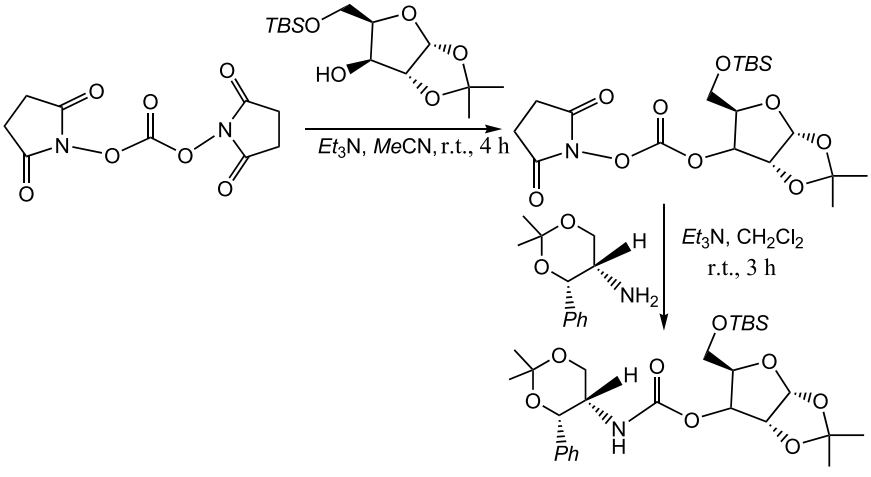


Scheme 41

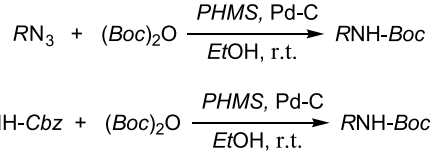
Aresta et al. [58] have reported the synthesis of carbamate esters by reaction of aromatic amines with *DMC* or diphenyl carbonate (*DPC*) in the presence of organo phosphorous acids ($Ph_2P(O)OH$, $(PhO)_2P(O)OH$, $(BuO)_2P(O)OH/(BuO)P(O)(OH)_2$ equimolar mixtures) (Scheme 41). Here organo phosphorus compounds have been used as promoters which give 100% selectivity for carbamate synthesis. The catalytic role played by the P-acid has been investigated and rationalized in terms of a reaction mechanism involving the intermediate formation of a carbonic phosphinic anhydride $X_2P(O)OC(O)OR$ ($X = Ph$, PhO, $R = Me$, Ph).



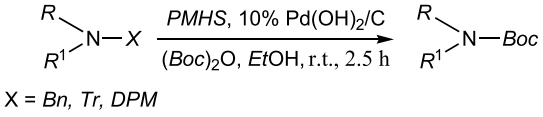
Scheme 42



Scheme 43



Scheme 44



Scheme 45

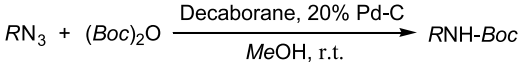
Use of disuccinimidyl carbonate has been reported [59] in an efficient synthesis of functionalized urethanes from azides and alcohols as shown in Scheme 42.

Disuccinimidyl carbonate has also been used [60] in the synthesis of carbamates from amines and alcohols (Scheme 43).

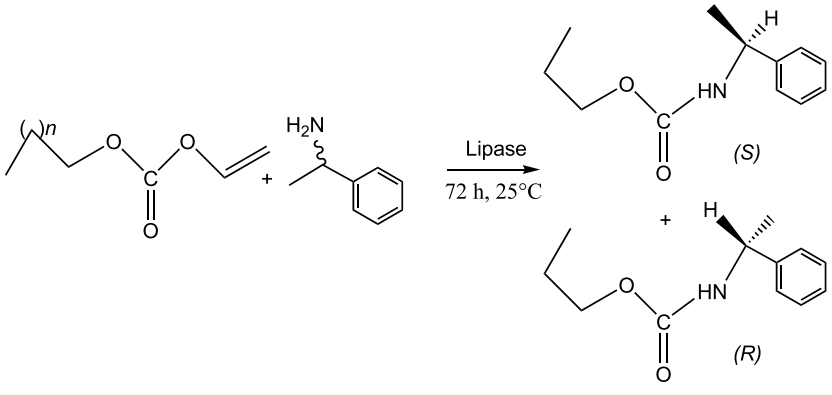
Chandrasekhar et al. [61] have reported an excellent one-pot method for the synthesis of carbamates from azides and benzyl carbamates to *t*-butylcarbamate using the inexpensive and safe hydride source polymethylhydrosiloxane (*PMHS*) under Pd–C catalysis (Scheme 44).

