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## Review

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### Use Of Carbon Dioxide In The Synthesis Of Organic Carbamates



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#### ABSTRACT

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 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. © 2006 Trade Science Inc. - INDIA

#### INTRODUCTION

Organic carbamates are the stable class of compounds derived from the unstable carbamic acid by the substitution of amino and ester ends and identified by the presence of O-CO-NH linkage. When carbamate linkage is present in a cyclic system, it is referred to as cyclic carbamates or oxazolidin-2-one.

Carbamation of amines has frequently been utilized in the synthesis of organic carbamates<sup>[1]</sup>, which hold unique applications in the field of pharmaceuticals<sup>[2]</sup> and agriculture<sup>[3]</sup>. Organic carbamates have

also been played an important role in the area of synthetic organic chemistry, particularly as synthetic intermediates<sup>[4]</sup>, for the protection of amino groups in peptide chemistry<sup>[5]</sup>, and as linkers in combinatorial chemistry<sup>[6]</sup>. Functionalization of amines as carbamates offers an attractive method for the generation of derivatives, which may have interesting medicinal and biological properties<sup>[7]</sup>. However, the scope of existing methodologies for carbamate formation are limited by the need of specialized reagents and an operational complexity due to the use of either toxic or cumbersome reagents, such as phos-

# Review

gene<sup>[8]</sup>, its derivatives<sup>[9]</sup>, and carbon monoxide<sup>[10]</sup>. 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<sup>[11]</sup> or supercritical<sup>[12]</sup> state or in an electrochemical process<sup>[13]</sup>. Besides, it has also been used for C-C, C-N, and C-O bond forming reactions<sup>[14]</sup>. In the present review we-

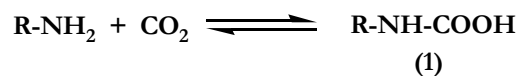
## 2. Classification of Carbamates

Classification of carbamates (figure 1) will focus on the synthesis of organic carbamates using various conditions and forms of carbon dioxide.

## 3. Synthesis of carbamates using carbon dioxide

### 3.1 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).



SCHEME 1

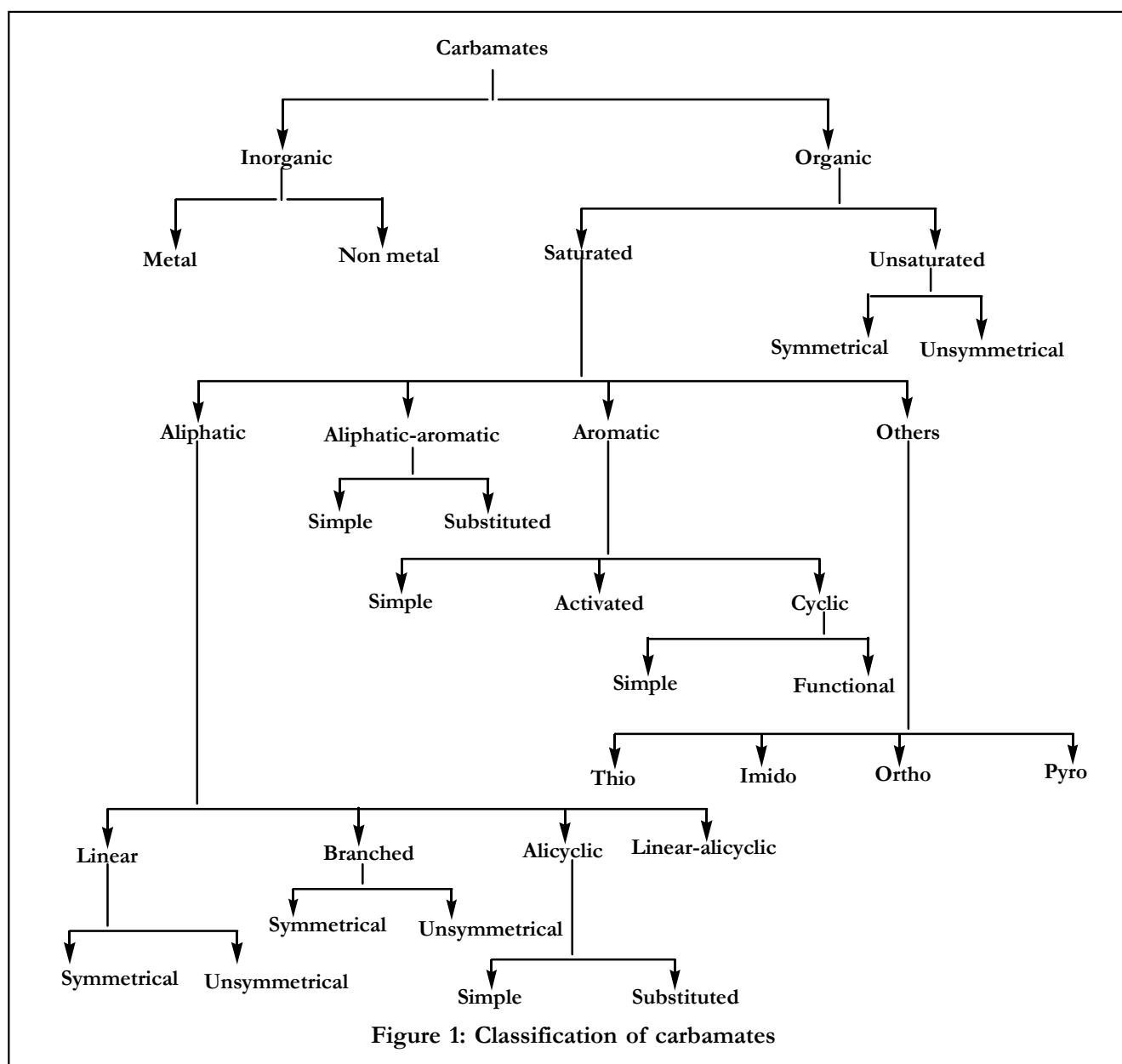
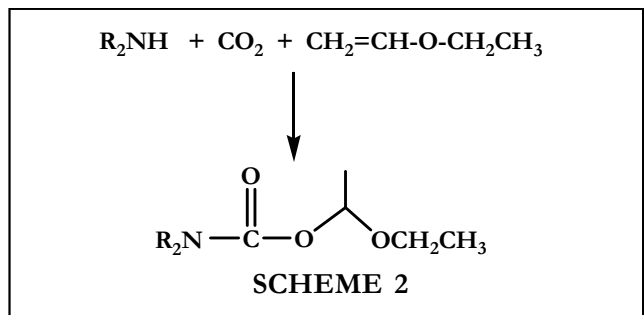


