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Recent Developments on the Carbamation of Amines

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Abstract: Organic carbamates represent an important class of compounds showing various interesting properties. They find wide utility in various areas as pharmaceuticals, agrochemicals (pesticides, herbicides, insecticides, fungicides *etc.*), intermediates in organic synthesis, protection of amino group in peptide chemistry, and as linker in combinatorial chemistry *etc*. Classical synthesis of carbamates involves use of harmful reagents such as phosgene, its derivatives and carbon monoxide. Recently, various kinds of synthetic methods have been developed for the synthesis of organic carbamates. In the present review, I would like to highlight the recent developments on the synthesis of organic carbamates using variety of reagents.

Keywords: Carbamation, amines, carbamates.

1. INTRODUCTION

Organic carbamates are the stable class of compounds derived from the unstable carbamic acid (H_2N-COOH) by the substitution of amino and acid ends through the various kinds of structurally diverse alkyl/aryl, aryl-alkyl or substituted alkyl/aryl and aryl-alkyl groups, and are identified by the presence of the linkage O-CO-NH- [1, 2]. When the carbamate linkage is present in a cyclic system, this class of compounds is referred to as cyclic carbamates [3]. When the carbamate group is attached with any inorganic atom either metal or non metal, such compounds are referred to as inorganic carbamates [4].

The reaction of carbamation of amines has frequently been utilized in the synthesis of organic carbamates which holds unique applications in the field of pharmaceuticals [5], agrochemicals (pesticides, herbicides, insecticides, fungicides *etc.*) [6], intermediates in organic synthesis [7], for the protection of amino groups in peptide chemistry [8], as linkers in combinatorial chemistry [9] *etc.* Functionalization of amines as carbamates offers an attractive method for the generation of derivatives, which may have interesting medicinal and biological properties [10]. Organic carbamates have been extensively used as useful synthons for the synthesis of structurally diverse synthetic intermediates/molecules of biological significance [11]. Therefore, considerable interest has been generated in the recent past for the development of efficient and safe methodologies for carbamate esters synthesis.

Organic carbamates have frequently been employed as demandable pharmaceuticals in the forms of drugs and prodrugs [12]. In recent years, several reports have indicated that carbamate linkage present in between the active pharmacophores of various structurally diverse molecules increases manifold biological activities of semisynthetic/synthetic natural/synthetic molecules [13]. Further-

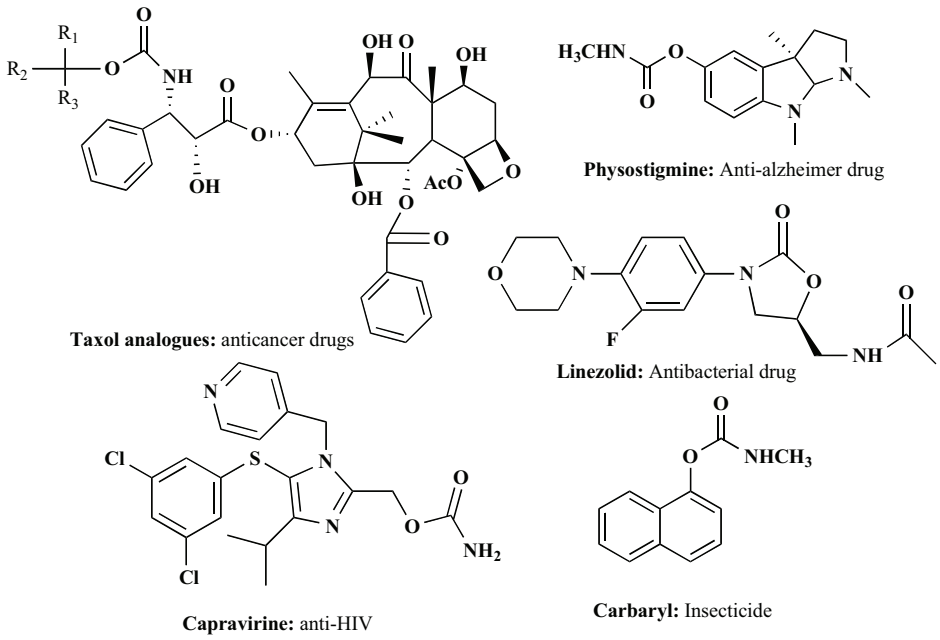

Fig. (1). Biologically active drug molecules bearing carbamate linkage.

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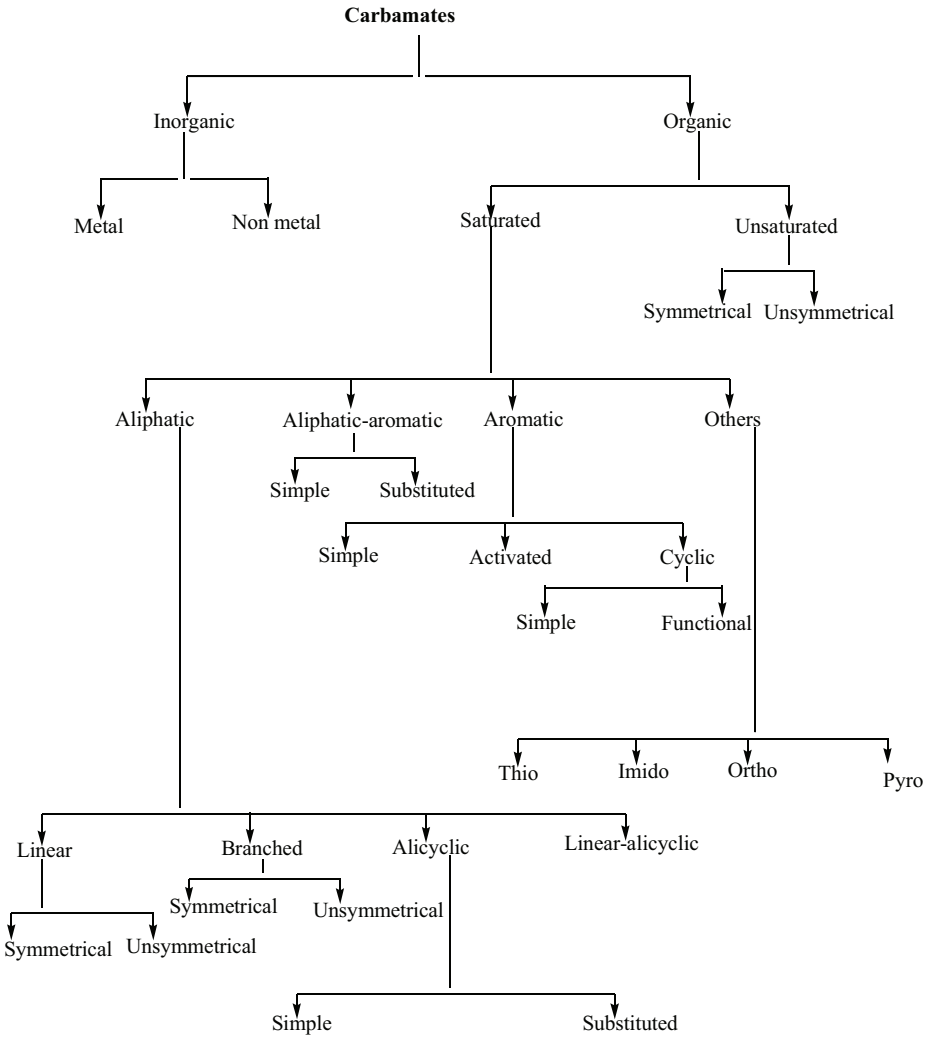


Fig. (2). Classification of carbamates.

more, the role of carbamate linkage have been extensively studied in structurally diverse natural/semisynthetic molecules against various disease such as anti-cancer, anti-bacterial, anti-fungal, anti-malarial, anti-viral, anti-HIV, anti-estrogenic, anti-progestational, anti-osteoporosis, anti-inflammatory, anti-filarial, anti-tubercular, anti-diabetic, anti-obesity, anti-convulsant, anti-helminthes, Alzheimer disease, CNS and CVS active *etc* [14, 15, 13, 5]. Some of the important biologically active drug molecules bearing carbamates have shown in Fig. (**1**).

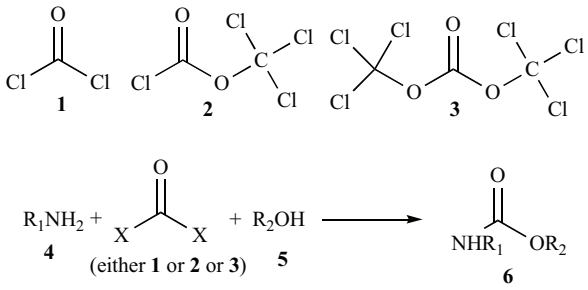
2. CLASSIFICATION OF CARBAMATES

Carbamates can be mainly classified into two groups, namely inorganic and organic. Depending upon the structural variations on the attached moieties they are further classified as shown in Fig. (**2**).

3. METHODS OF PREPARATION

3.1. Phosgenation Technique

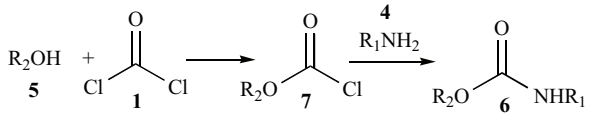
Phosgene (**1**) is a potentially useful, versatile building block in organic synthesis [16]. It offers the possibility of binding two nucleophilic units to the same carbon atom and such two-component system is particularly well suited for the combinatorial synthesis of carbonate, ureas and carbamate (Scheme **1**). Phosgene is extremely toxic which limits its use. Safer substitutes have been proposed such as 1,1,1-Trichloromethylformate (Diphosgene, **2**) [17], and *bis*-(1,1,1-trichloromethyl) carbonate (Triphosgene **3**) [18], which are frequently used in recent years. Depolymerization of **3** into **1** has widely replaced phosgene by triphosgene, which is relatively safer to use [19]. Thus, carbamates **6** synthesis has been achieved through the reaction of an amine **4** with an alcohol **5** using either **1**, or **2** or **3** as source of carbonyl equivalent (Scheme **1**).



Scheme 1.

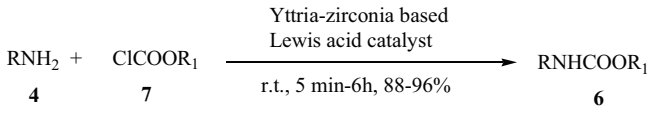
Chloroformates and isocyanates are intermediates produced from phosgene, have frequently been employed in the synthesis of organic carbamates. Chloroformates [20] **7**, can be obtained through the reaction of alcohol/phenol **5** with phosgene **1**, reacts with

amines/substituted amines **4** (*i.e.* aminolysis) afforded carbamates [21] **6** (Scheme **2**). Carbamates synthesis through the chloroformates route has been achieved using different reaction conditions such as use of strong bases [22] (NaOH, $NaHCO_3$, Et_3N, pyridine and triphenylphosphene), metals [23], ultrasound [24], *bis*(trimethylsilyl)acetamide [21] in combination with azides [23].



Scheme 2.

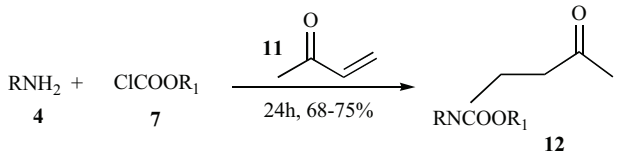
In recent years, there has been much attention on the synthesis of carbamates using chloroformates as key intermediate. Thus, Pandey *et al* have reported [25] an efficient synthesis of carbamates **6** through the reaction of variety of amines **4** with chloroformates **7** using catalytic amount of Yttria-Zirconium based Lewis acid catalyst (Scheme **3**).



Scheme 3.

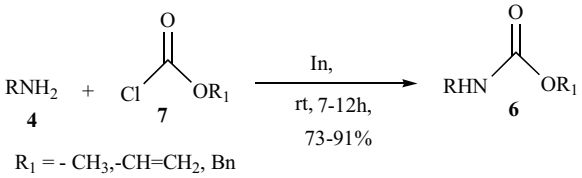
Later on, Mormeneo *et al* have reported [26] a versatile method for the synthesis of carbamates **6** through an *in-situ* generated polymer supported chloroformate resin **9**. Bis-trichloromethyl carbonate (BTC) has been used as a phosgene equivalent to afford a supported chloroformate **9**, which on sequential one-pot reaction of variety of alcohols **5** with amines **4** afforded the corresponding carbamates **6** in high yields (Scheme **4**).

ketone **11** in the presence of Sn^{4+} modified Zeolite Hβ (Hβ-SnA) at room temperature (Scheme **5**).



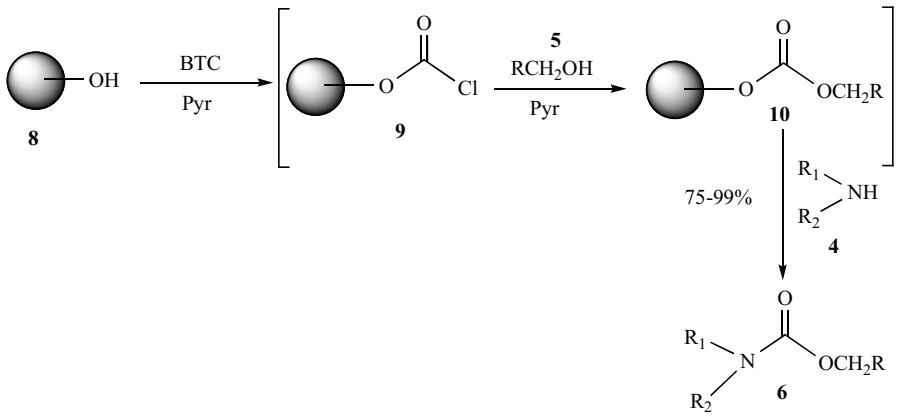
Scheme 5.

More recently, Kim and Jung have reported [28] a simple and efficient synthesis of carbamates **6**, through reacting equimolar amounts of amines **4**, chloroformates **7**, and Indium metal (Scheme **6**). Thus, carbamates of structurally diverse substituted aliphatic, aromatic, heterocyclic amines were prepared using various kinds of chloroformates.

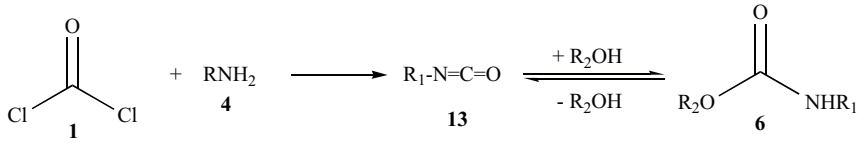


Scheme 6.

Isocyanates [29] **13**, obtained through the reaction of phosgene **1** and amines **4**, react with hydroxy compounds **5** (*i.e.* alcohols/phenols) afforded the corresponding carbamates (Scheme **7**) [30]. Polyurethanes [31], the building blocks of isocyanates have been used in industry. Synthesis of carbamates starting from isocyanates could be achieved through the use of strong bases [32], and metal halides [33] *etc.* Carbamates could be converted into isocy-



Scheme 4.



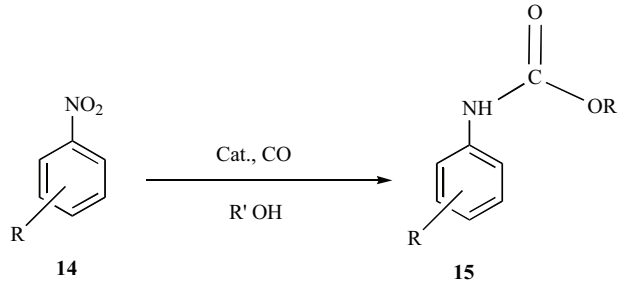
Scheme 7.

Raje *et al* have reported [27] an efficient, one-pot synthesis of *N*-substituted (3-oxobutyl) carbamates **12**, *via* tandem condensation of primary amines **4**, with methyl chloroformate **7** followed by the conjugate addition of the resulting carbamates with methyl vinyl anates by thermal decomposition at higher temperatures using different reaction conditions such as use of metal catalysts [34], chlorocatecholborane/boron halides with triethylamine [35], silanes [36], chlorosilanes [37], dichlorosilanes [38], Mitsunobu's reaction

conditions [39], montmorillonite K-10 [40], Bi_2O_3 [41], and recently used basic metal oxide nanoparticles [42] *etc*.

3.2. Reductive Carbonylation of Nitro-aromatics

The reductive carbonylation of aromatic nitro-compounds **14** to the corresponding carbamates is an interesting approach towards synthesis of carbamates **15** (Scheme **8**) [43]. The carbonylation reaction of nitro-aromatics is an exothermic reaction and is catalyzed by palladium, ruthenium, and to a lesser extent rhodium. Furthermore, platinum [44], iridium [45], and iron [46] have also been reported to be active in this reaction.



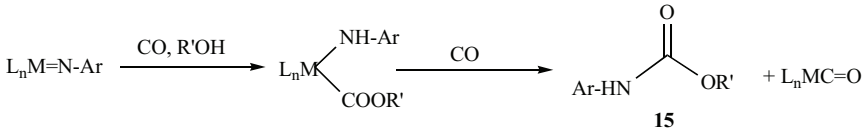
Scheme 8.

For a reductive carbonylation of aromatic nitro-compounds carried out in alcohol, it might generally be considered that the carbamate **15** is formed by reaction of aromatic isocyanates ArNCO, with an alcohol R-OH, outside the coordination sphere of the metal [47]. However, Cenini has found in the case of $Ru_3(CO)_{12}$ with NEt_4Cl as a cocatalyst that the alcohol participates in the catalytic cycle, since when it was absent, practically no isocyanate was obtained (Scheme **9**).