Later on, *Chandrasekhar et al.* [62] reported the synthesis of *t*-butyl carbamates in high yields from the corresponding *N*-benzyl, *N*-trityl, and *N*-diphenylmethyl precursors in a single-step reductive transformation employing *PMHS* and di-*t*-butyl dicarbonate under $Pd(OH)_2/C$ catalysis (Scheme 45).

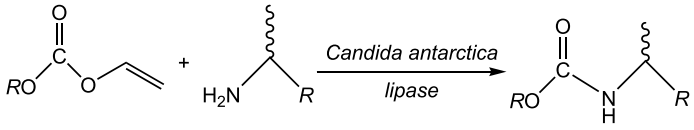
Conversion of azides to *t*-butyl carbamates [63] could also be effected using di-*t*-butyl dicarbonate, decaborane (20 mol%) and 20% Pd–C at room temperature in methanol (Scheme 46).



Scheme 46



Scheme 47



Scheme 48

The enzyme lipase has also been used as a catalyst in the synthesis of chiral carbamates [64] starting from racemic amines and alkyl-vinyl carbonates (Scheme 47).

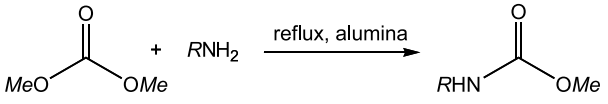
Chiral carbamates [65] have also been synthesized through an enzymatic alkoxy carbonylation reaction with vinyl carbonates and racemic amines using *Candida antarctica* lipase (Scheme 48).

Vauthey et al. [66] have reported the synthesis of carbamates and ureas from the reaction of amines with *DMC* catalyzed by γ-Al_2O_3 in excellent yields (85–100%) (Scheme 49).

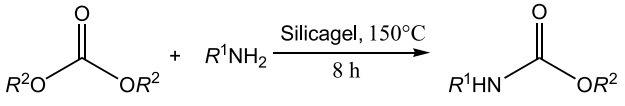
Silicagel [67] has also been used as catalyst in the conversion of carbonates to carbamates (Scheme 50).

Selva et al. [68] have reported the synthesis of carbamate esters from primary aliphatic amines with dialkyl carbonates in supercritical CO_2 (Scheme 51).

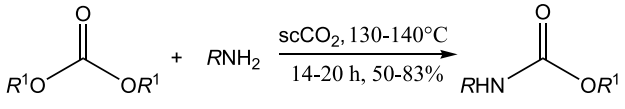
Recently *Curini et al.* [69] have reported that Yb(O*Tf*)$_3$ can be efficiently used for the preparation of carbamates from amines and *DMC* under solvent-free conditions (Scheme 52).



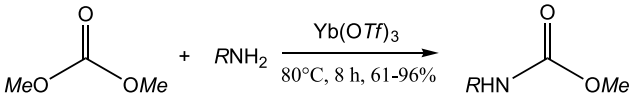
Scheme 49



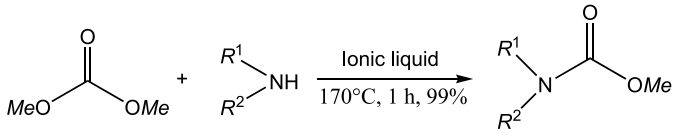
Scheme 50



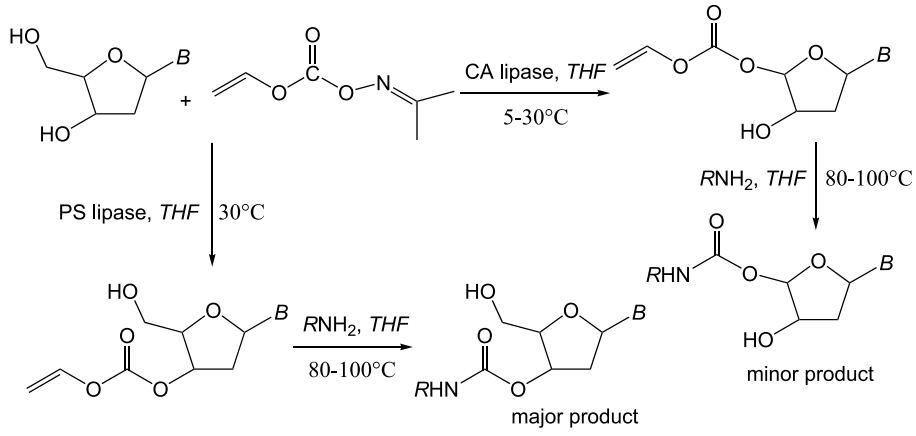
Scheme 51



Scheme 52



Scheme 53



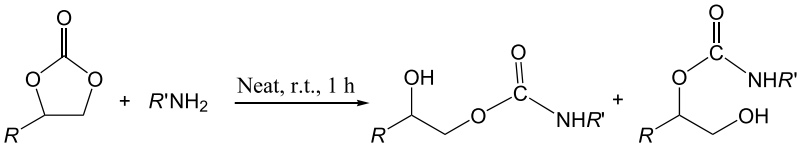
Scheme 54

In the same year, *Sima et al.* [70] have reported the synthesis of carbamates from the reaction of primary and secondary aliphatic amines with *DMC* in ionic liquids (Scheme 53).