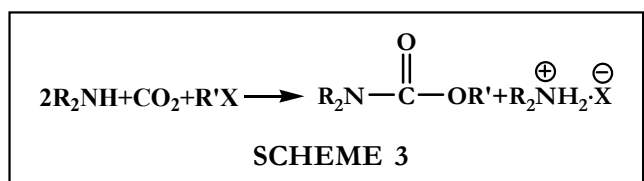
Figure 1: Classification of carbamates

## Review

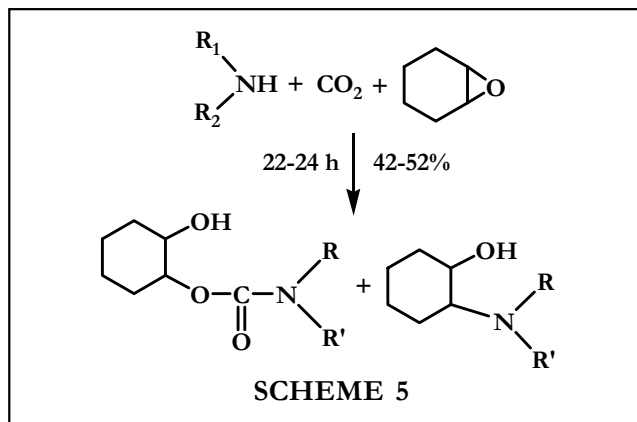
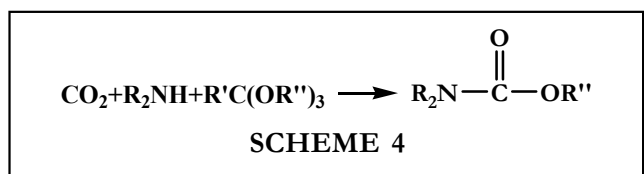


However, Yoshida et al.<sup>[15]</sup> have reported the synthesis of carbamates from  $\text{CO}_2$ , amines, and unsaturated ethers (SCHEME 2). But in this method only secondary aliphatic amines could be used. Moreover, it takes long reaction times ( $\sim 70$ - $80$  h) and it results in low yields (3-12%).

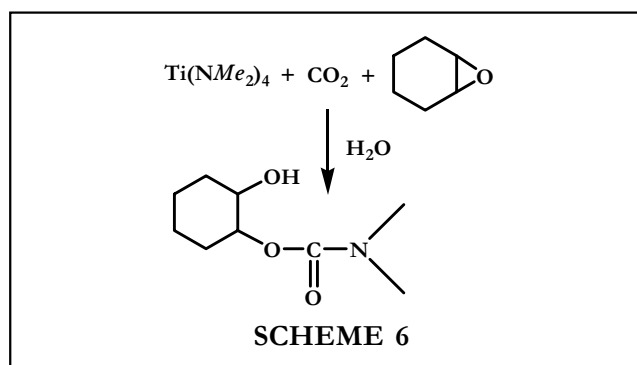
Later on, Yoshida et al.<sup>[16]</sup> have also reported a carbamate esters synthesis starting from  $\text{CO}_2$  and using two equivalents of amine and an alkyl halide in a one-pot reaction (SCHEME 3). This method is also limited to primary and secondary aliphatic amines, takes long reaction times ( $\sim 45$  h), and the carbamates are obtained in only 6-25% yields.



Later on, Ishii et al.<sup>[17]</sup> have reported the synthesis of carbamates from the  $\text{CO}_2$  and ortho esters (SCHEME 4). This reaction takes long reaction times, but is useful for the carbamates derived from primary and secondary amines.