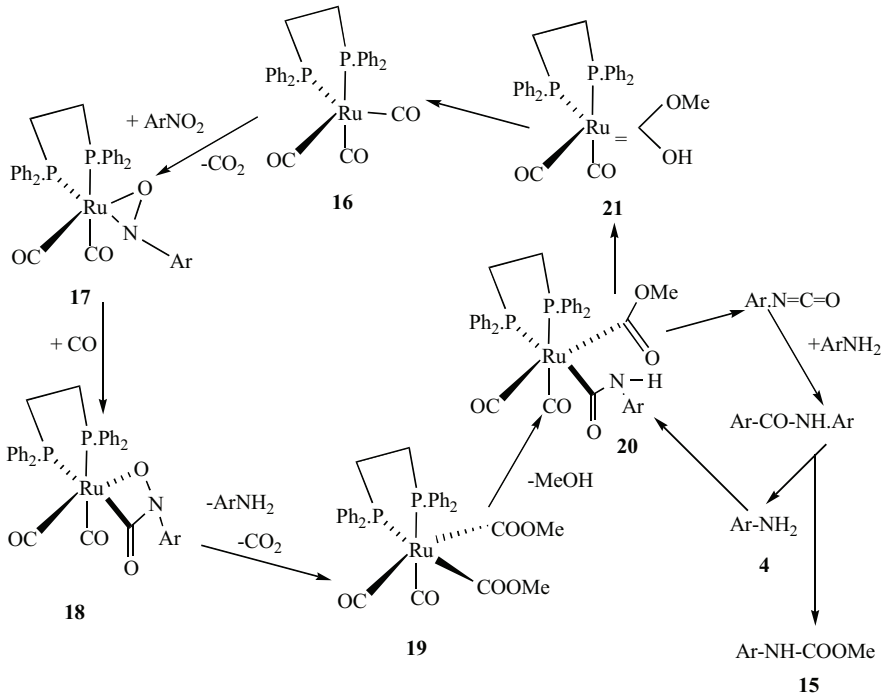
Several reports have been published by Gladfelter and Cenini giving more insight into the mechanism of the catalytic cycle of the rhodium and ruthenium catalysts. Gladfelter [48] has proposed a mechanism using Ru(dppe) $(CO)_3$ **16** (dppe = *bis*(diphenylphosphene)-ethane as a catalyst, in which an aromatic amine **4** is suggested as a linker intermediate (Scheme **10**).

Very similar results were obtained by Cenini using $[(PPh_3)_2N][Rh(CO)_4]$ **22** as a catalyst (Scheme **11**) [49].

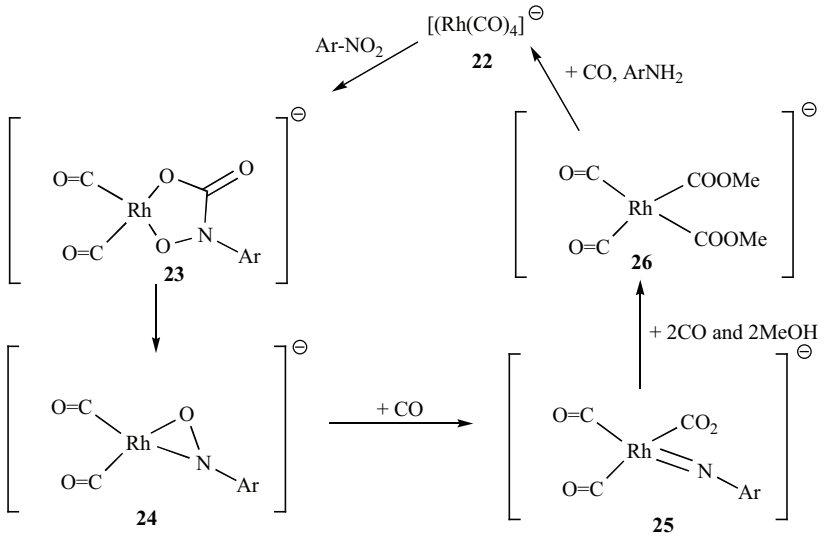
Most previously reported catalytic systems for the reductive carbonylation of aromatic nitro-compounds usually have employed corrosive Lewis acids and or a base [50] such as pyridine or triethylamine in excess amounts. For example, supported palladium is inactive in the absence of a Lewis acid even in the presence of an excess of pyridine, whereas $PdCl_2$ exhibits, good activity in the absence of Lewis acids but requires excess of base. Palladium (II) complexes of the type $[Pd(Py)_2Cl_2]$ can catalyze the reaction at low Py:Pd ratio but the method requires promotors such as $FeCl_3$ or $MoCl_5$ and aprotic solvents such as chlorobenzene [51]. On the other hand reductive carbonylation of aromatic nitro-compounds could be catalyzed by palladium anchored to montmorillonite [52], supported Pd-1,10-phenanthroline derivatives in the presence of a Bronsted acid [53] Pd complexes with 1,10-phenanthroline derivatives [54], and Pd heteropolyanion is an approach to this problem. In addition to this ruthenium carbonyl complexes such as $Ru_3(CO)_{12}$ or $Ru(CO)_3(PPh_3)_2$ are efficient homogeneous catalysts in



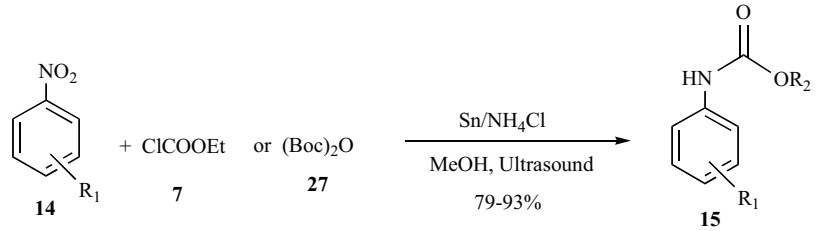
Scheme 9.



Scheme 10.



Scheme 11.

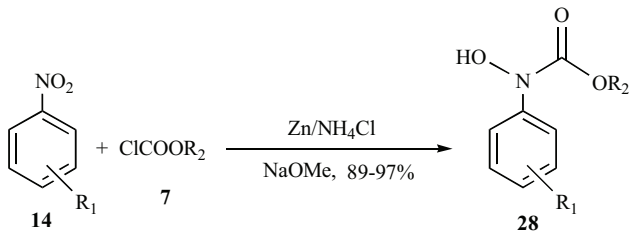


Scheme 12.

the reductive carbonylation of aromatic nitro-compounds to carbamates if additives such as alkylammonium salts [55] chelating ligands [56] or anilines [57] are used. Palladium [58] has been often applied as catalyst in the homogeneous and heterogeneous catalyst systems. Rhodium [59] catalysts also have been applied less often to the reductive carbonylation of nitrobenzene than ruthenium and palladium catalysts.

Chandrasekhar *et al* have reported [24] an efficient protocol for the synthesis of carbamates **15** through reductive carbonyltion of aromatic-nitro compounds **14** with either $(Boc)_2O$, or ClCOOEt using Sn/NH_4Cl system under ultrasound radiation (Scheme **12**).

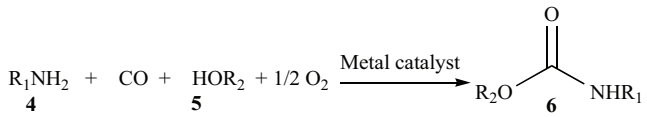
More recently, Tomkinson and coworkers have reported [60] an efficient protocol for the synthesis of *N*-aryl *N*-hydroxy carbamates **28**, through one-pot procedure involving zinc-mediated reduction of nitroarenes **14** in the presence of chloroformates **7** (Scheme **13**).



Scheme 13.

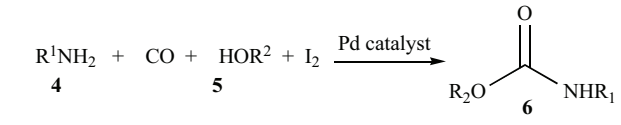
3.3. Oxidative Carbonylation of Amines

Carbamates **6**, have been prepared in good to excellent yields through the reaction of amines **4**, alcohols **5**, carbon monoxide and oxygen in the presence of novel metal catalysts. The metallic catalysts used during the oxidative carbonylations are palladium [61], platinum and alkali metal halides [62], CO, Cu and Rh (Scheme **14**) [63]. Pd and Cu halides have also been employed as a catalysts during the oxidative carbonylation process [64].



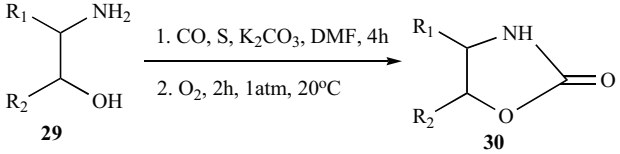
Scheme 14.

Use of Iodine promoted Pd-catalyzed [65], and Gold-complex with triphenylphosphine [66] have also been reported in the synthesis of carbamates (Scheme **15**).



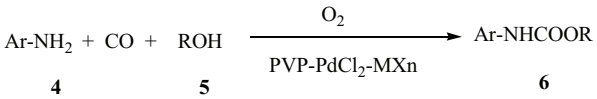
Scheme 15.

Mizuno *et al* have reported [67] the synthesis of 2-oxazolidinone derivatives in which 2-aminoethanols **29** were easily subjected to the thiocarboxylation with CO promoted by elemental sulfur followed by oxidative cyclization with molecular oxygen to afford the corresponding 2-oxazolidinones **30** in good yields under mild conditions (Scheme **16**).



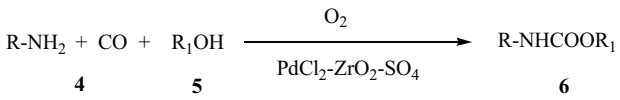
Scheme 16.

Wan *et al* have reported [68] an efficient synthesis of carbamate esters **6**, through the oxidative carbonylation of amines **4** with alcohols **5** using polymer-supported palladium manganese bimetallic catalyst (Scheme **17**).



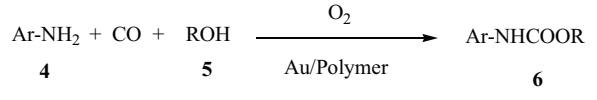
Scheme 17.

Later on, Shi *et al* have reported [69] a novel synthesis of carbamates **6** through the oxidative carbonylation of amines **4** with alcohols **5** using $PdCl_2/ZrO_2$-SO_4^{2-}catalyst system at 170°C (Scheme **18**).



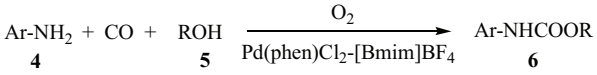
Scheme 18.

Shi *et al* have reported [70] an efficient and clean synthesis of carbamates **6** through oxidative carbonylation of aromatic amines **4** using polymer immobilized gold catalysts (Scheme **19**).



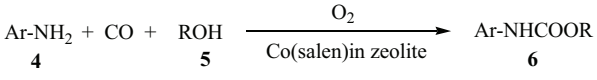
Scheme 19.

Later on, Shi *et al* have also reported [71] a high yielding efficient carbonylation of amines **4** with variety of alcohols **5** using palladium complex-ionic liquid afforded carbamates **6**. The desired products could be precipitated by adding water into the resulting reaction mixture and the catalysts system could be reused with slight loss of catalytic activity (Scheme **20**).



Scheme 20.

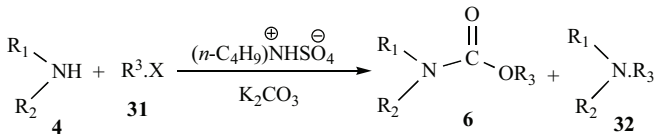
Recently, Mei and coworkers have reported [72] the methyl *N*-phenyl carbamates **6** through the oxidative carbonylation of aniline **4**, using a series of recoverable Co(salen) in zeolite Y as catalysts wherein Co(salen) complexes were successfully encapsulated in zeolite Y by a flexible ligand method (Scheme **21**). They have studied the catalytic activity of various kinds of Co(salen) over zeolite based catalysts.



Scheme 21.

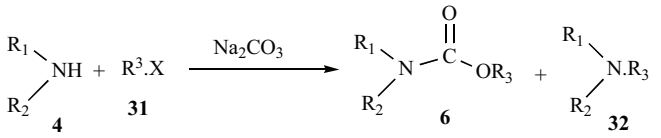
3.4. Using Metal/Non-Metal Carbonates/ Bicarbonates

Carbonates and bicarbonates have been effectively employed for providing carbonyl functionality for the preparation of carbamates. Variety of metal carbonates such as potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), and cesium carbonate (Cs_2CO_3) has been used alone and in combination with different catalytic systems. Synthesis of carbamates **6** through the reaction of variety of secondary amines **4** with structurally diverse alkyl halides **31** was achieved using K_2CO_3/tetra-*n*-butylammonium hydrogen sulfate (Scheme **22**) [73]. This method produces carbamates **6** as a major product along with the minor amount of *N*-alkylated amines **32**.



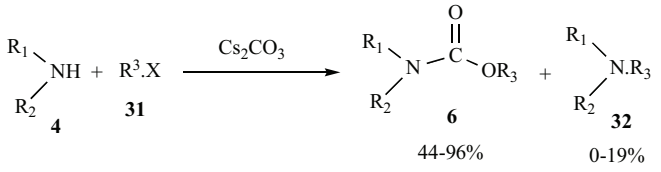
Scheme 22.

Sodium carbonate have also been used in the synthesis of carbamates [74]. Moreover, this method was not efficient for production of only *O*-alkylated carbamates **6** due to the exclusive formation of *N*-alkylated amines **32** (Scheme **23**).



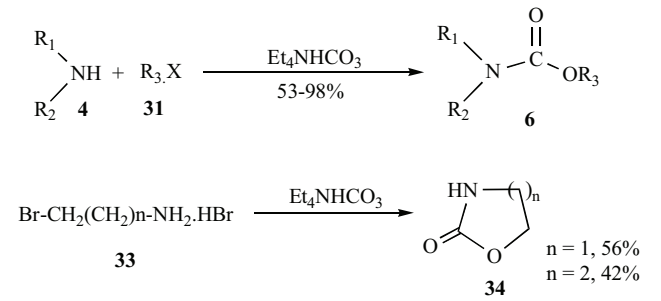
Scheme 23.

The role of Cs_2CO_3 in minimizing the synthesis of *N*-alkylated tertiary amines **32** during the one-pot, efficient synthesis of carbamates **6** from the corresponding alkyl halides **31** and amines **4** was first investigated by Butcher [75] (Scheme **24**). He found that Cs_2CO_3 was much better than K_2CO_3 in yielding better yields of carbamates from their corresponding alkyl halides and amines.



Scheme 24.

Several bicarbonates have been used for the synthesis of carbamates. Of these sodium bicarbonate ($NaHCO_3$) has found use in peptide chemistry [76]. Inesi and their coworkers have reported [77] the synthesis of linear carbamates **6** starting from corresponding primary and secondary amines **4** and alkyl halides **31** using tetra-ethylammoniumhydrogen carbonate (Et_4NHCO_3) as the carbonyl source (Scheme **25**). The yields of carbamates were affected by the nature of alkyl halides used. They have further extended their methodology for the synthesis of cyclic carbamates **33** starting from the corresponding haloamines **34** using Et_4NHCO_3.



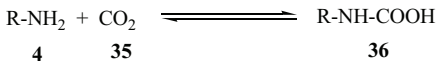
Scheme 25.

3.5. Syntheses of Carbamates Using Carbon Dioxide

Carbon dioxide has been frequently used in its various conditions and forms, as a cheap and safe alternative for the synthesis of carbamates [78], carbonates [79], and several other interesting organic transformations [80]. Carbamates synthesis using various forms of carbon dioxide such as gaseous, electrochemical, and supercritical has been achieved in recent years employing diversity of reagents and catalytic systems.

3.5a. Gaseous Carbon Dioxide

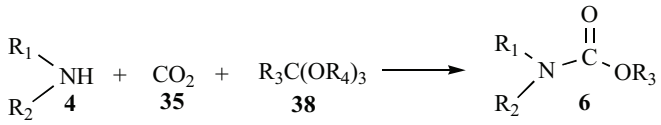
Although carbon dioxide **35** has low reactivity [81] *e.g.* with amines **4** it forms unstable carbamic acids **36**, which revert to their corresponding starting materials (Scheme **26**).



Scheme 26.

However, Yoshida *et al* have reported [82] the synthesis of carbamates **6** starting from CO_2 **35**, amines **4**, and unsaturated ethers **37** (Scheme **27**). This method limits carbamates synthesis only from secondary aliphatic amines. Moreover, it requires longer reaction times (~70-80 h) and afforded low yields (3-12%).

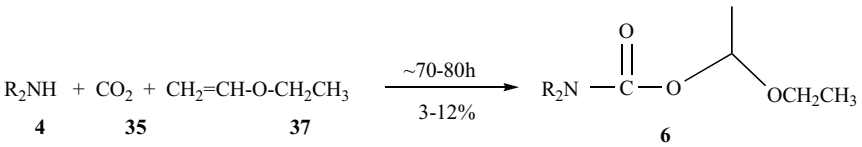
Later on, Ishii *et al* have reported [84] the synthesis of carbamates **6** through the one-pot reaction of primary or secondary aliphatic amines **4** with ortho-esters **38** using gaseous CO_2 (Scheme **29**). This method takes longer reaction times and afforded carbamates in low yields.