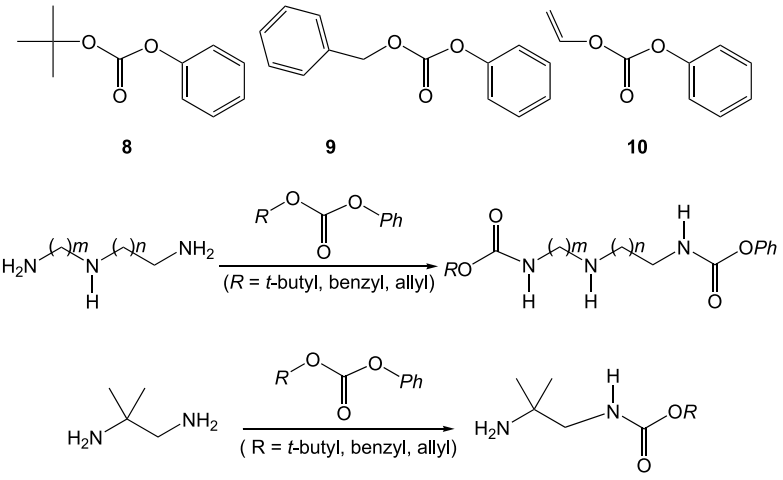
Garcia-Alles et al. [71] have reported the chemoenzymatic synthesis of a 2′-deoxynucleoside urethane. 2′-Deoxynucleoside-5′- and -3′-alkylcarbamates were synthesized in a two step procedure using lipase in the regioselective vinyloxycarbonylation step (Scheme 54). The regioselectivity of the reaction depends upon the type of lipase used. Total regioselectivity is obtained in the presence of PS lipase and only a small amount of the regioselective product is obtained when the reaction is catalyzed by CA lipase.

Iwasaki et al. [72] have reported the synthesis of hydroxyalkyl carbamates from cyclic five-membered carbonates and primary amines at room temperature (Scheme 55).

Pittelkow et al. [73] have recently reported the synthesis of carbamate protected polyamines using alkyl phenyl carbonates. This is an economical, practical and versatile method for selective *Boc*, *Cbz*, and *Alloc* protection of polyamines and amines in the presence of secondary amines. Also, this method allows monocarbamate protection of simple symmetrical aliphatic α, ω-alkanediamines in high



Scheme 55



Scheme 56

yields with respect to the diamine. Furthermore, the method allows selective carbamate protection of a primary amine located on a primary carbon in the presence of a primary amine located on a secondary or a tertiary carbon in excellent yields (Scheme 56). The alkyl phenyl carbonates investigated in this study were *t*-butyl phenyl carbonate (**8**), benzyl phenyl carbonate (**9**), and allyl phenyl carbonate (**10**), which introduce the *Boc*, *Cbz*, and *Alloc* protecting groups.

Conclusion

This review gives a comprehensive survey regarding the synthesis of organic carbamates using cheap, easily available, and harmless reagents as the source of the carbamate functionality, *i.e.* CO_2. Organic carbamates have clearly been demonstrated to be extremely useful and stable reagents, exhibiting unique physical, chemical, and biological properties. Furthermore, in organic synthesis organic carbamates have shown to be a powerful instrument serving mainly as protecting groups for amines as well as synthons for other functional group manipulations. Organic carbamates have become excellent templates for the formation of C–C and carbon-hetero atom bonds. Organic carbamates have also been utilized in the introduction of oxygen moieties as well as in the activation of various functional groups, which allows for a plethora of other applications. Organic carbamates have been frequently employed in organic synthesis for a variety of targets including carbohydrates, nucleosides, natural products, and pharmaceutical substances. In addition, organic carbamates have made a great impact in the fields of polymer science, biology, and medicine. Organic carbamates are used in industry as well and thus made their way into everyday life. This important functional group class, although often overlooked, holds potential and no doubt will offer new and exiting chemistry in the future.

Acknowledgements

The authors are grateful to Dr. *N. Anand* for fruitful discussions.

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