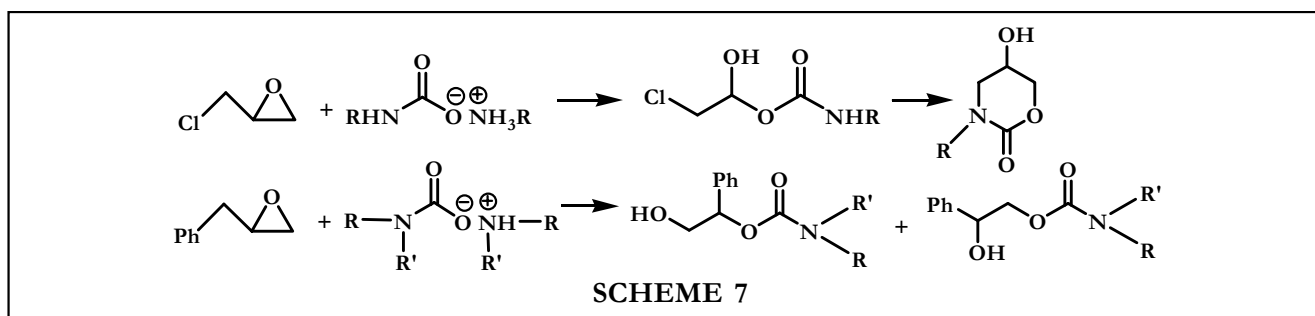
Mono-carbamates of 1,2-diols from the corresponding 1,2-epoxides have been prepared<sup>[18]</sup> by reaction with  $\text{CO}_2$  and primary and secondary aliphatic amines (SCHEME 5). However, about half of the epoxide is lost due to the accompanying nucleophilic ring opening by the amine.



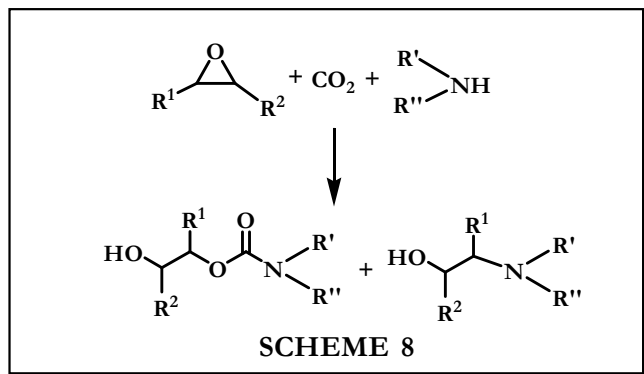
The mono-carbamates could also be obtained from an epoxide using tetrakis(dimethyl)-titanium (IV) and  $\text{CO}_2$  (SCHEME 6)<sup>[19]</sup>. But this reaction was not satisfactory due to its long reaction time ( $\sim 3$ - $4$  d) and low yields (5-20%).

Similarly, chloromethyl oxirane or phenyl oxirane on reaction with  $\text{CO}_2$  and aliphatic amines in methanol gave carbamates (2-17%) (SCHEME 7)<sup>[20]</sup>.

Later on, better yields have been reported by

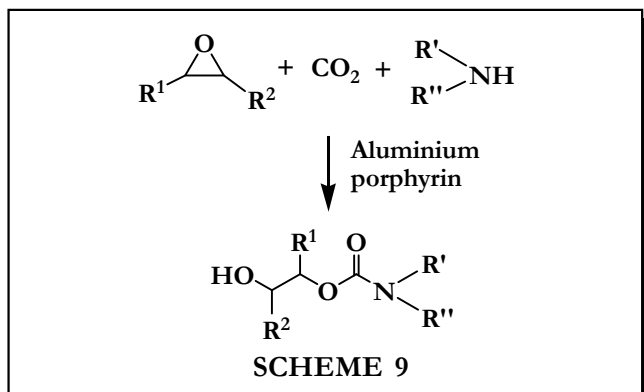


# Review

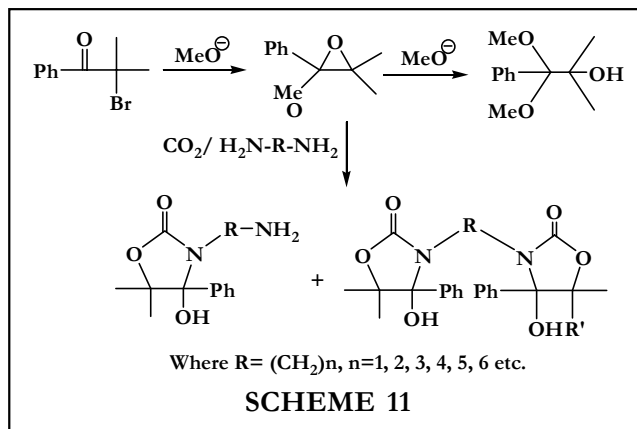
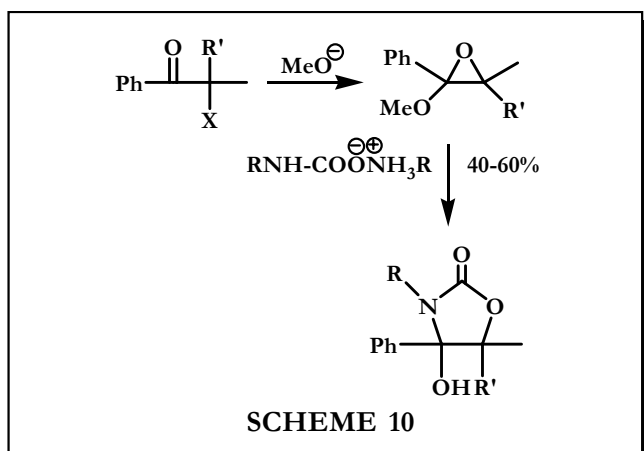