Scheme 29.

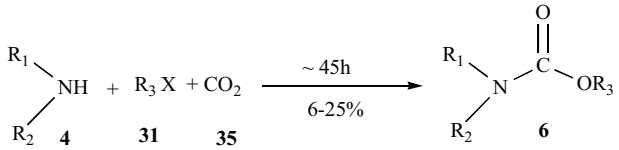
Monocarbamates of 1,2-diols **40** have been synthesized [85] from the corresponding 1,2-epoxides **39** through the reaction of primary and secondary aliphatic amines using gaseous CO_2 (Scheme **30**). However, about half of the epoxide is lost due to the accompanying nucleophilic ring opening by the amine afforded *N*-alkylated product **41**.

Monocarbamates **40** could also be obtained [86] starting from an epoxide **39** using tetrakis(dimethyl)-titanium(IV) and gaseous



Scheme 27.

Later on, Yoshida *et al* have also reported [83] synthesis of carbamates **6** through the one-pot reaction of amines **4** with alkyl halides **31** using gaseous CO_2 (Scheme **28**). Carbamates obtained in this method are also limited to primary and secondary aliphatic amines, require longer reaction times (~45 h), and affording 6-25% yields.



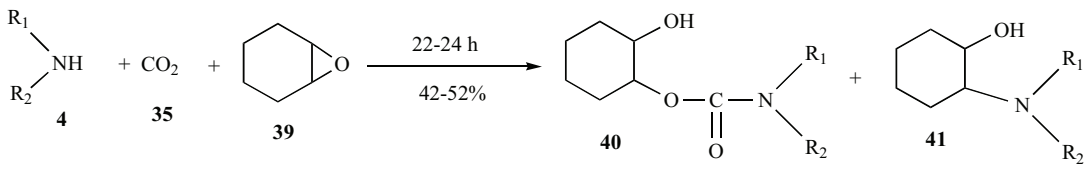
Scheme 28.

CO_2 (Scheme **31**). But this method was not satisfactory due to its longer reaction time (~3-4 d), and low yields (5-20%).

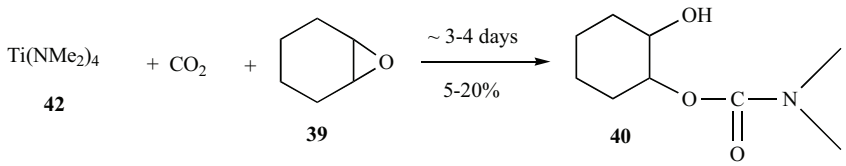
Similarly, chloromethyl oxirane **43** or phenyl oxirane **44** on reaction with CO_2 and aliphatic amines in methanol gave various kinds of substituted carbamates [87] in 2-17% yields (Scheme **32**).

Later on, better yields have been reported by Yoshida *et al* through the reaction of various epoxides **50**, with variety of amines **4** using gaseous CO_2 **35** (Scheme **33**) [88] However, this method suffers from leading to isomeric mixtures.

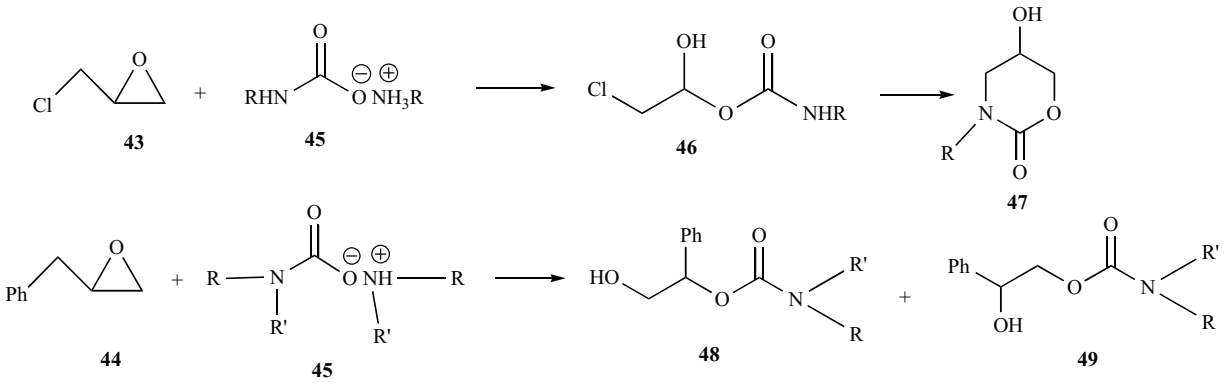
Kojima *et al* have reported [89] carbamates synthesis from epoxides **50**, amines **4**, and CO_2 **35**, wherein the latter was previously fixed on an aluminium porphyrin (Scheme **34**).



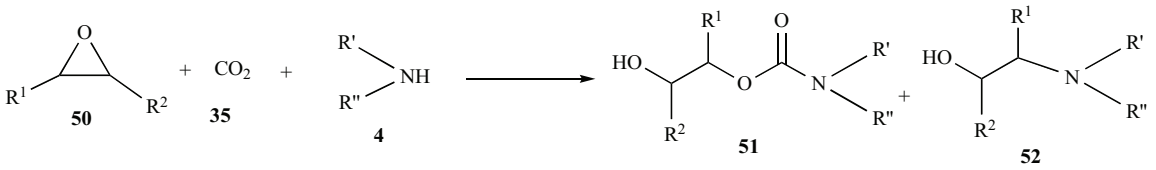
Scheme 30.



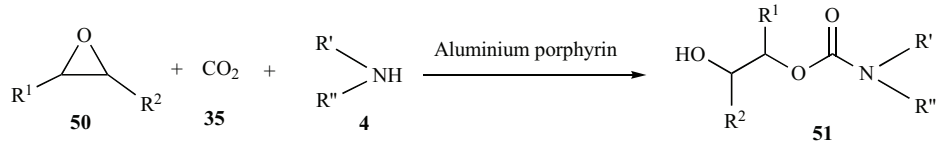
Scheme 31.



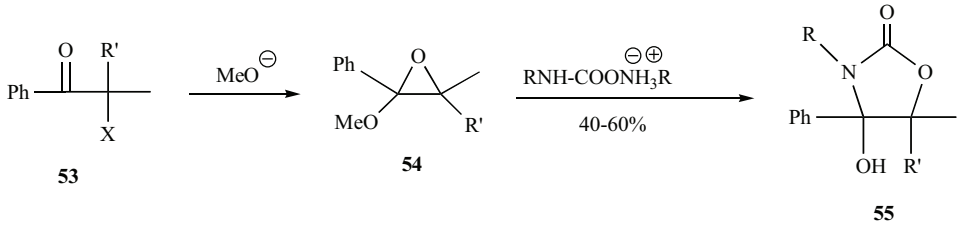
Scheme 32.



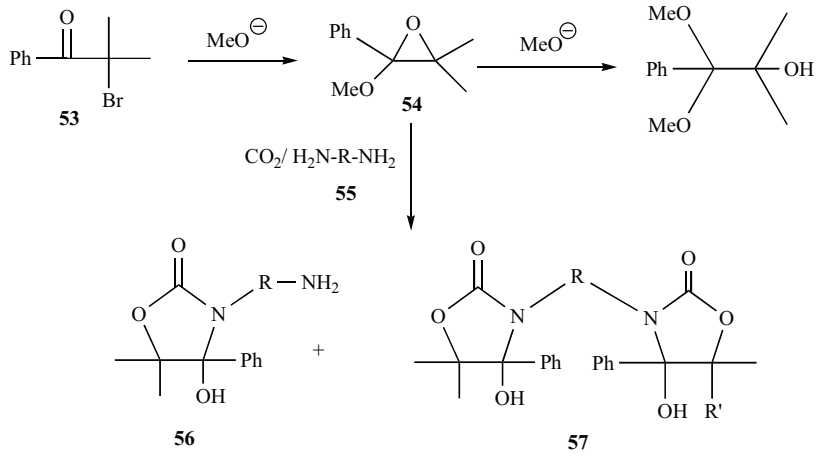
Scheme 33.



Scheme 34.



Scheme 35.



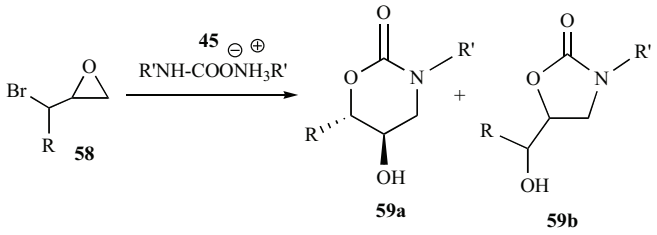
Where R= (CH_2)n, n=1, 2, 3, 4, 5, 6 etc.

Scheme 36.

Toda *et al* have reported [90] the synthesis of cyclic carbamates **55** (*i.e.* oxazolidinones) through the reaction of carbon dioxide with α-bromoacylophenones **53** in the presence of aliphatic primary amines **4** in methanol afforded 3-alkyl-4-hydroxy oxazolidone-2 derivatives **55** under mild reaction conditions (Scheme **35**).

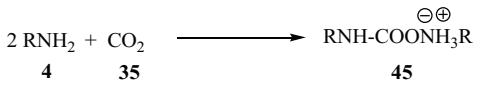
This reaction led to the formation of *bis*(2-oxazolidinones) [91] **57** when 2-methoxy 3,3-dimethyl-2-phenyloxirane **54** or α-bromo-*i*-butyrophenone **53** was reacted with CO_2 and aliphatic α,ω-diamines **56** (Scheme **36**).

Reaction of 2-(1-haloalkyl)-oxiranes **58** with carbon dioxide and aliphatic primary amines gave five-and six-membered cyclic carbamates **59** (Scheme **37**) [92].



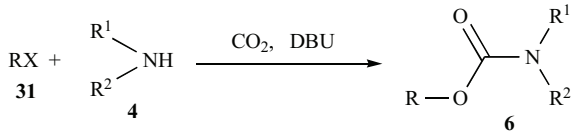
Scheme 37.

In the above reaction it was shown that there is an ionic species **45** involved which is formed when 2 molar ratio of amine **4** was reacted with CO_2 (Scheme **38**).



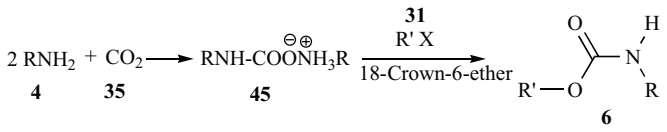
Scheme 38.

An improvement in the yields of carbamate formation has been achieved by using different basic reagents, which might be helpful in increasing the nucleophilicity of the ionic species **43**. Thus, Hori *et al.* have reported [93] the synthesis of carbamates **6** through the reaction of primary and secondary amines **4**, CO_2, and alkyl halides **31** in the presence of a strong proton acceptor like DBU (Scheme **39**).



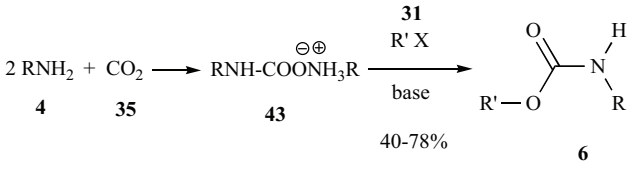
Scheme 39.

Aresta *et al.* have reported [94] synthesis of carbamates **6** employing ionic species **45** through the alkylation with alkyl halides **31** using 18-Crown 6-ether as a phase transfer catalyst (Scheme **40**).



Scheme 40.

However, this method was useful for the preparation of carbamates of only primary and secondary aliphatic amines. The effect of several strong bases (CyTMG, TMG, DBU, MTDB, CyTEG*, etc*) in increasing the nucleophilicity of **45** resulting the formation of carbamates **6**, was studied by McGhee *et al* [95] They have demonstrated the role of various strong bases in yielding *O*-alkylated carbamate products using various kinds of alkylating agents (Scheme **41**).



Scheme 41.

O-Allyl carbamates [96] **62** could be obtained by the addition of preformed carbamate ion **60** [R.R'NH-COO H^+Base] generated from various primary and secondary amines **4** and CO_2, to a THF solution of allylic chlorides **61** containing a palladium/phosphine catalyst (Scheme **42**).

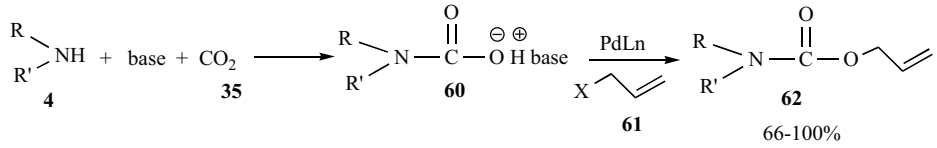
Later on, Perez *et al.* have reported [97] synthesis of *N*-alkyl carbamates **6** in good to excellent yields through a clean and mild transcarboxylation of several amines **4** with the previously synthesized DBU-CO_2 complex and subsequent *O*-alkylation by different alkyl halides **31** (Scheme **43**).

Cyclic carbamates [98] **66** could be obtained in good yields (33-93%) under mild reaction conditions from amino alcohols **65** and carbon dioxide using phosphorus (III) reagents **63** [*i.e.* Ph_3P, $(PhO)_3P$] and halogenoalkanes **64** (*i.e.* CCl_4 and $CCl_3.CCl_3$) (Scheme **44**).

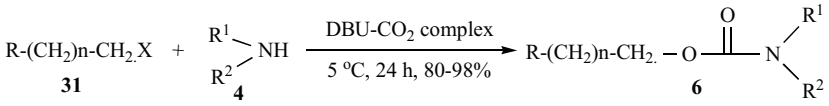
Tominaga *et al.* have reported [99] an efficient protocol for the synthesis of 2-oxazolidinones from CO_2 and 1,2-amino alcohols **65** catalyzed by *n*-Bu_2SnO afforded 53-94% yields (Scheme **45**).

Synthesis of cyclic carbamates **67a** and **67b** from amino alcohols **65** involves sequential carboxylation with carbon dioxide followed by a Mitsunobu's reaction was reported by Dinsmore and Mercer [100]. Unexpectedly, the stereochemical course of the Mitsunobu's reaction is dependent on whether the carbamic acid intermediate is *N*-substituted with hydrogen (retention) or carbon (inversion) (Scheme **46**).

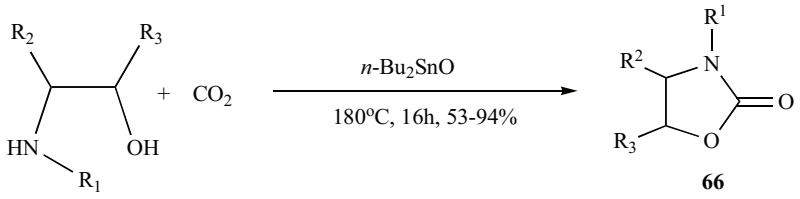
We have reported [101] an efficient, one-pot, high yielding protocol for the synthesis of carbamates **6** through the reaction of vari-



Scheme 42.

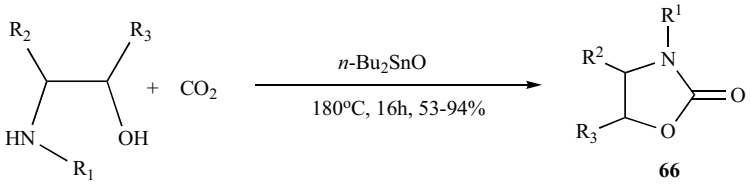


Scheme 43.



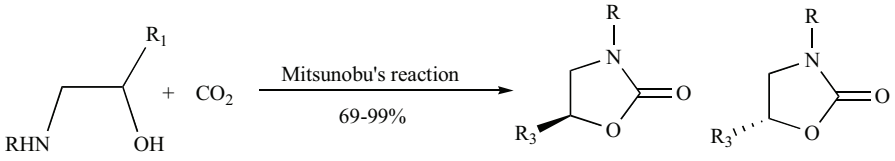
65 **66**

Scheme 44.



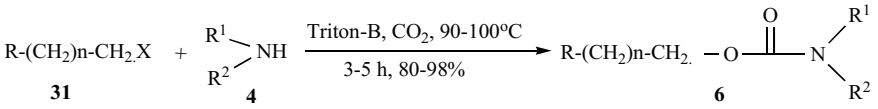
65 **66**

Scheme 45.

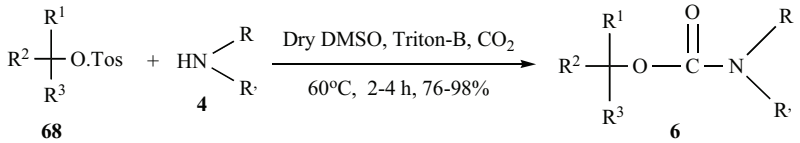


65 **67a** **67b**

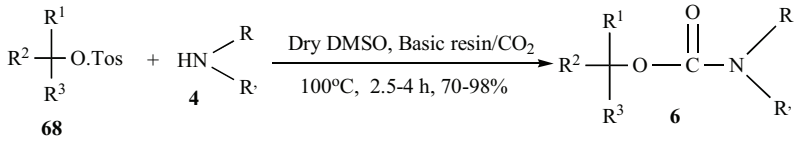
Scheme 46.



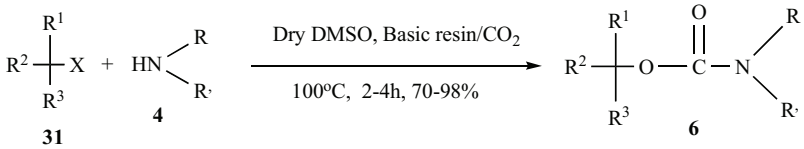
Scheme 47.



Scheme 48.



Scheme 49.



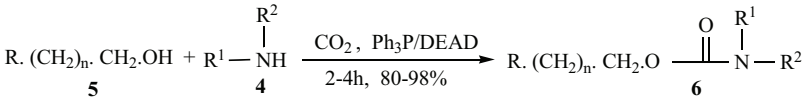
Scheme 50.

ous amines **4** with variety of alkyl halides **31** using benzyltrimethylammonium hydroxide (Triton-B)/CO_2 system (Scheme **47**).

We have also reported [102] the synthesis of carbamates **6** in high yields through the reaction of a variety of alcoholic tosylates **68** with various amines **4** using Triton-B/CO_2 system (Scheme **48**).

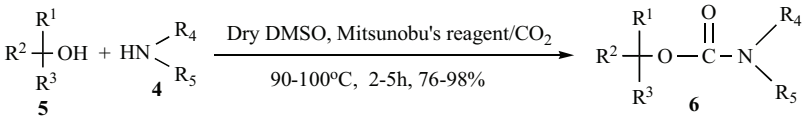
Use of Amberlite IRA 400 resin (basic resin) in the synthesis of carbamates **6** in high yields through the reaction of corresponding variety of alcoholic tosylates **68** with various amines **4** was also reported by our group (Scheme **49**) [103].

The utility of basic resin in the synthesis of carbamates **6** in high yields from the corresponding alkyl halides **31** and amines **4** using gaseous CO_2 was also investigated by our group (Scheme **50**) [104].



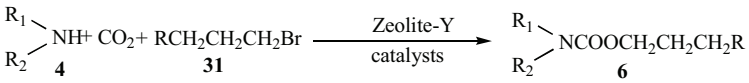
5 4 6

Scheme 51.



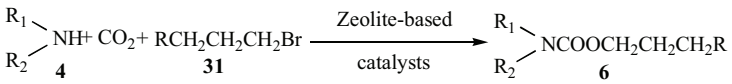
5 4 6

Scheme 52.



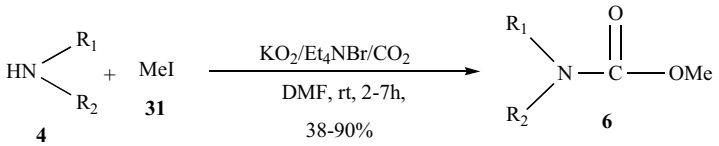
4 31 6

Scheme 53.



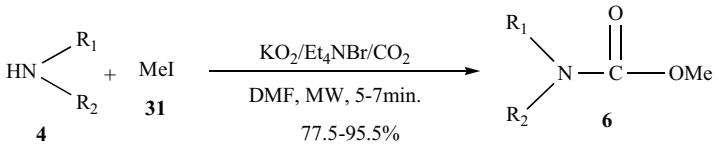
4 31 6

Scheme 54.



4 31 6

Scheme 55.



4 31 6

Scheme 56.

A direct synthesis in high yields of carbamates **6** from the primary alcohols **5** and amines **4** using Mitsunobu's reagent/CO_2 system has been first reported by our group (Scheme **51**) [105].

The above method for the preparation of carbamates **6** was further extended from a variety of primary, secondary and tertiary alcohols **5** and amines **4** using Mitsunobu's reagent/CO_2 system by our group (Scheme **52**) [106].

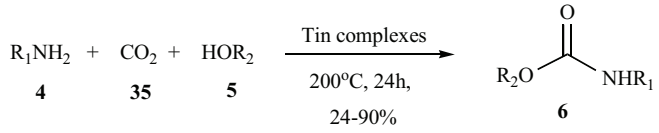
The use of zeolite-based catalysts in the synthesis of carbamates **6** was investigated by Srivastava *et al* [107] through the reaction of corresponding amines **4**, gaseous CO_2, and alkyl halides **31** over either titano-silicate molecular sieves or metal phthalocyanine complexes encapsulated in Zeolite–Y. The catalysts could be used with little or no loss in activity (Scheme **53**).

Srivastava *et al* have also reported [108] efficient protocol for the synthesis of carbamates **6** using CO_2 mediated by Zeolite-based organic-inorganic hybrid catalysts (Scheme **54**).

Recently, Singh have reported synthesis of various kinds of methyl carbamates [109] **6** through the corresponding amines **4** and methyl iodide **31** using tetra-ethyl ammonium bromide-superoxide/CO_2 system (Scheme **55**).

Singh and coworkers have further investigated [110] the improved and efficient protocol for the synthesis of methyl carbamates **6**, through the reaction of corresponding amines **4** with methyl iodide **31** using tetra-ethyl ammonium bromide-superoxide/CO_2 system under microwave conditions (Scheme **56**).

Carbon dioxide has been converted into carbamates **6** through the reaction of various amines **4** with variety of alcohols **5** catalyzed by tin complexes [111]. The addition of acetals as dehydrating agent under high CO_2 pressure is the key to achieve high yields (Scheme **57**).



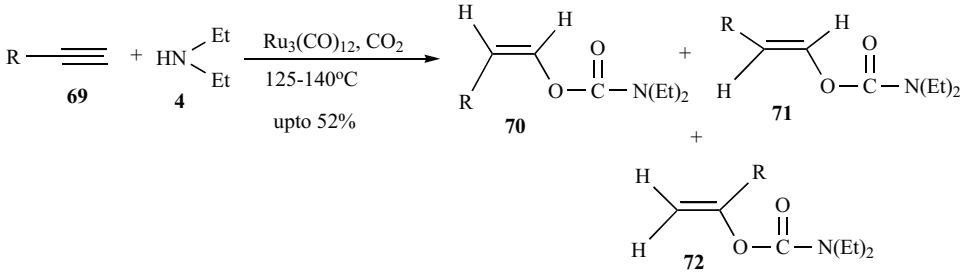
4 35 5 6

Scheme 57.

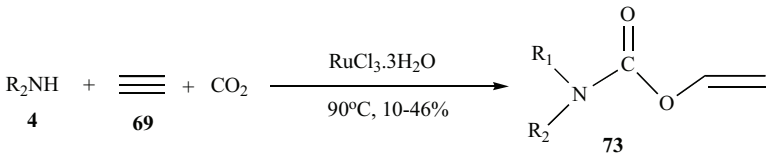
Sasaki and Dixneuf have first reported [112] synthesis of vinyl carbamates (**70**, **71**, **72**) starting from diethylamine **4**, and alkynes **69** using CO_2 in presence of a ruthenium catalyst $Ru_3(CO)_{12}$ (Scheme **58**).The overall yields of the products is poor in most of the reactions.

Later on, Sasaki and Dixneuf have reported [113] the a direct synthesis of vinyl carbamates **73** in good yields through direct reaction of secondary amines **4** with acetylene **69** using gaseous CO_2 in presence of catalytic amount of $RuCl_3.3H_2O$ (Scheme **59**).

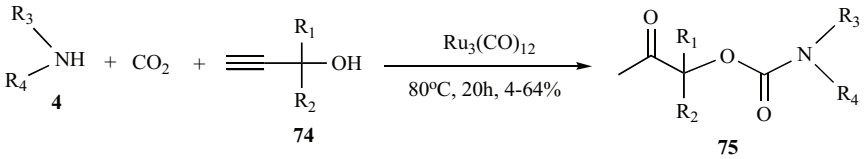
Sasaki and Dixneuf have also reported [114] the synthesis of 2-oxoalkyl substituted carbamates **75** in good yields through the reaction of secondary amines **4**, α-ethynyl alcohols **74** and CO_2 using $Ru_3(CO)_{12}$ catalyst (Scheme **60**).



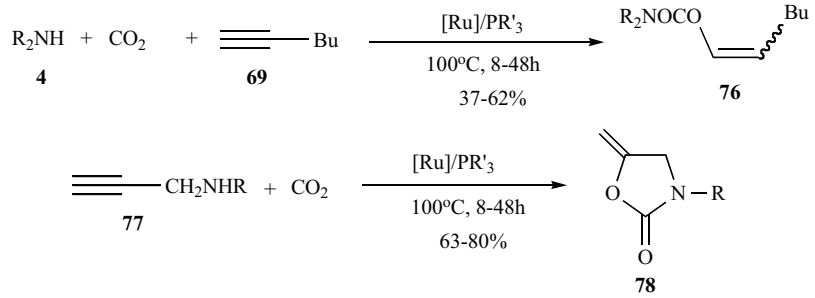
Scheme 58.



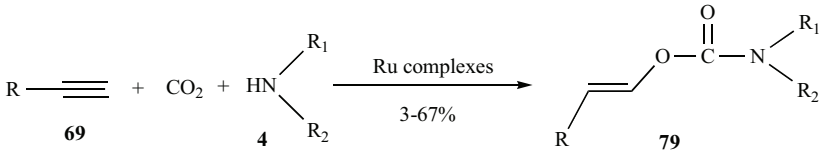
Scheme 59.



Scheme 60.



Scheme 61.



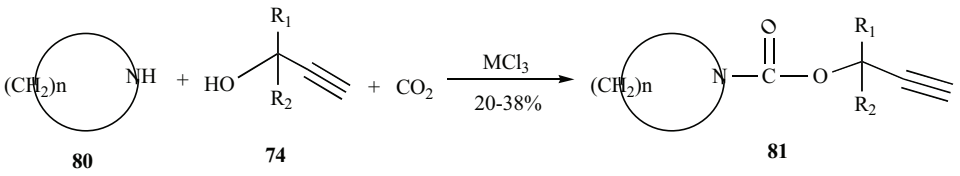
Scheme 62.

Matsudo and coworkers have reported [115] synthesis of enol carbamates **76** in good yields with high regio and stereoselectivity through the reaction of amines **4**, terminal alkynes **69** and using gaseous CO_2 in presence of catalytic amount of (η^4-cyclooctadiene) (η^6-1,3,5-cyclooctatriene)ruthenium [Ru (COD) (COT)] and tertiary phosphine (Scheme **61**). They have further extended their methodology for the synthesis of cyclic enol carbamates **78** using *N*-substituted propargyl amines **77** and CO_2.

Later on, Dixneuf *et al* have also reported [116] the synthesis of vinyl carbamates **79** through the reaction of an alkyne **69** with an amine **4** using gaseous CO_2 in presence of various kinds of ruthenium complexes *i.e.* $RuCl_2(PR_3)$carene) and $RuCl_2$(norbornadiene)$(pyridine)_2$ (Scheme **62**). They have studied the catalytic role of different Ru-complexes in affording better yields of vinyl carbamates.

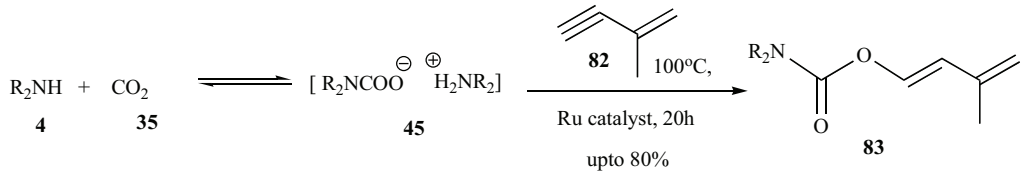
Shim *et al* have synthesized [117] carbamates **81** through the reaction of amines **80**, acetylenic alcohols **74**, and carbon dioxide using a lanthanide catalyst. Thus, the reaction of perhydro-azepine **80** with 3,3-dimethyl prop-1-yne-3-ol **74** and CO_2 in presence of MCl_3 (M = Ce, Pr, Nd, Gd) gave carbamates **81** (n = 6) in 20-38% yields. They have also prepared the carbamates (n = 4, 5) in 31 and 21% yields (Scheme **63**).

Dixneuf and coworkers have reported [118] regioselective synthesis of *O*-1-(1,3-dienyl)carbamates **83** through regioselective addition of CO_2 and secondary amines **4** to isopropenylacetylene **82** in the presence of $[Ph_2P(CH_2)_nP.Ph_2]Ru(\eta^3\text{-}CH_2\text{-}C(Me)=CH_2)_2$ catalyst (Scheme **64**). The yields were dependent on the nature of legand used in catalyst. They have realized that legand wherein n = 2, afforded better yields of the products. The addition is favored in case of secondary cyclic amines.



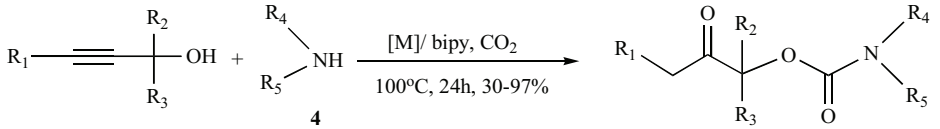
80 **74** **81**

Scheme 63.



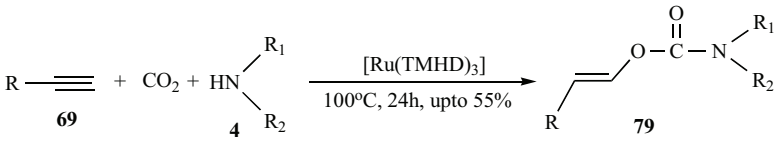
4 **35** **45** **83**

Scheme 64.



74 **4** **84**

Scheme 65.



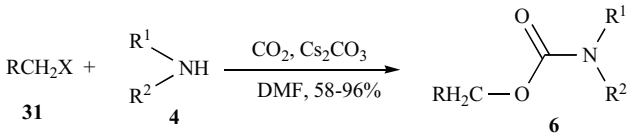
69 **4** **79**

Scheme 66.

Kim and coworkers have reported [119] the synthesis of carbamates **84** through the reaction of various kinds of propargyl alcohols **74** with variety of amines **4** using gaseous CO_2 in presence of catalytic amount of [Cu (1) $(BF_4)_2$ (1 = 2, 5, 19, 22, tetraaza [6, 6] (1, 1') ferrocenophane, 1,5-diene) (Scheme **65**).

Recently, Bhanage *et al* have reported [120] synthesis of vinyl carbamates **79** through reaction of various kinds of alkynes **69**, amines **4**, and CO_2 using ruthenium *tris*(2,2,6,6-tetramethyl 3,5-heptanedionate) metal complex as a catalyst (Scheme **66**).

Carbon dioxide providing the carbonyl functionality for the synthesis of carbamates is not sufficient itself in yielding high yields of desired carbamates. Therefore, several researchers have considered that by adding basic reagents to reaction mixture may increase the basicity and nucleophilicity of the ionic species **43**. Consequently, it has been proposed that metal carbonates such as Na_2CO_3, K_2CO_3, Cs_2CO_3 *etc* are good basic reagents, which could provide carbonyl functionality in addition to its basic properties. Based on this concept there are many reports appreared in the recent past on the use of metal carbonates/CO_2 system for the synthesis of carbamates. Thus, Butcher have reported [121] a carbamate synthesis **6** in good to excellent yields (58-96%) from various alkyl halides **31** and amines **4** using the cesium carbonate/CO_2 system (Scheme **67**).

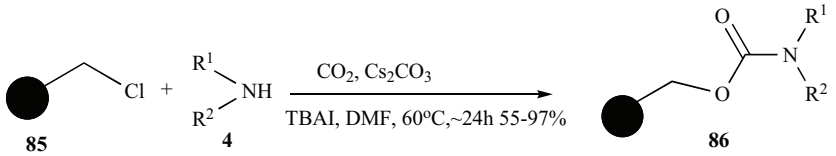


31 **4** **6**

Scheme 67.

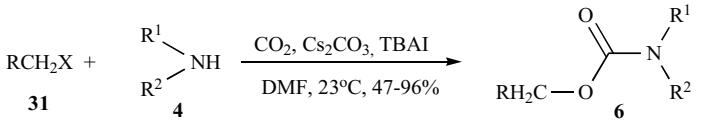
Later on, Jung and coworkers have reported [122] synthesis of carbamates **86** using solid phase Merrifield resin **85** in good to excellent yields using cesium carbonate/CO_2 and TBAI as phase transfer catalyst (Scheme **68**).

Later on, they have also reported synthesis of carbamates [123] **6** in solution phase through the reaction of various kinds of structurally diverse aliphatic, aromatic, and heterocyclic amines **4** with variety of alkyl halides **31** using cesium carbonate/CO_2 system in presence of a catalytic amount of TBAI (Scheme **69**).

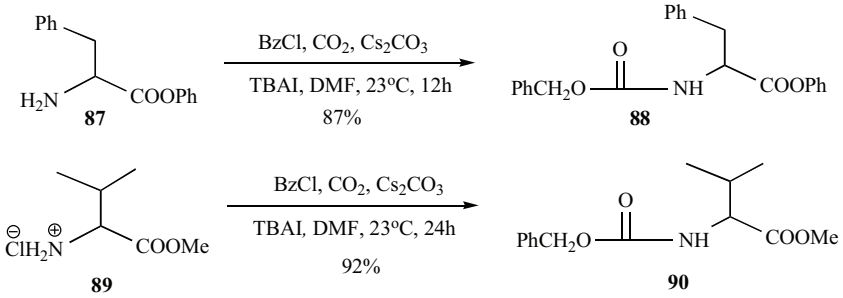


85 **4** **86**

Scheme 68.



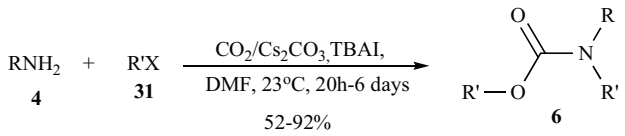
Scheme 69.