Yoshida et al.<sup>[21]</sup> (SCHEME 8). However, the latter syntheses suffer from leading to isomer mixtures

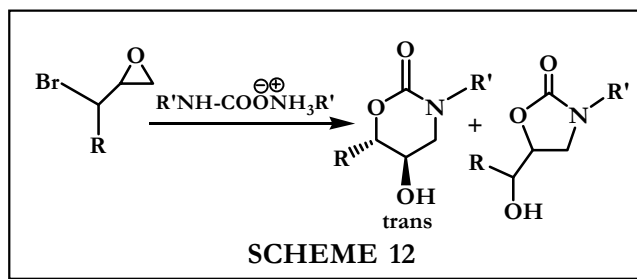
Kojima et al.<sup>[22]</sup> have reported carbamates synthesis from epoxides, amines, and CO<sub>2</sub> where the latter was previously fixed on an aluminium porphyrin (SCHEME 9).



Toda et al.<sup>[23]</sup> have reported the synthesis of cyclic carbamates (i.e. oxazolidinones). Reaction of carbon dioxide with  $\alpha$ -bromoacylophenones in the presence of aliphatic primary amines in methanol afforded 3-alkyl-4-hydroxy oxazolidone-2 derivatives under mild conditions (SCHEME 10).

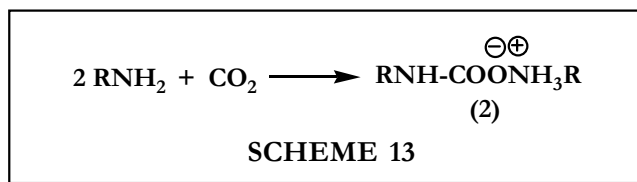


This reaction led to the formation of bis(2-oxazolidinones)<sup>[24]</sup> when 2-methoxy 3,3-dimethyl-2-phenyloxirane or  $\alpha$ -bromo-i-butyrophenone was reacted with CO<sub>2</sub> and aliphatic  $\alpha,\omega$ -diamines (SCHEME 11).



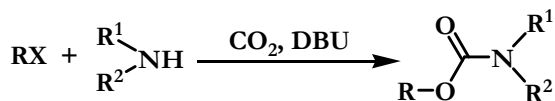
Reaction of 2-(1-haloalkyl)-oxiranes with carbon dioxide and aliphatic primary amines gave five- and six-membered cyclic carbamates<sup>[25]</sup> (SCHEME 12).

In the above reaction it was shown that there are ionic species **2** involved which is formed from 2 mol amine reacting with CO<sub>2</sub> as shown in SCHEME 13.

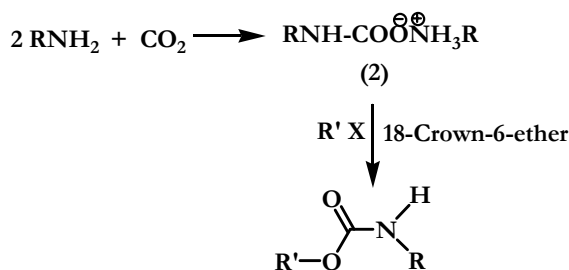


An improvement in the yields of carbamate formation has been achieved by using different basic reagents, which help in the stabilization of the intermediate ionic species **2**. Thus, Hori et al.<sup>[26]</sup> have reported the synthesis of organic carbamates from primary and secondary amines, CO<sub>2</sub>, and alkyl halides in the presence of a strong proton acceptor like DBU (SCHEME 14).

# Review



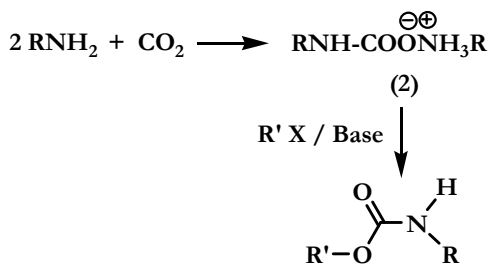
SCHEME 14



SCHEME 15

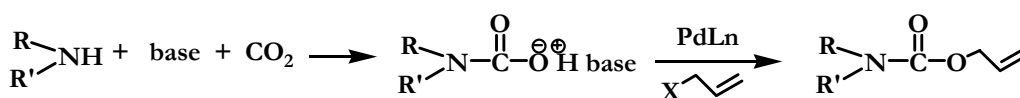
Aresta et al.<sup>[27]</sup> have reported a carbamate synthesis from the ionic species **2** by alkylation with alkyl halides using 18-Crown 6-ether as a phase transfer catalyst (SCHEME 15).