Scheme 70.

They have extended their methodology in the synthesis of peptidomimetic using various kinds of protected amino acids (Scheme **70**).

A direct synthesis of *N*-alkyl carbamates **6** from primary amines **4**, and alkyl halides **31** using cesium carbonate/CO_2 system has also been reported by Jung and their coworkers (Scheme **71**) [124].

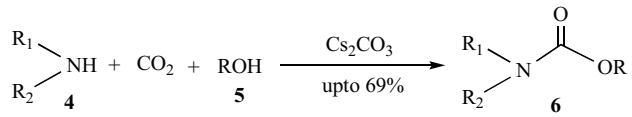


Scheme 71.

A study on comparative yields of carbamates **6** using different metal carbonates and bases on *O*-as well as *N*-alkylated products was reported by Shi and Shen (Scheme **72**) [125]. They have realized that best yields (> 87%) of carbamates could be achieved using DBU/CO_2 system.

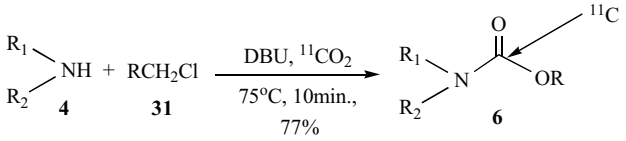
We have reported [126] a convenient, high yielding, one-pot synthesis of carbamate esters in high yields (70-90%) from corresponding alcoholic tosylates **68**, and amines **4** using the K_2CO_3/CO_2 system in the presence of a catalytic amount of tetra-*n*-butylammonium iodide (Scheme **73**). This method has been used for carbamates derived from various aliphatic primary, secondary, and aromatic amines.

Recently, Vos and coworkers have reported [127] an efficient and green synthesis of carbamates **6** through the coupling of various amines **4** with variety of alcohols **5** using Cs_2CO_3/CO_2 system (Scheme **74**).



Scheme 74.

A very recent report for the synthesis of radio-labeled carbamates **6** through the incorporation of [^{11}C] CO_2 using various kinds of alkyl halides **31**, amines **4** and catalytic amount of DBU was reported by Hooker and coworkers (Scheme **75**) [128].

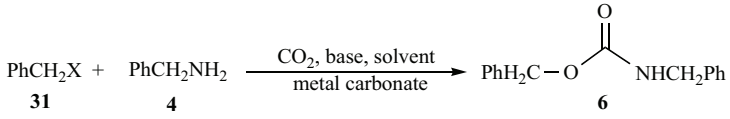


Scheme 75.

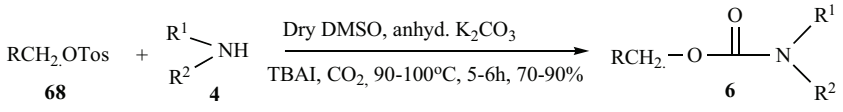
3.5b Electrochemical Carbon Dioxide

Inesi and coworkers have first reported [129] the synthesis of linear carbamates and cyclic carbamates (**6** & **34**) from the corresponding amines **4**, alkyl halides **31** or haloalkylamines **33** using electrogenerated-superoxide activated carbon dioxide ($O_2^{\cdot -}/CO_2$) (Scheme **76**).

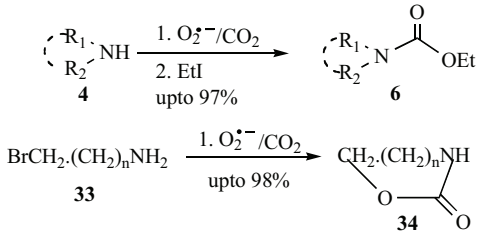
Later on, Inesi and coworkers have also reported [130] synthesis of carbamates **6** using carbon dioxide through an electrochemical process (Scheme **77**). This synthesis is based on the reaction of amines **4**, with the electrochemically generated base **92** (associated with the Et_4N^+ cation) from 2-pyrrolidone **91** followed by sequen-



Scheme 72.

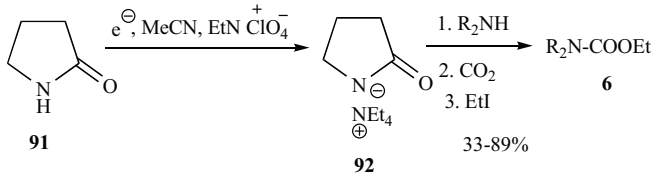


Scheme 73.



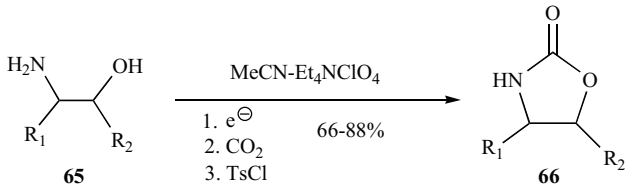
Scheme 76.

tial addition of CO_2 and ethyl iodide, afforded carbamates in high yields.



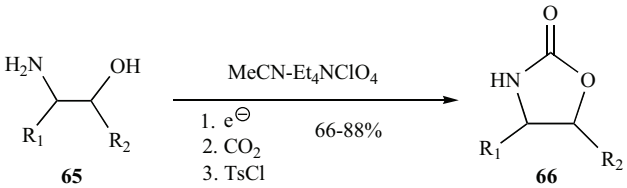
Scheme 77.

Later on, Inesi *et al* have also reported [131] an improved electrochemical synthesis of chiral oxazolidin-2-ones **66** starting from the corresponding chiral 1,2-amino alcohols **65**. Subsequent CO_2 bubbling and addition of tosyl chloride afforded desired cyclic carbamates **66** in high yields (Scheme **78**).



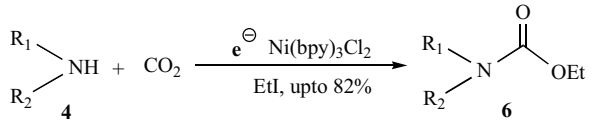
Scheme 78.

The utility of electrochemically generated cyanomethyl anion/carbon dioxide system in affording high yields of carbamates **6** using various kinds of amines **4** and alkyl halides **31** was further investigated by Inesi and their coworkers (Scheme **79**) [132].



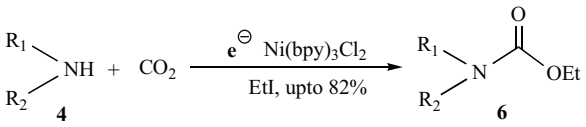
Scheme 79.

Recently, Inesi and coworkers have reported [133] a new electrochemical procedure for the synthesis of carbamates **6** in high yields starting from the corresponding amines **4**, and alkyl halides using electrochemical carbon dioxide-saturated room temperature ionic liquid [Bmim]BF_4 solutions (Scheme **80**).



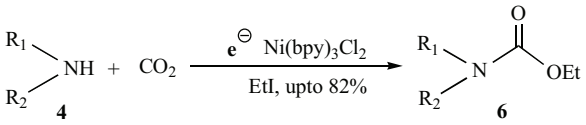
Scheme 80.

Dunach and Tascedda have reported [134] a new and selective electrochemical procedure for the synthesis of five membered ring cyclic carbamates **94** & **95** involving nickel-catalyzed CO_2 incorporation into aziridines **93** under mild electrochemical conditions (Scheme **81**). Out of several Ni catalysts used, Ni $(bipy)_3(BF_4)_2$ was shown to be an efficient catalyst for this transformation afforded 100% yields of desired carbamates.



Scheme 81.

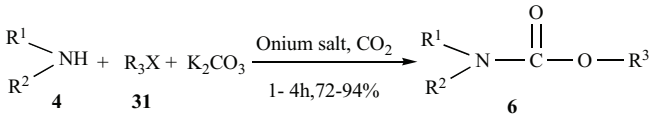
Recently, Lu and coworkers have reported [135] a new and efficient electrochemical synthesis of carbamates through the electrochemical incorporation of carbon dioxide into amines catalyzed by an electrogenerated Ni complex $[Ni(bpy)_3Cl_2]$ using tetraethylammonium bromide (Scheme **82**).



Scheme 82.

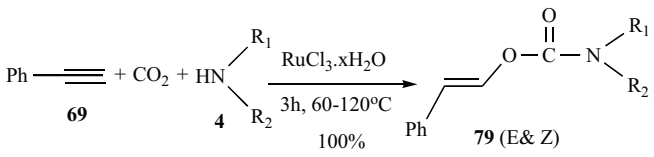
3.5c. Supercritical Carbon Dioxide

Yoshida *et al* have first reported [136] the synthesis of carbamates **6** in good yields starting from the corresponding amines **4** and alkyl halides **31** using supercritical CO_2/K_2CO_3 in presence of tetra-*n*-alkylammonium halides acting as phase transfer catalyst (Scheme **83**). They have also demonstrated the role of different phase transfer catalysts on carbamates synthesis and found that tetrabutylammonium bromide was best among all in affording high yields of carbamates.



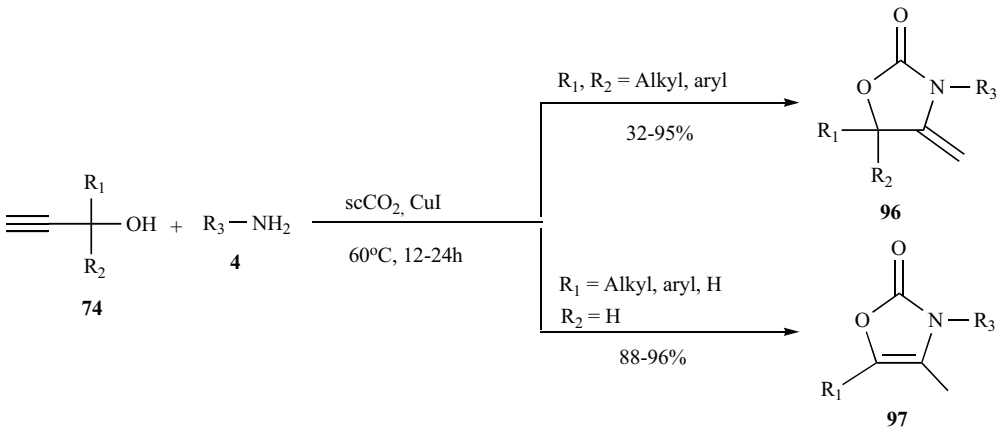
Scheme 83.

Later on, Baker and coworkers have reported [137] solvent free ruthenium-catalyzed synthesis of vinyl carbamates **79** through the reaction of phenyl acetylene **69** with diethyl amine **4** using supericritical CO_2 (Scheme **84**). They have also studied the effect of temperature on the catalytic activity of Ru-complexes and found that the best yields of vinyl carbamates were obtained at 120°C.

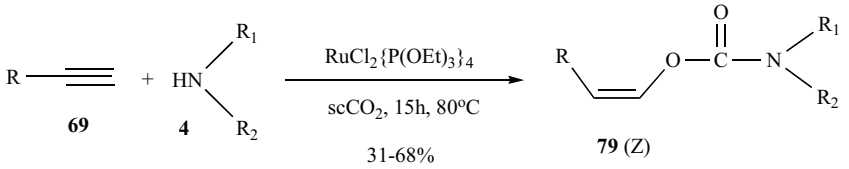


Scheme 84.

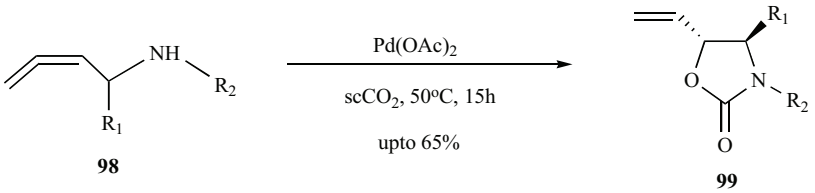
Recently, Jiang and coworkers have demonstrated [138] a new and efficient protocol for the synthesis of oxazolidinones **96** and oxaolones **97** through the cycloaddition reaction of CO_2 with propargyl alcohols **74** and amines **4** under supercritical conditions (Scheme **85**).



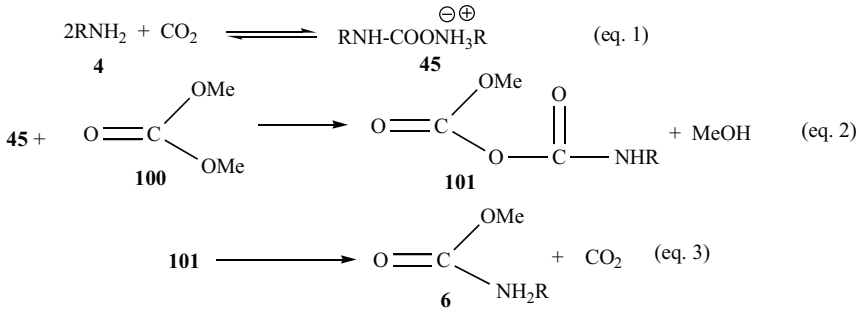
Scheme 85.



Scheme 86.



Scheme 87.



Scheme 88.

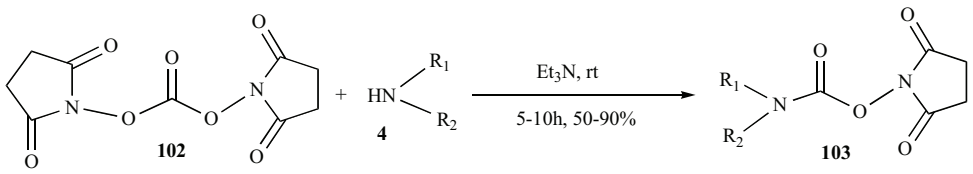
Recently, Ikariya and coworkers have reported [139] the stereoselective synthesis of Z-alkenyl carbamates **79** from the corresponding amines **4** and alkynes **56** using CO_2-soluble ruthenium-$P(OEt)_3$ catalyst under supercritical conditions (Scheme **86**).

Very recently, Ikariya and coworkers have also reported [140] the synthesis of 5-vinyl 1,3-oxazolidine-2-ones **99**, through carboxylative transformation of 2,3-allenic amines **98** and CO_2 promoted by palladium catalysts under supercritical conditions (Scheme **87**).

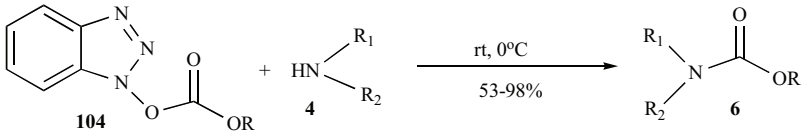
3.5d. Organic Carbonates and Carbon Dioxide

Organic carbonates constitute an important source for carbonyl functionality during the synthesis of carbamates. Their reaction with amines represents an alternative synthetic route to carbamates that has gained growing attention in the last few years as a non-phosgene route to the synthesis of organic carbamates [141]. Nowadays, dimethyl carbonate (DMC) **100** can be produced on a large scale by oxidative carbonylation of methanol [142]. Other organic carbonates can be easily obtained by transesterification of DMC with phenols [143] and long chain high boiling alcohols [144]. The reaction between primary and secondary amines and dialkyl carbonates needs a suitable catalyst in order to get satisfactory conversion rates and high selectivities. Strong bases such as alkali metal alkoxides, Zn, Co, Sn, Al, and Tin compounds have been widely employed as catalysts in the carboalkoxylation of anilines and more generally of aromatic amines [145]. Moreover, Lewis acids, such as $AlCl_3$, $SnCl_2$, $ZnCl_2$, $Zn(OAc)_2.2H_2O$, $FeCl_3$, or metal(Rh, Ru) complexes have proved to be effective in promoting the conversion of propyl amine and diethyl carbonate selectively to propyl and ethyl carbamate [142].

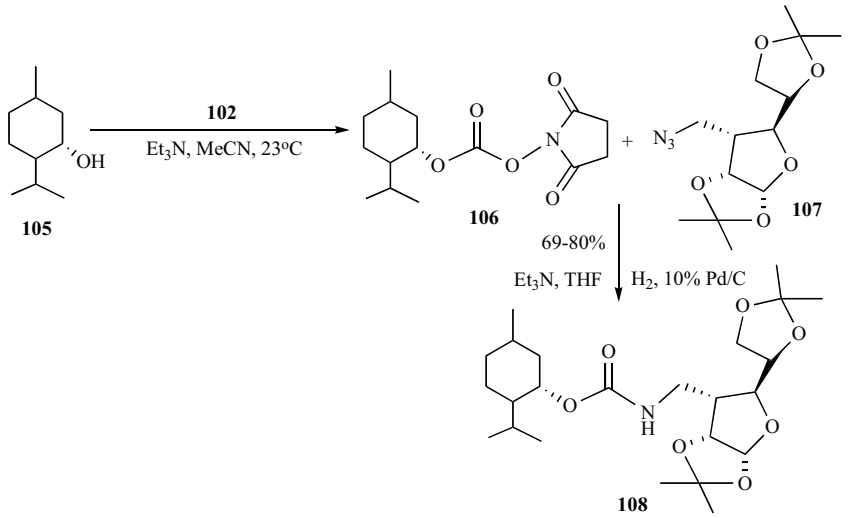
Primary and secondary aliphatic amines can react with CO_2 according to equilibrium (eq.1) afforded monoalkylammoniumalkylcarbamate ion [78**]** **45** that serves as a convenient source of carbamate moiety in the synthesis of carbamates using DMC **100** (Scheme **88**) [146]. *O*-Carbomethoxylation of carbamate anion is the first step eq. 2, to afford a mixed carbamic-carbonic anhydride



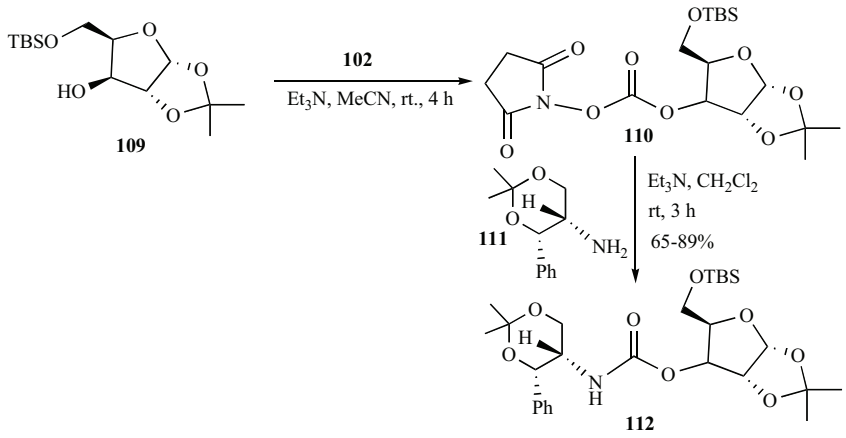
Scheme 89.