However, this method is useful for the preparation of carbamate esters of only 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.<sup>[28]</sup>. In presence of alkylating agents this leads to the formation of carbamates (SCHEME 16) in good yields (40-78%).



SCHEME 16

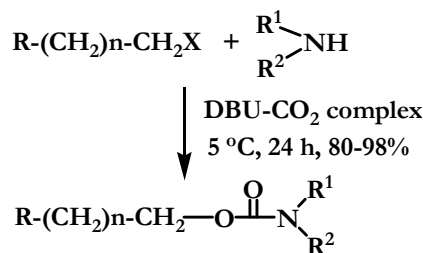
O-Allyl carbamate<sup>[29]</sup> could be obtained by the addition of preformed carbamate ion  $[\text{R}'\text{R}'\text{NH}-\text{COO}^{\ominus}\text{H}^{\oplus}\text{Base}]$  generated from various primary and secondary amines and  $\text{CO}_2$ , to a THF solution of allylic



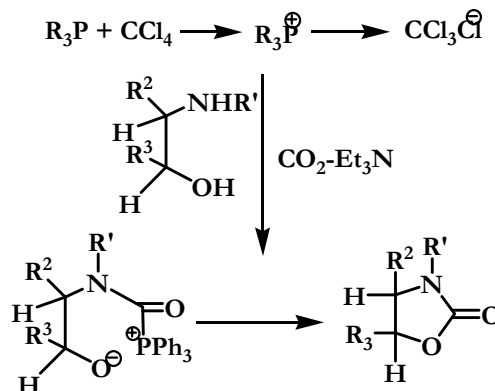
SCHEME 17

chlorides under 800-100 psig carbon dioxide at room temperature containing a palladium/phosphine catalyst in 66-100% yields (SCHEME 17).

Recently, Perez et al.<sup>[30]</sup> have reported the synthesis of N-alkyl carbamates in good to excellent yields by a clean and mild transcarboxylation of several amines with the previously synthesized DBU- $\text{CO}_2$  complex and subsequent O-alkylation by different alkyl halides (SCHEME 18).



SCHEME 18

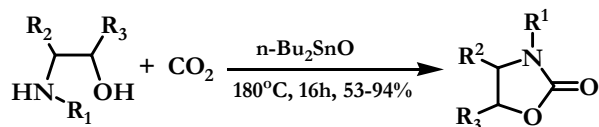


SCHEME 19

Cyclic urethanes<sup>[31]</sup> could be obtained in good yields (33-93%) under mild conditions from amino alcohols and carbon dioxide using phosphorus(III) reagents [i.e.  $\text{Ph}_3\text{P}$ ,  $(\text{PhO})_3\text{P}$ ] and halogenoalkanes (i.e.  $\text{CCl}_4$  and  $\text{CCl}_3\text{CCl}_3$ ) (SCHEME 19).

Tominaga et al.<sup>[32]</sup> have reported the synthesis of 2-oxazolidinones from  $\text{CO}_2$  and 1,2-amino alcohols catalyzed by  $n\text{-Bu}_2\text{SnO}$  (SCHEME 20). The dehydrative condensation of 1,2-aminoalcohols with  $\text{CO}_2$  was found to proceed in NMP as the solvent. 2-

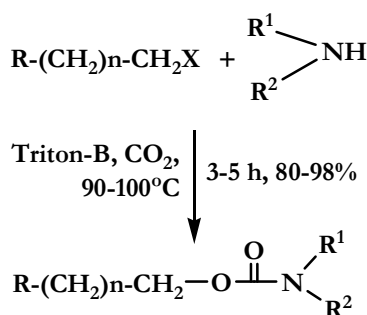
# Review



SCHEME 20

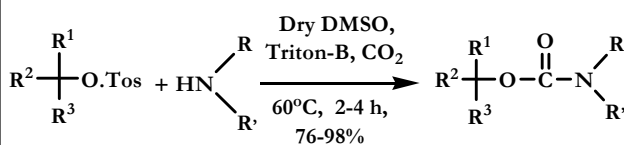
Oxazolidinones were obtained in 53-94% yields when the commercially available  $n\text{-Bu}_2\text{SnO}$  was used as the catalyst.

Recently, we have reported<sup>[33]</sup> an efficient, one-pot, high yielding carbamate synthesis from  $\text{CO}_2$ , amines, and alkyl halides using Triton-B as the catalyst (SCHEME 21).

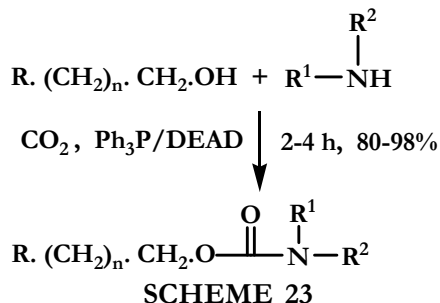


SCHEME 21

We have also reported<sup>[34]</sup> the synthesis of carbamates in high yields from a variety of alcoholic tosylates and amines using the Triton-B/ $\text{CO}_2$  system (SCHEME 22).