Scheme 90.



Scheme 91.



Scheme 92.

RNH-COOCOMe **101**. This step could be catalyzed by acidic species, such as RNH_3^+, RNH-COOH, present at equilibrium. Selective decarboxylation of **101** through expulsion of a CO_2 molecule from its carbamic moiety leads to the formation of carbamate **6**.

Organic carbonates have received much attention in recent years as cheap and safe alternatives to the non-phosgene routes for the synthesis of organic carbamates. Therefore, several researchers over the world have become interested to synthesize carbamates through this route.

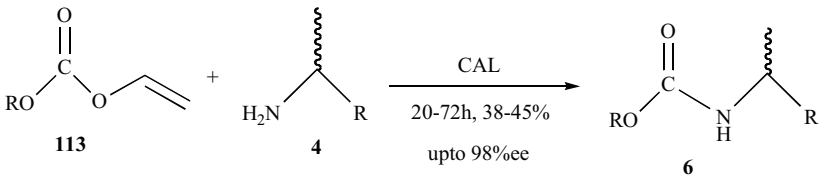
Ogura and coworkers have first reported [147] an efficient synthesis of *N*-succinimidyl carbamates **103** through the reaction of corresponding amines **4** with *N,N'*-disuccinimidyl carbonate (DSC) **102** using triethyl amine (Scheme **89**).

Later on, Ogura and their coworkers have demonstrated [148] an efficient protocol for the synthesis of carbamates **6** through the reaction of corresponding amines **4** with benzotriazole carbonate **104 (**Scheme **90**).

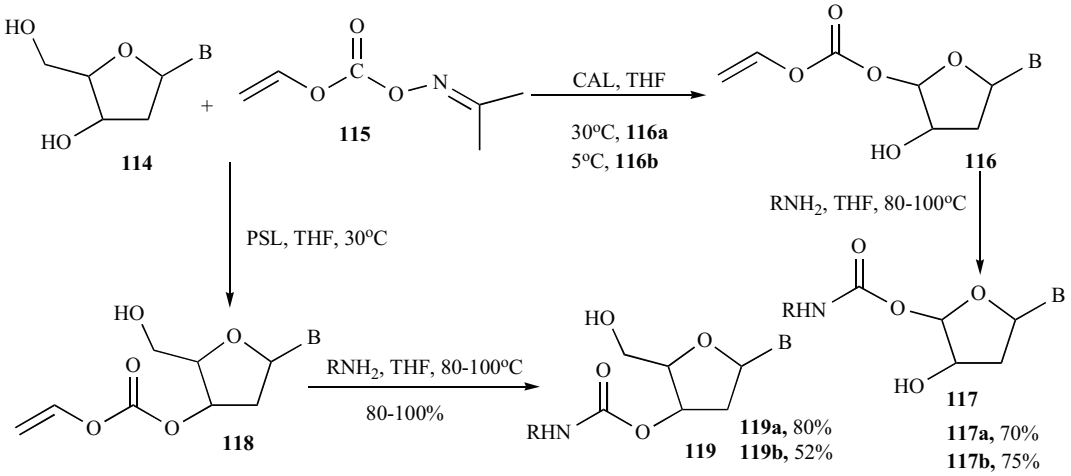
Use of *N,N'*-disuccinimidyl carbonate **102** has been further explored for the synthesis of carbamates [149] **108** from azides **107** and mixed carbonates **106** by Ghosh and coworkers (Scheme **91**).

Ghosh and coworkers have also reported [150] synthesis of carbamates **112** in high yields starting from the corresponding amines **111** and a mixed carbonate **110**, which is obtained through a reaction of alcohol **109** with DSC **102** (Scheme **92**).

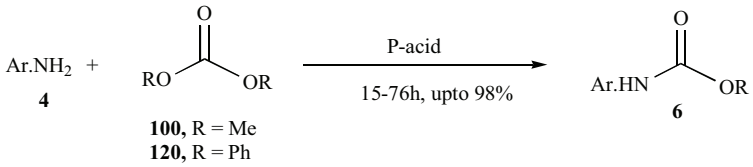
Chiral carbamates **6** have also been synthesized through an enzymatic alkoxy-carbocylyzation reaction with vinyl carbonates **113**



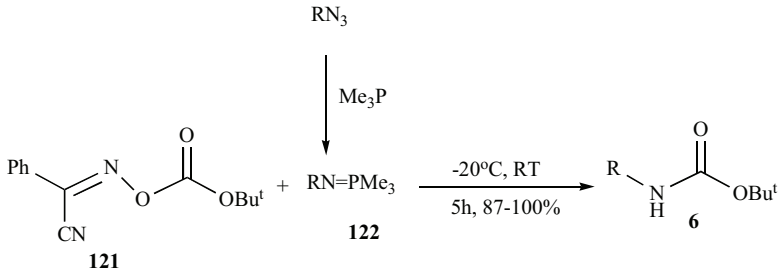
Scheme 93.



Scheme 94.



Scheme 95.



Scheme 96.

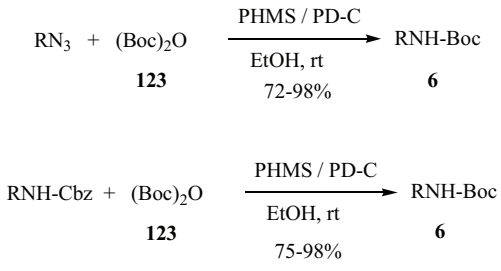
and racemic amines **4** using *Candida antarctica* lipase, CAL was reported by Pozo and Gotor (Scheme **93**) [151].

Gotor and coworkers have reported [152] the chemoenzymatic synthesis of a 2'-deoxynucleoside urethan. 2'(Deoxynucleoside 5' and 3'(*N*-alkyl)carbamates (**117** & **119**) were synthesized in a two-step procedure using lipase catalysis in the regioselective vinyloxy carbonylation step (Scheme **94**). The regioselectivity of the reaction depends upon the type of lipase enzyme 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.

Aresta *et al* have reported [153] the synthesis of carbamates **6** through the reaction of aromatic amines **4** with DMC **100** or diphenyl carbonate (DPC) **120** 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 **95**). They have further realized that better yields of carbamates were obtained using DPC.

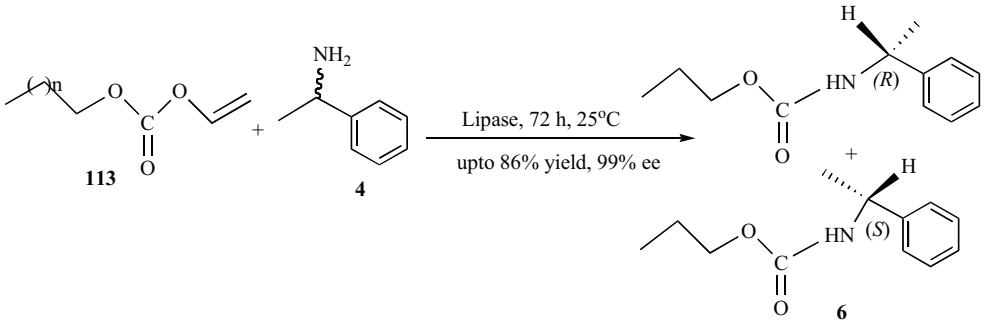
Urpi and coworkers have reported [154] an efficient protocol for the synthesis of *tert*-butyl carbamates **6** through reaction of azides with trimethyl phosphine followed by addition of 2-(*tert*-butoxycarbonyloxyamino)-2-phenylacetonitrile **121** at -20°C (Scheme **96**).

Chandrasekhar *et al* have reported [155] an excellent one-pot method for the synthesis of carbamates **6** through reaction of azides with di-*tert*-butylcarbonates (Boc) **123** using the inexpensive and safe hydride source i.e. polymethylhydrosiloxane (PMHS) under Pd-C catalysis (Scheme **97**).



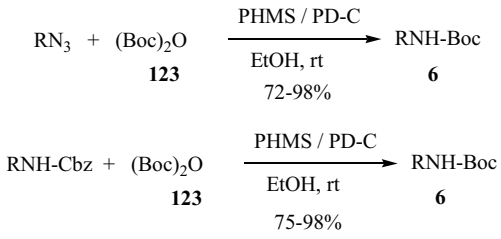
Scheme 97.

The enzyme lipase has also been used as a catalyst in the synthesis of chiral carbamates [156] **6** starting from racemic amines **4** and alkylvinyl carbonates **113** (Scheme **98**).



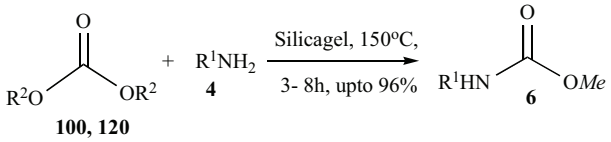
Scheme 98.

Lemaire and coworkers have reported [157] efficient synthesis of carbamates **6** through the reaction of amines **4** with DMC **100** catalyzed by γ-Al_2O_3 (Scheme **99**).



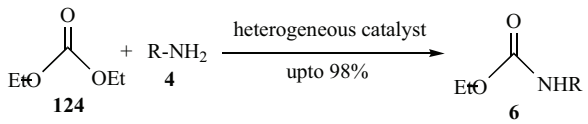
Scheme 99.

Chaudhari and coworkers have reported [158] an efficient protocol for the synthesis of carbamates **6** through the reaction of various carbonates (**100**, **120**) with variety of amines **4** catalyzed by silicagel (Scheme **100**).



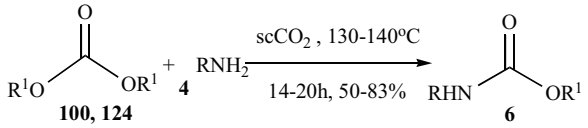
Scheme 100.

Carloni and coworkers have reported [159] synthesis of carbamates **6** through reaction of diethyl carbonate **124** with variety of amines **4** using a heterogeneous catalyst a hybrid organic-inorganic material prepared by anchoring TBD to MCM-41 silica. (Scheme **101**).



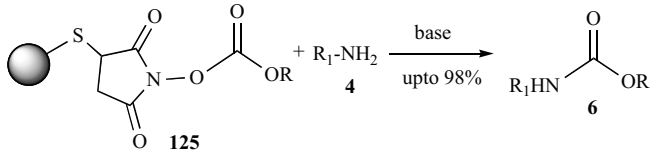
Scheme 101.

Selva and workers have reported [160] an efficient synthesis of carbamates **6** from primary aliphatic amines **4** with dialkyl carbonates (**100** & **124**) in supercritical CO_2 (Scheme **102**).



Scheme 102.

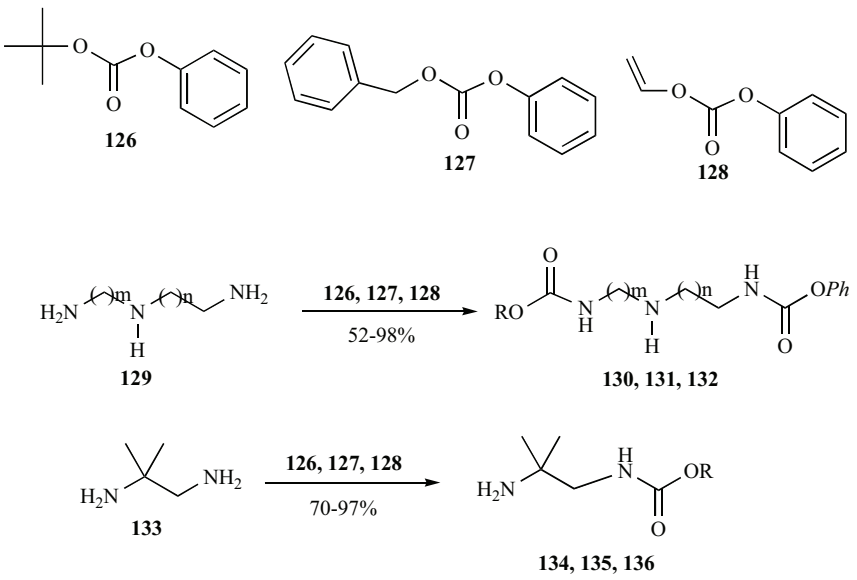
Sodeoka and coworkers have reported [161] a convenient method for the synthesis of carbamates **6** through reaction of various amines **4** with variety of polymer-supported *N*-hydroxy succinimide substituted carbonates **125** (Scheme **103**).



Scheme 103.

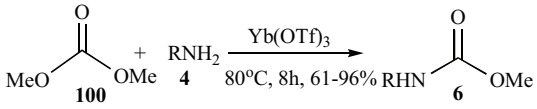
Later on, Christention and coworkers have reported [162] the synthesis of carbamate protected polyamines (**130**, **131**, **132**, **134**, **135**, **136**) using alkyl phenyl carbonates (**126**, **127**, **128**). This is an economical, practical and versatile method for selective Boc, Cbz, and Alloc protection of polyamines. This method allows Boc, Cbz, and Alloc protection of primary amines in the presence of secondary amines by reaction of polyamines with alkylphenyl carbonates. Also, this method allows monocarbamation of simple symmetrical aliphatic α,ϖ-alkanediamines in high 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 **104**). The alkyl-phenyl carbonates investigated in this study were *tert*-butylphenylcarbonate (**126**), benzylphenylcarbonate (**127**), and allylphenylcarbonate (**128**), which introduces the Boc, Cbz, and Alloc protecting groups.

Later on, Curini and workers have reported [163] that ytterbium triflate, Yb(O*Tf*)$_3$ can be efficiently used for the preparation of car-



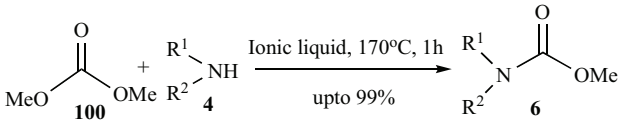
Scheme 104.

bamates **6**, through reaction of various amines **4** with DMC **100** under solvent free conditions (Scheme **105**).



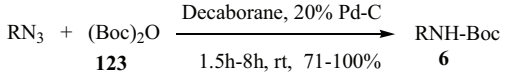
Scheme 105.

Later on, Deng and coworkers have reported [164] the synthesis of carbamates **6** through the reaction of primary and secondary aliphatic amines **4** with DMC **100** using ionic liquids (Scheme **106**).



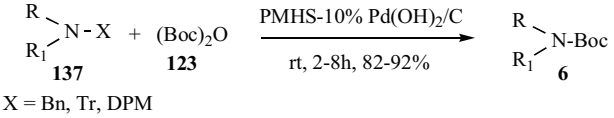
Scheme 106.

Conversion of azides to *tert*-butyl carbamates [165] **6** could also be synthesized using di-*tert*-butyl dicarbonate **123**, decaborane (20 mol%) and 20% Pd-C at room temperature in methanol (Scheme **107**).



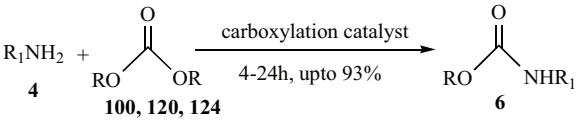
Scheme 107.

Chandrasekhar and coworkers have reported [166] the one-step conversion of *N*-benzyl, *N*-trityl, *N*-diphenyl amines **137** to *tert*-butyl carbamates **6** using Boc **123** in the presence of polymethylhydrosiloxane (Scheme **108**).



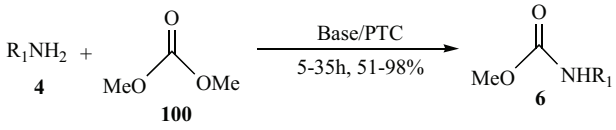
Scheme 108.

Chaudhari and coworkers have reported synthesis of carbamates [167] **6** through the reaction of various organic carbonates (**100**, **120**, **124**) with various amines **4**, using various catalysts (Scheme **109**). Out of several catalysts used, *n*-butyltin oxide was found to be best in affording good yields of the carbamates.



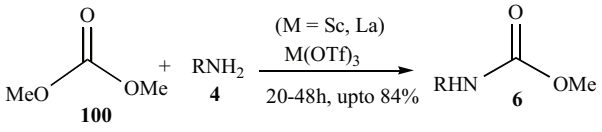
Scheme 109.