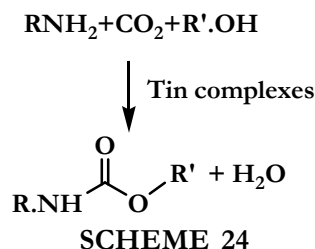
SCHEME 22



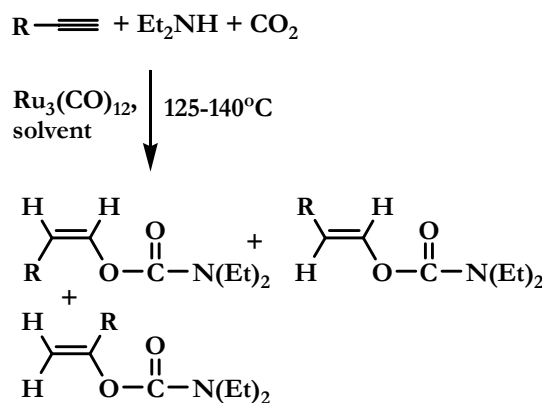
SCHEME 23

A direct synthesis in high yields of carbamates from primary alcohols and amines using Mitsunobu's reagent/ $\text{CO}_2$  system was reported by our group<sup>[35]</sup> (SCHEME 23).

Recently, carbon dioxide has been converted into carbamates<sup>[36]</sup> through reaction with amines and alcohols catalyzed by tin complexes. The addition of acetals as dehydrating agent under high  $\text{CO}_2$  pressure is the key to achieve high yields (SCHEME 24).

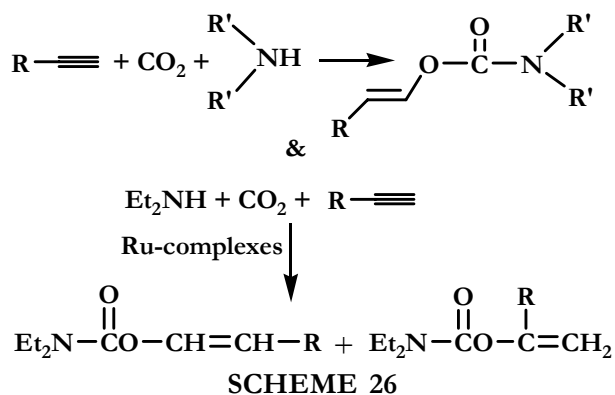


SCHEME 24



SCHEME 25

Vinyl carbamates<sup>[37]</sup> have been synthesized from  $\text{CO}_2$ , diethylamine and alkynes in presence of a ruthenium catalyst (SCHEME 25).

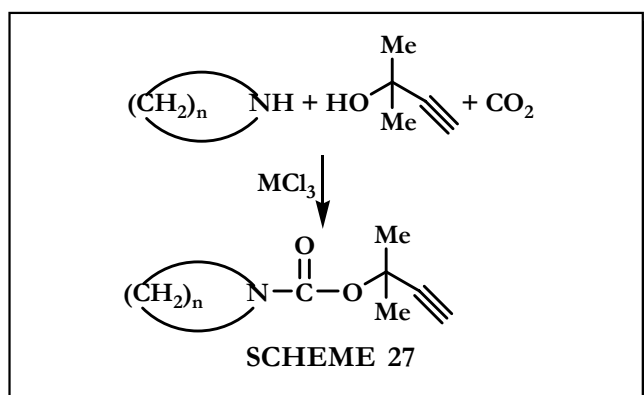


SCHEME 26

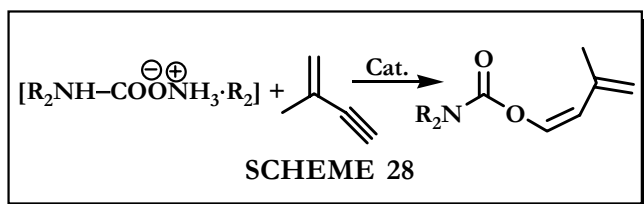
# Review

Better yields of vinyl carbamates<sup>[38]</sup> were obtained using CO<sub>2</sub> and ruthenium complexes [i.e. RuCl<sub>2</sub>(PR<sub>3</sub>)carene) and RuCl<sub>2</sub>(norborna diene) (pyridine)<sub>2</sub>] (SCHEME 26).

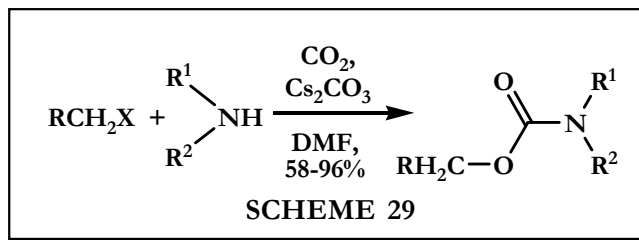
Shim et al.<sup>[39]</sup> have synthesized of carbamates from amines, acetylenic alcohols, and carbon dioxide using a lanthanide catalyst. Thus the reaction of perhydro-azepine with 3,3-dimethyl prop-1-yne-3-ol and CO<sub>2</sub> in presence of MCl<sub>3</sub> (M=Ce, Pr, Nd, Gd) gave carbamates (n=6) in 20-38% yields. They have also prepared the carbamates (n=4, 5) in 31 and 21% yields (SCHEME 27).



Regioselective synthesis of O-1-(1,3-dienyl) carbamates<sup>[40]</sup> was carried out by regioselective addition of CO<sub>2</sub> and secondary amines to isopropenyl acetylene in the presence of  $[Ph_2P(CH_2)_n PPh_2]Ru(\eta^3-CH_2-C(Me)=CH_2)_2$  catalyst (SCHEME 28).

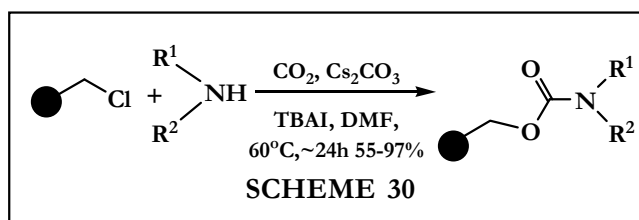


Carbon dioxide providing the carbonyl functionality for the carbamates is not sufficient itself for the excellent production of carbamates. The basicity of the ionic species **2** is increased by adding basic reagents. Furthermore, it has been proposed that metal carbonates, like Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, Cs<sub>2</sub>CO<sub>3</sub> etc. are good basic reagents, which could provide carbonyl functionality in addition to its basic properties. Based on this concept there are many reports on the use of metal carbonates for carbamate synthesis. Thus, Butcher<sup>[41]</sup> have reported a carbamate synthe-

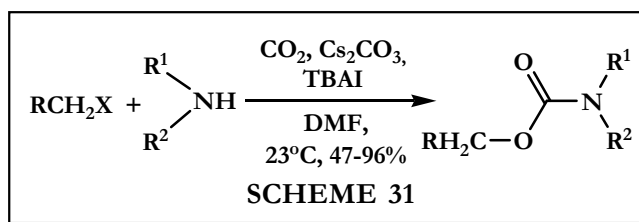


sis in good to excellent yields (58-96%) from alkyl halides using the cesium carbonate/CO<sub>2</sub> system (SCHEME 29).

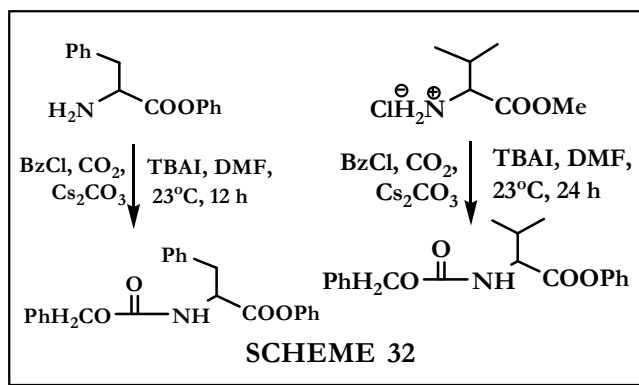
Later on, Salvatore et al.<sup>[42]</sup> have reported a carbamate synthesis on a solid phase Merrifield resin in good to excellent yields using cesium carbonate/CO<sub>2</sub> and TBAI as phase transfer catalyst (SCHEME 30).



Carbamate<sup>[43]</sup> synthesis was also carried out in solution using aliphatic, aromatic, and heterocyclic amines in a cesium carbonate/CO<sub>2</sub> system in presence of a catalytic amount of TBAI (SCHEME 31).

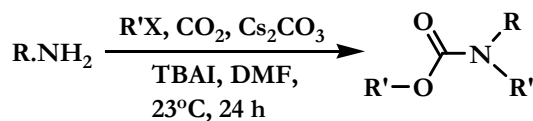


Besides using different amines they have also used the same technique in peptidomimetic synthesis (SCHEME 32).



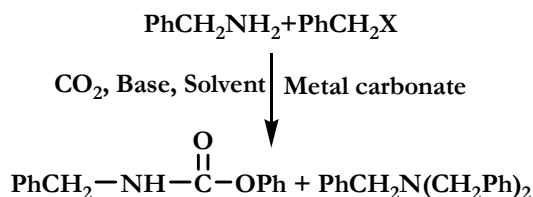
## Review

A direct synthesis of N-alkyl carbamates from primary amines, and alkyl halides using the cesium carbonate/ $\text{CO}_2$  system has been reported<sup>[44]</sup> by Salvatore et al. (SCHEME 33).



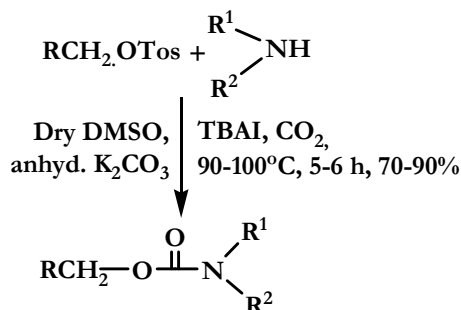
SCHEME 33

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  $\text{CO}_2$  and different metal carbonates and bases have been reported by Shi Min et al.<sup>[45]</sup> (SCHEME 34).