Shen *et al* have reported [168] a facile synthesis of *N*-methyl *N*-aryl carbamates from aromatic amines **4** and DMC **100** in the presence of potassium carbonate and tetrabutylammonium bromide under solvent free conditions (Scheme **110**).



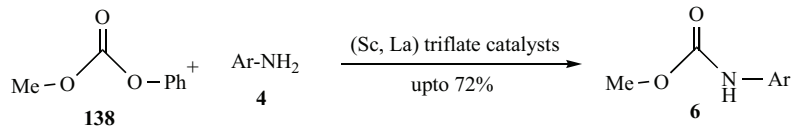
Scheme 110.

Distaso and Quaranta have reported [169] a high yielding synthesis of carbamates **6** through reaction of various aliphatic amines **4** and dimethyl carbonate **100** catalyzed by group III metal (Sc, La) triflates, under mild reaction conditions (Scheme **111**). $Sc(OTf)_3$ is more effective than La salt.

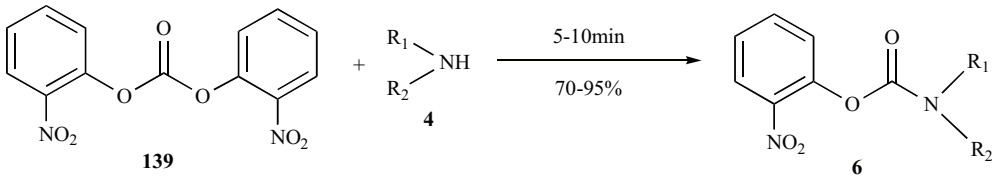


Scheme 111.

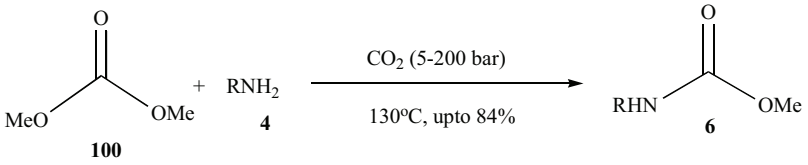
Distaso and Quaranta have also reported [170] carbomethylating reactivity of methyl phenyl carbonate **138** towards aromatic amines **4** in the presence of group 3 metal (Sc, La) triflate catalyst under mild conditions to afford the corresponding carbamates **6** in high yields (Scheme **112**). They have optimized the effect of the various catalysts at different temperature, time, and molar ratio of



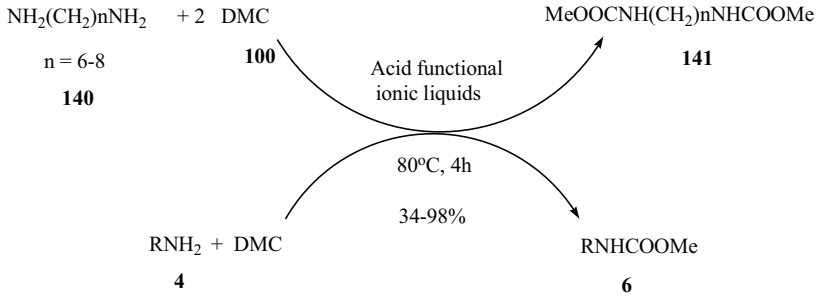
Scheme 112.



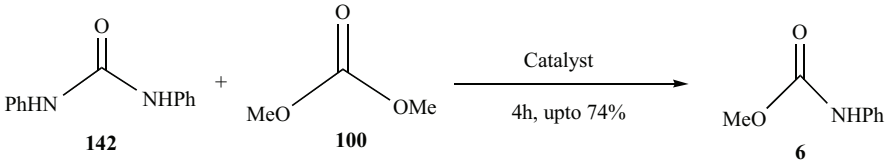
Scheme 113.



Scheme 114.



Scheme 115.



Scheme 116.

amines on the yields of the carbamates. $Sc(OTf)_3$ is more effective than La salt.

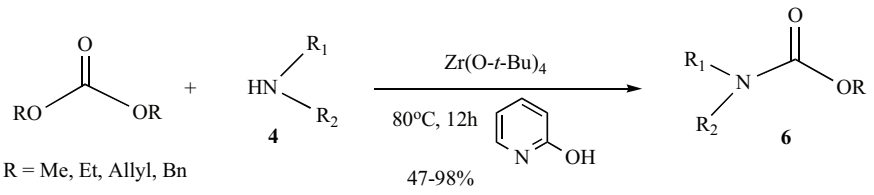
Cotarca and workers have reported [171] an efficient synthesis of *o*-nitrophenyl carbamates **6** through the reaction of bis(o-nitrophenyl)carbonate **139** with aliphatic amines **4** under mild reaction conditions (Scheme **113**).

Later on, Selva and coworkers have reported [172] a high yielding one-pot synthesis of methyl carbamates **6** from primary aliphatic amines **4** and dimethyl carbonates **100** using supercritical CO_2 (Scheme **114**). The pressure of CO_2 largely influences both the reaction conversion and the selectivity towards urethanes. Generally, conversion goes through a maximum (70-80%) in the mid-range (40 bar) and drops at lower and higher pressures, whereas selectivity is continuously improved (from 50% up to 90%) by an increase of pressure.

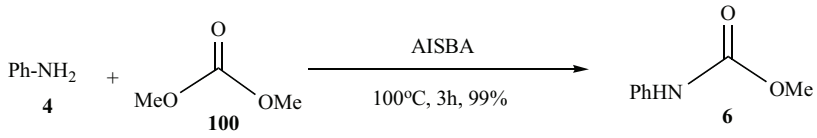
Deng and coworkers have reported [173] synthesis of carbamates **6** and dicarbamates **141** through reaction of variety of aliphatic amines **4** and bisamines **140** with dimethyl carbonate **100** catalyzed by acid functionalized ionic liquids (Scheme **115**). They have realized that $-SO_3H$ functionalized ionic liquids were found to be most effective among the applied ionic liquids.

Later on, Li and coworkers have reported [174] synthesis of methyl-*N*-phenyl carbamates **6** through the reaction of dimethyl carbonate **100** with 1,3-diphenyl urea **142** under atmospheric pressure (Scheme **116**). Among various catalysts used, NaOMe was found to be best in affording high yields of carbamates.

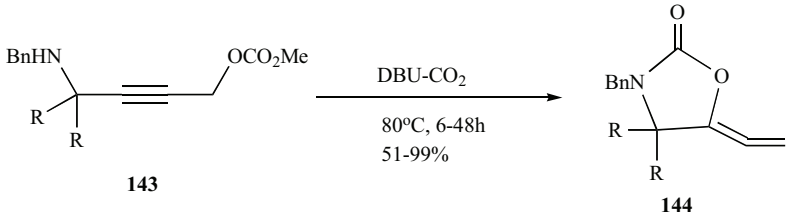
Later on, Han and Porco have reported [175] an efficient protocol for the synthesis of structurally diverse carbamates **6** through the reaction of various amines **4** with variety of carbonates (**100**, **120**, **124** *etc*) using zirconium (IV) catalyzed exchange process using 2-hydroxy pyridine as catalytic additives (Scheme **117**).



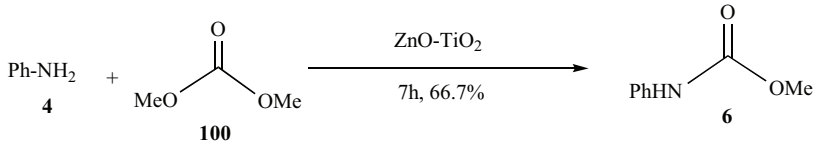
Scheme 117.



Scheme 118.



Scheme 119.



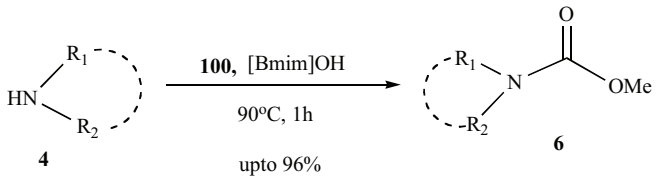
Scheme 120.

Use of DMC **100** in the synthesis of methyl-*N*-phenyl carbamates **6** using aromatic amines using ordered AISBA-15 catalyst was recently reported by Halligudi and coworkers (Scheme **118**) [176].

Recently, Yoshida and coworkers have reported [177] an efficient protocol for the synthesis of 5-vinylidineoxazolidin-2-ones **144** by DBU-mediated CO_2-fixation reaction of 4-(benzylamino)-2-butynyl carbonates and benzoates **143** (Scheme **119**).

Use of DMC **100** was further explored in the synthesis of methyl-*N*-phenyl carbamates **6** from aromatic amines **4** catalyzed by ZnO-TiO_2 catalyst (Scheme **120**) [178].

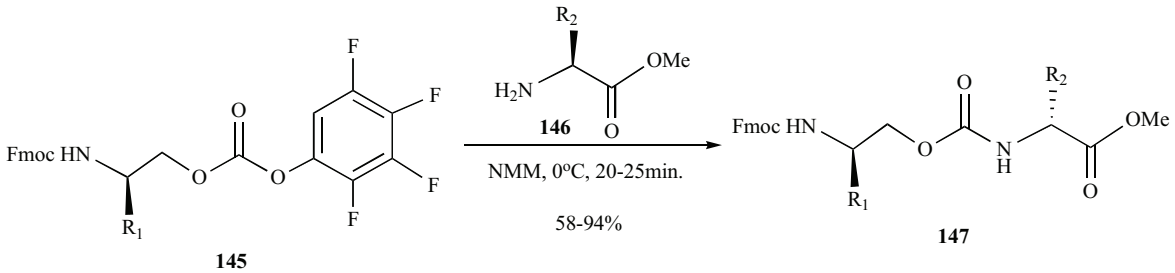
N-Heterocyclic carboxymethylation of amines **4** using DMC **100** catalyzed by ionic liquid, afforded corresponding carbamates **6** in high yields was reported by Gao and coworkers (Scheme **121**) [179].



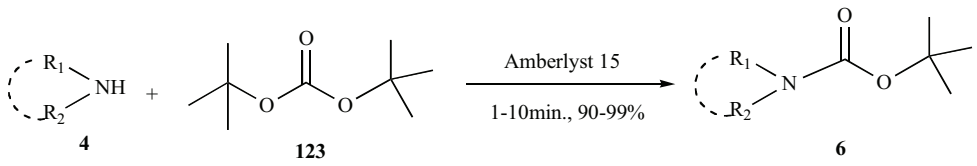
Scheme 121.

Recently, Sureshbabu and Hemantha have reported [180] the synthesis of dipeptidyl carbamates **147** through the reaction of an amino acid **146** with their synthesized F-moc aminoalkoxy pentafluorophenyl carbonate **145**. They have further explored the utility of **145** in synthesis of oligopeptidyl carbamates using variety of amino acids (Scheme **122**).

A most recent report for an efficient preparation of *N-tert*-butyl carbamates **6** of various amines **4** using di-*tert*-butyl carbonate **123**

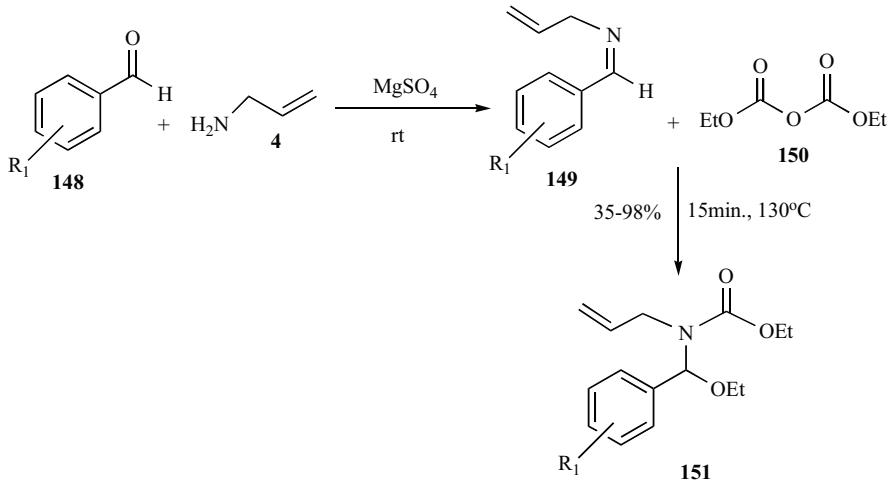


Scheme 122.



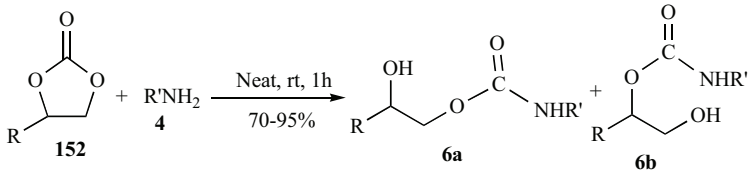
4 **123** **6**

Scheme 123.



148 **4** **149** **150** **151**

Scheme 124.



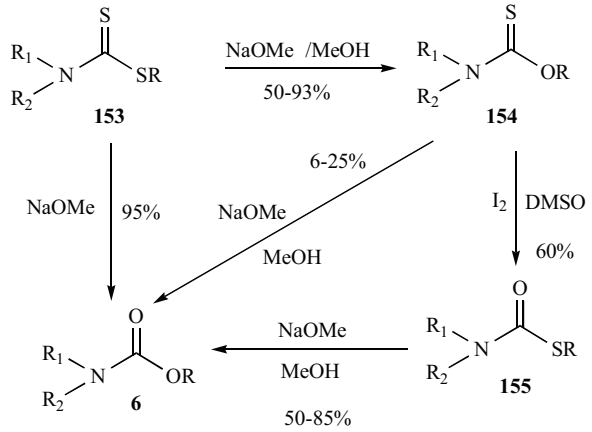
152 **4** **6a** **6b**

Scheme 125.

in presence of Amberlyst 15 under solvent free conditions was reported by Pal and their coworkers (Scheme **123**) [181].

More recently, A direct conversion of various allylic imines **149** to their corresponding α-ethoxy carbamates **151** using diethyl pyrocarbonate **150** was reported by Grognec and coworkers (Scheme **124**) [182]. The imines were synthesized from the corresponding aldehydes **148** using allylic amines **4**.

Iwasaki and coworkers have reported [183] the synthesis of hydroxy carbamates **6** (**a** & **b**) from cyclic five-membered carbonates **152** and primary amines **4** at room temperature (Scheme **125**).



153 **154** **155** **6**

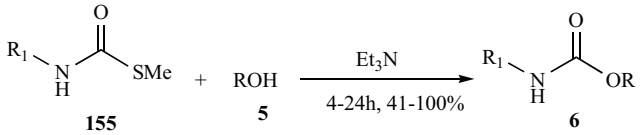
Scheme 126.

3.6. Carbamates Synthesis from Dithiocompounds

3.6a. Using Dithiocarbamates/Thiocarbamates

Tandel and coworkers have reported an efficient synthesis of carbamates **6** from dithiocarbamate **153** through either series of transformations or direct conversion using NaOMe/MeOH afforded carbamates **6** (Scheme **126**) [184]. The overall yields in carbamates from dithiocarbamates during three step is 36%, whereas the direct conversion afforded 95%.

Recently, Fochi and coworkers have reported an efficient protocol for the synthesis of various kinds of carbamates **6** through reaction of corresponding thiocarbamates **155** with alcohol **5** in triethylamine (Scheme **127**) [185].

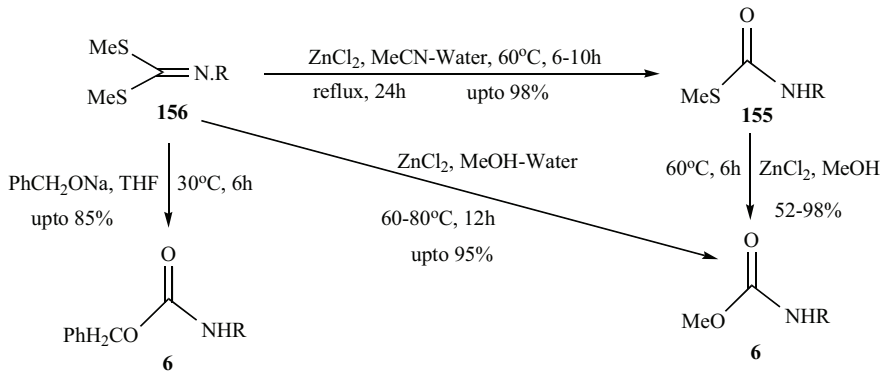


155 **5** **6**

Scheme 127.

3.6b. From Carbon-Imido Dithiolates

Rajappa and coworkers have reported [186] that carbon-imido dithiolates **156** are important precursors for the synthesis of carbamates **6** and can be first converted into S-methyl thiocarbamates [187] **155** using zeolite catalyzed partial hydrolysis. This method therefore provides an alternative route to methyl carbamates **6**



Scheme 128.

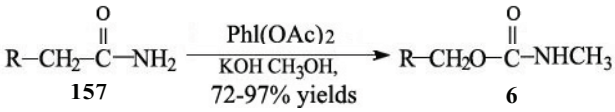
[188]. The carbon di-imidodithiolates can also be converted into carbamates **6** through one-step synthesis (Scheme **128**).

3.7. Carbamates Synthesis Through Rearrangement Reactions

3.7a. Hoffmann Rearrangement

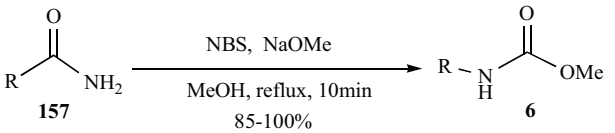
Generally, Hoffmann rearrangement [189] converts primary carboxamides to amines using aqueous NaOH and Br_2. In recent years, it has been used for the synthesis of carbamates **6** through the involvement of an isocyanate intermediate. Several researchers have directed their efforts on this rearrangement reaction in order to achieve an efficient synthesis of carbamates.

Moriarty and coworkers have reported [190] an efficient protocol for the synthesis of methyl carbamates **6** from primary alkyl and aryl carboxamides **157** using hypervalent iodine. They have treated a series of primary alkyl/aryl carboxamides **157** with $PhI(OAc)_2$ in KOH-MeOH at 5-10°C afforded the corresponding methyl carbamates **6** in good to excellent yields (Scheme **129**). These conditions avoids the use of elemental bromine or heavy metal reagents such as $Pb(OAc)_4$, AgOAc, $Hg(OAc)_2$, while taking advantage of the commercial availability of $PhI(OAc)_2$.



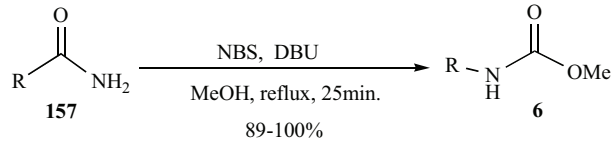
Scheme 129.

Later on, Huang and coworkers have reported [191] the synthesis of methyl carbamates **6** *via* a modified Hoffmann rearrangement. They have treated a series of *p*-substituted aromatic and primary aliphatic carboxamides **157** with NBS and NaOMe in methanol heated to reflux for ten minutes for the conversion of the carboxamides to their corresponding primary amino methyl carbamates **6** in nearly quantitative yields (Scheme **130**). The mild oxidative conditions of this modified Hoffmann rearrangement are shown to be particularly useful for the preparation of *p*-substituted anilines.



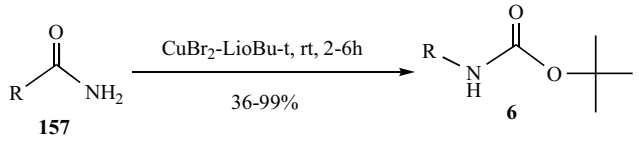
Scheme 130.

They have further elaborated [192] the synthesis of methyl carbamates **6** through the involvement of Hoffmann rearrangement using NBS and DBU in methanol **(**Scheme **131**). This method has been widely useful for the conversion of alkyl and aryl carboxamides **157** to their corresponding methyl carbamates **6** in excellent yields under extremely mild conditions.



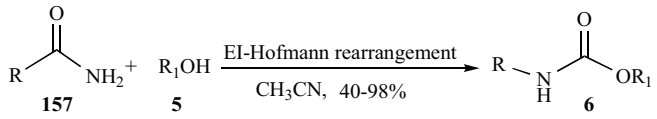
Scheme 131.

The synthesis of *N-tert*-butoxy carbamates **6** from primary carboxamides **157** using copper (II) reagent (prepared from copper (II) bromide and lithium tertiary butoxide *i.e.* $CuBr_2$-LiOBu-t) afforded good to high yields, has also been reported by Yamaguchi and their coworkers (Scheme **132**) [193].



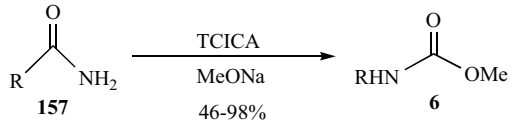
Scheme 132.

Later on, Matsumara and coworkers have reported [194] the electrochemical synthesis of carbamates **6** from primary carboxamides **157** and the process has been referred to as" Electrochemically induced Hoffmann rearrangement" which under new solvent systems containing a variety of alcohols **5** was developed since the reaction proceeds under mild conditions (neutral). An epoxy functional group in the amide and alcohol remains intact during the electrolysis (Scheme **133**).



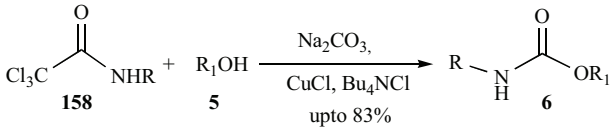
Scheme 133.

Later on, Hiegel and Hogenaur have reported [195] a base catalyzed synthesis of *N*-substituted carbamates **6** through the rearrangement of *N*-chloroamides (Scheme **134**). These *N*-chloramides were obtained by the chlorination of amides **157** using trichloro isocyanuric acid (TCICA).



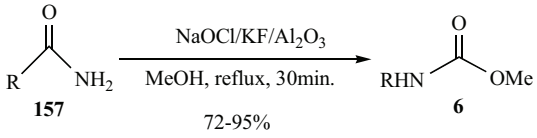
Scheme 134.

Nishikawa and coworkers have reported the synthesis of carbamates **6** through the rearrangement reaction of trichloroacetamides **158** using variety of alcohols **5** (Scheme **135**) [196].



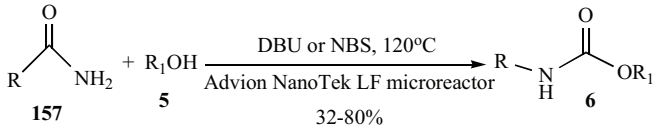
Scheme 135.

Gogoi and Konwar have reported [197] synthesis of methyl carbamates **6** through the modification of Hoffmann rearrangement. Thus, a series of methyl carbamates **6** were synthesized in good to excellent yields using NaOCl as an oxidant in the presence of KF/Al_2O_3/ MeOH at reflux conditions (Scheme **136**).



Scheme 136.

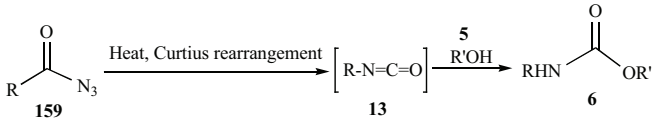
A most recent method for the synthesis of carbamates **6** starting from the corresponding amines **157** through Hoffmann rearrangement using microreactor technique has been reported by Ley and their coworkers (Scheme **137**) [198].



Scheme 137.

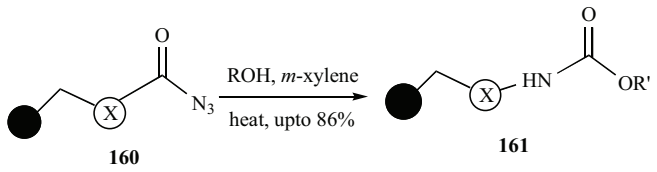
3.7b. Curtius Rearrangement

Curtius rearrangement involves the pyrolysis of acyl azides **159** to yield isocyanates **13** (Scheme **138**) [199]. Isocyanates **13** can treated with alcohols **5** to afford the corresponding carbamates **6**. In recent years, much interest has been developed among the chemists to synthesize the carbamates through Curtius rearrangement by trapping of isocyanate intermediate with an alcohol.



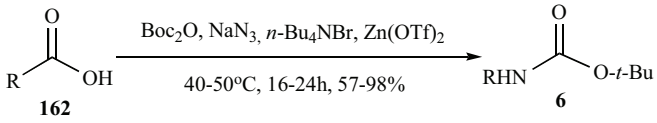
Scheme 138.

Richer and Andersen have reported [200] the synthesis of carbamates **161** solid supports using polystyrene resin. They have prepared an acid azide derivative **160**, which was previously loaded on polystyrene resin and treated with appropriate alcohol in *m*-xylene. The carbamates were obtained in excellent yields (Scheme **139**).



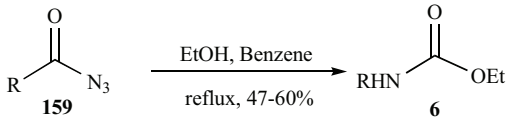
Scheme 139.

Lebel and Leogane have reported [201] an efficient protocol for the preparation of *tert*-butyl carbamates **6** from the corresponding acid **162**. The reaction of carboxylic acid **162** with di-*tert*-butyl dicarbonate **123** and sodium azide allowed the formation of an acyl azide **159**, which undergoes a Curtius rearrangement in the presence of tetrabutylammonium bromide and zinc(II)triflate afforded the corresponding carbamates **6** through the trapping of isocyanate intermediate (Scheme **140**). They have also extended the same protocol for the direct synthesis of carbamates of aromatic amines using aromatic acid [202, 203].



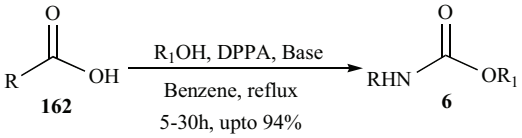
Scheme 140.

Dussault and Xu have reported a direct conversion of various acid azides **159** to their corresponding carbamates **6** through Curtius rearrangement using an alcohol **5** (Scheme **141**) [204]. Similar kind of approach was adopted by Saigo and coworkers for the synthesis of fullerene carbamates through reaction of corresponding fullerene acid azide with an alcohol [205].



Scheme 141.

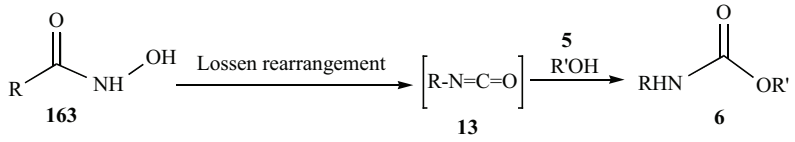
Ikegami and coworkers have reported synthesis of carbamates **6** of various sugar and other functionalities using corresponding acid **162.** *Insitu* conversion of acid **162** to the corresponding azides **159** was achieved using diphenylphosphoryl azides (DPPA), followed by addition of an alcohol afforded corresponding carbamates (Scheme **142**) [206]. They have further explored their methodology for the synthesis of carbamate linked glycoconjugates using various kinds of sugar acids and DPPA [207].



Scheme 142.

3.7c. Lossen rearrangement

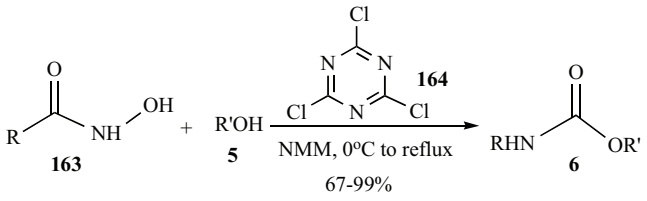
The Lossen rearrangement is a useful chemical reaction in which *O*-activated hydroxamic acids **163** can be converted into the corresponding isocyanates **13** (Scheme **143**) [208]. Carbamate **6** can be synthesized through *insitu* trapping of an isocyanate intermediate **13** through an alcohol **5**. In recent years, based on the above concept researchers become interested to synthesize carbamates using hydroxamic acids through the Lossen rearrangement reaction.



163 **13** **6**

Scheme 143.

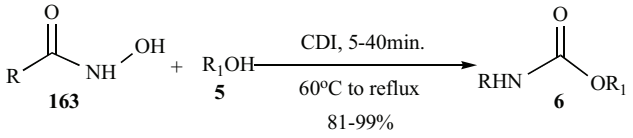
Recently, Papot and coworkers have reported an efficient synthesis of carbamates **6** through the reaction of a hydroxamic acid **163** with an alcohol **5** promoted by 2,4,6-trichloro-1,3,5-triazine **164** (cyanuric chloride, TCT) in presence of excess of *N*-methyl morpholine (NMM) through Lossen rearrangement reaction (Scheme **144**) [209].



163 **5** **6**

Scheme 144.

A most recent method for the synthesis of carbamates **6** through the reaction of hydroxamic acids **163** with an alcohol **5** using carbonyl diimidazole (CDI) through Lossen rearrangement was reported by Dube and coworkers (Scheme **145**) [210].



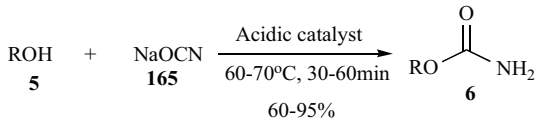
163 **5** **6**

Scheme 145.

3.8. Miscellaneous Methods for the Synthesis of Carbamates

3.8a. Carbamates Synthesis Using Sodium Cyanate

Recently, use of sodium cyanate **165** in the synthesis of primary carbamates **6** through reaction with alcohol **5** using various kinds of acidic catalysts such as trichloroacetic acid, silica supported-sulfuric acid, silica supported-perchloric acid, and $Al(HSO_4)_3$ has been realized by Modaressi-Alam and coworkers (Scheme **146**) [211-214].

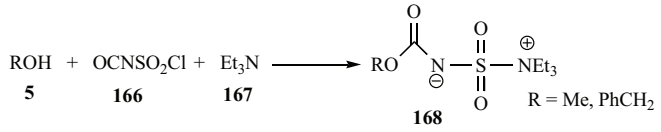


5 **165** **6**

Scheme 146.

3.8b. Carbamates Synthesis Using Burgess Reagent

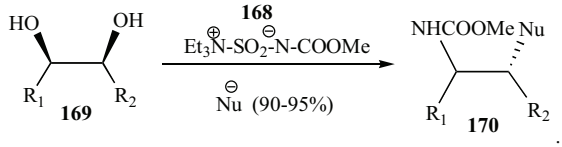
Burgess reagent [215] **168** is prepared from a reaction of an alcohol **5** with chlorosulfonyl isocyanate **166** and triethyl amine **167** (Scheme **147**), has been shown to be an efficient for the stereospecific *cis*-dehydration of secondary and *tert*. to provide olefins. Primary alcohols do not undergo elimination due to competing (and predominant) displacement reaction to form corresponding methyl carbamates. Several kinds of alcohols have been used in order to get more efficient Burgess reagent which could afford carbamates in high yields. In recent years, researchers have directed their efforts to synthesize carbamates through Burgess reagent.



5 **166** **167** **168**

Scheme 147.

Nicolaou and coworkers have reported [216] an efficient, one-pot synthesis of methyl carbamates **170** through the corresponding *cis*-diols **169** using methyl-Burgess reagent **168** (Scheme **148**).



169 **170**

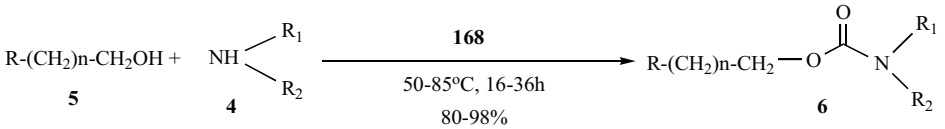
Scheme 148.

Later on, Wood and coworkers have reported [217] a novel, one-step conversion of primary alcohols **5** into carbamate-protected **6** amines using benzyl-Burgess reagent **168** (Scheme **149**).

Conversion of Baylis-Hillman adducts **171** of *β*-amino acids into corresponding methyl carbamates **172** using methyl Burgess reagent **168** was reported by Mamaghani and Badrian (Scheme **150**) [218].

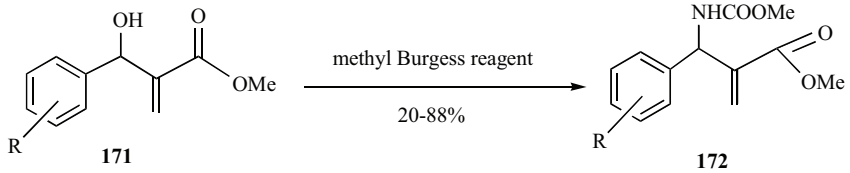
3.8c. Synthesis of Carbamates from Oximes

Goti and coworkers have reported the synthesis of various substituted aromatic carbamates **174** through the reaction of variety of



5 **4** **6**

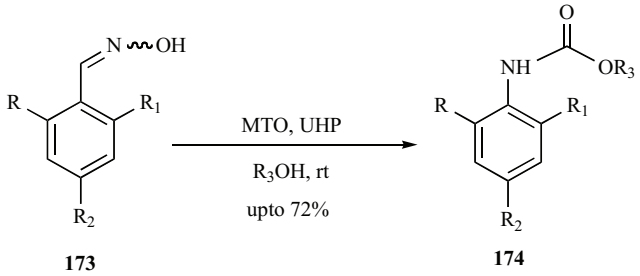
Scheme 149.



171 **172**

Scheme 150.

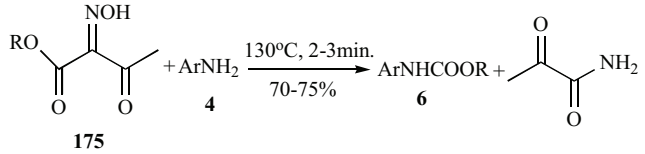
aromatic oximes **173** with alcohols using methyltrioxorhenium (MTO) and urea-hydrogen peroxide (UHP) (Scheme **151**) [219].



173 **174**

Scheme 151.

Recently, Elghamry have reported the synthesis of carbamates **6** through the reaction of oximinoacetoacetate **175** with variety of aromatic amines **4** under solvent free conditions (Scheme **152**) [220].



175

Scheme 152.

4. CONCLUSIONS

This review gives a comprehensive survey regarding the synthesis of organic carbamates through the various starting materials from the beginning to the recent reports (covering upto December, 2009). 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 several 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 frequently been used a demandable synthons for the synthesis of various structurally diverse synthetic intermediates which have broad applications in drug discovery synthesis. In recent years, it has been realized by various researchers that introduction of carbamate functionality in various biologically active synthetic/natural/semisynthetic molecules increases many fold biological activities. 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. Their wide utility as useful agrochemicals makes their further demand for their synthesis. This important functional group class, although often overlooked, holds potential and no doubt will offer new and exiting chemistry in the near future.

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