SCHEME 34

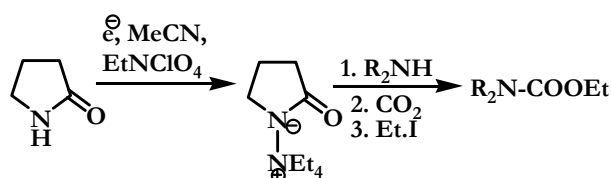
We have reported<sup>[46]</sup> a convenient, high yielding, one-pot synthesis of carbamate esters in very good yields (70-90%) from alcoholic tosylates and amines using the  $\text{K}_2\text{CO}_3/\text{CO}_2$  system in presence of a catalytic amount of tetra-n-butylammonium iodide (SCHEME 35). This method has been used for carbamate esters starting from aliphatic primary, secondary, and aromatic amines.



SCHEME 35

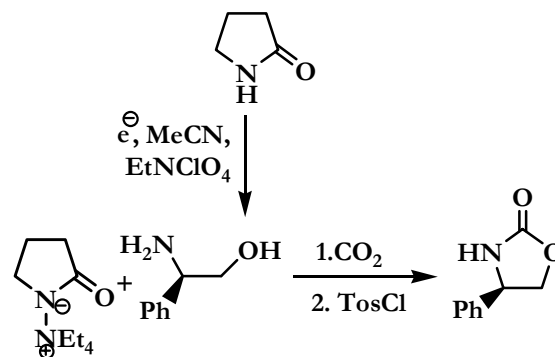
### 3.2 Electrochemical Synthesis Using Carbon dioxide

Inesi et al.<sup>[47]</sup> have reported carbamate synthesis by using the carbon dioxide 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  $\text{Et}_4\text{N}^+$  cation) followed by sequential addition of  $\text{CO}_2$  and ethyl iodide.



SCHEME 36

Recently Inesi et al.<sup>[48]</sup> have reported an improved electrochemical synthesis of chiral oxazolidin-2-ones from chiral 1,2-amino alcohols. They are obtained by direct electrolysis of a solution of MeCN-TEAP containing the amino alcohol with subsequent  $\text{CO}_2$  bubbling and addition of TosCl. This synthesis avoids any addition of bases or probases and oxazolidinones are obtained in high yields (SCHEME 37).



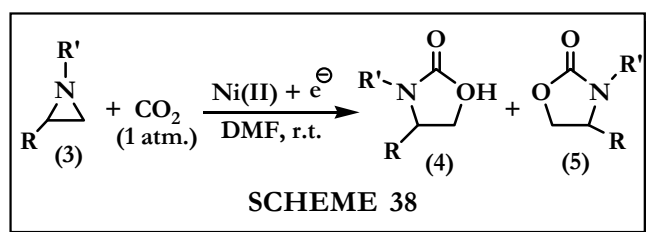
SCHEME 37

A new and selective method of 2-oxazolidinone synthesis using a simple electrochemical procedure by which the cyclic carbamate **4** and **5** can be obtained in good yields from the direct reaction of substituted aziridines **3** with  $\text{CO}_2$  has been recently reported<sup>[49]</sup>. Carbon dioxide insertion into the C-N bond takes place under very mild conditions at room temperature and with atmospheric carbon dioxide pres-



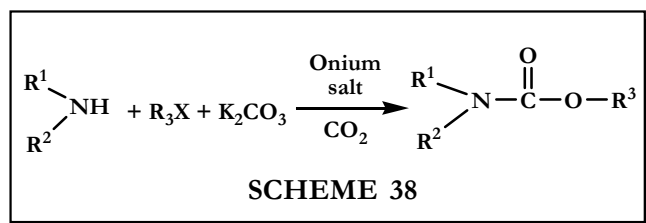
# Review

sure. The reaction was catalyzed by a Ni(II) complex (10 mol%) and was carried out in a single compartment cell fitted with a consumable magnesium 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<sub>2</sub> 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 a very low yield of cyclic carbamates was obtained (<10%).



### 3.3 Supercritical Carbon Dioxide

Yoshida et al.<sup>[50]</sup> have reported the synthesis of carbamates in good yields from amines and alkyl halides using supercritical CO<sub>2</sub>, the potassium carbonate system, and tetra-n-alkylammonium halides acting as phase transfer catalyst (SCHEME 39). They have also demonstrated the effect of different catalysts on carbamates synthesis



### CONCLUSION

This review gives a comprehensive survey regarding the synthesis of organic carbamates using cheap, easily available, and harmless reagents as the source of carbamate the functionality i.e. CO<sub>2</sub>. Organic carbamates have clearly been demonstrated to be extremely useful and stable reagents, exhibiting unique physical and chemical and biological properties. Furthermore, in organic synthesis, organic car-

bamates 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 have been utilized 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.S.Ray for his fruitful discussions.

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