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Role of the Macrocyclic Polyether in the Synthesis of N-Alkylcarbamate Esters from Primary Amines, CO_2 and Alkyl Halides in the Presence of Crown-Ethers.

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Abstract: Primary amines, RNH_2 1, and CO_2 easily afford monoalkylammonium N-alkylcarbamates, $[RNH_3][O_2CNHR]$ 2, that have been reacted with alkyl halides, R'X, in the presence of crown-ethers to give organic carbamates in good yield. We report here the synthesis and spectroscopic characterization of some alkylammonium carbamates 2, where R = benzyl 2a, allyl 2b, ter-butyl 2c, cyclohexyl 2d, and discuss their stability in solution and the conditions in which they can react with alkyl halides to give organic carbamates, RNHC(O)OR'. The role played by the macrocyclic ligand in modifying the reactivity of monoalkylammonium carbamates 2 towards R'X has been rationalized and the influence of parameters such as solvent, temperature and CO_2 pressure on the yield and selectivity of the process leading to organic carbamates has been also settled.

INTRODUCTION

The utilization of carbon dioxide in the synthesis of organic carbamates[1-5] can represent an alternative route to current processes based on the use of harmful compounds, such as phosgene[6] or isocyanates.[7] To set up new synthetic procedures involving less noxious starting materials such as carbon dioxide[8] responds to requirements of both environmental protection and utilization of carbon dioxide as a source of carbon.

Amines and alkyl halides are compounds virtually suitable for being employed as starting reagents in the synthesis of carbamates by reaction with CO_2. The

synthesis of carbamate esters by direct reaction of amines, alkyl halides and carbon dioxide has been investigated by Yoshida and coworkers[4b,h] who limited their studies essentially to secondary alifatic amines. Hori *et al.* reported the synthesis of organic carbamates from primary or secondary amines, CO_2 and alkyl halides in the presence of a strong proton acceptor (DBU, 1,8-diazabicyclo[5.4.0.]undec-7-ene).[4g]

Recently, we have developed a new method of synthesis of N,N-substituted carbamates $R_2NC(O)OR'$ from secondary amines, carbon dioxide and alkyl halides.[4c-e] This process involves the utilization of phosphorous compounds, $P(NR_2)_3$ [9] and $P(O_2CNR_2)_x(NR_2)_{3-x}$,[4e,10] as promoters. The extension of this method to the synthesis of N-monosubstituted organic carbamates, RNHC(O)OR', is quite problematic as it involves, as intermediates, aminophosphines $P(NHR)_3$, hard to synthesize.[11,14]

We have decided, thus, to explore other synthetic procedures for primary amines and have studied the reactivity of mono-alkylammonium alkylcarbamates $[RNH_3][O_2CNHR]$ **2** which can be easily obtained from primary amines **1** and carbon dioxide, eq. (1).[15]

$$\underset{\mathbf{1}}{2\ RNH_2} + CO_2 \longrightarrow \underset{\mathbf{2}}{[RNH_3][O_2CNHR]} \qquad (1)$$

In this paper we report the characterization and properties of some monoalkylammonium N-monoalkylcarbamates **2** and describe their reaction with alkyl halides, R'X, in the presence of a macrocyclic polyether to afford RNHC(O)OR' carbamate esters.[16] The role of the macrocyclic ligand in controlling the reactivity of alkylammonium carbamates **2** towards alkyl halides is highlighted.

RESULTS AND DISCUSSION

Synthesis, Characterization and Properties of Monoalkylammonium N-Alkylcarbamates

The ionic carbamates used as carbamation agents in this work, are $[(PhCH_2)NH_3][O_2CNH(CH_2Ph)]$ **2a**, $[(CH_2{=}CH\text{-}CH_2)NH_3][O_2CNH(CH_2\text{-}CH{=}CH_2)]$ **2b**, $[(t\text{-}Bu)NH_3][O_2CNH(t\text{-}Bu)]$ **2c** and $[(Cy)NH_3][O_2CNH(Cy)]$ **2d**. They were prepared by saturating with CO_2 solutions of the corresponding amines $[PhCH_2NH_2$ **1a**, $CH_2{=}CHCH_2NH_2$ **1b**, $(t\text{-}Bu)NH_2$ **1c**, $CyNH_2$ **1d**] in solvents such as benzene, toluene, THF, diethyl ether, CH_2Cl_2, CH_3CN.[17] In these media, unlike what observed in alcoholic solvents (methanol, ethanol), **2a-d** are, generally, sparingly soluble and, thus, they can be isolated as white microcrystalline solids and characterized.

As shown in Table 1, isotopic labeling of the carbamic carbon causes in $[(PhCH_2)NH_3][O_2{}^{13}CNH(CH_2Ph)]$ **2a*** the shift of ν (NCOO) from 1567 to 1559 cm^{-1}. Comparison with the data reported by Chisholm[19] for covalent transition metal

Table 1. Selected IR Data (cm^{-1}, nujol) for N-Alkylammonium Carbamates **2a-2d** and Other Representative Ionic or Covalent Metal Carbamates.[a]

Compound	$\nu_{carbamic\ NH}$	$\delta_{(RNH_3^+)}$	$\nu_{(NCOO)}$	"NCOO" skeletal vibrations[b]	$\omega_{(OCN)}$	$\delta_{(NCOO)}$
			IONIC MONO-ALKYLAMMONIUM N-ALKYLCARBAMATES			
2a	3294 (m-s)	1629 (m-s)	1567 (vs); [8]	1497 - 1282	815 (m); [25]	630 (m); [1]
2b	3315 (m, br)	1610 (m, br)	1560 (s, br)	1480 - 1255	815 (m-s)	[c]
2c	3440 (m, sh)	1645 (s)	1560 (s, br)	1480 - 1210	810 (m-s, sh)	[d]
2d	3390 (m, sh)	1620 (s)	1550 (vs, br)	1475 - 1235	815 (m, sh)	640 (m-w)
			IONIC METAL CARBAMATES			
$(K^+CE)(O_2CNMe_2)^-$[e]			1580 (s)	1345 (s)	815 (m-s)	600 (m-w)
$(K^+CE)(O_2CNEt_2)^-$[e]			1565 (s)	1295 (s)	810 (m)	[d]
			COVALENT METAL CARBAMATES			
$Zr(O_2CNMe_2)_4$[f] (bidentate)			1587 (vs); [22]	1509-1265	794 (s); [24]	659 (s); [0]
$W(NMe_2)_3((O_2CNMe_2)_3$[f] (monodentate)			1636 (vs); [39]	1276-1190	785 (m); [22] 791 (m); [21]	647 (s); [2]

[a] Values in square brackets express the isotopic shift (cm^{-1}) upon carbamic carbon ^{13}C labeling. [b] See Ref. 18. [c] Not assigned owing to broad absorptions obscuring the 690-600 cm^{-1} range. [d] No band was observed in the 690-600 cm^{-1} range. [e] From Ref. 4d-e. [f] From Ref. 19.

carbamates shows that the ν(NCOO) isotopic shift is smaller for ionic than for covalently bound carbamates.

All alkylammonium N-alkylcarbamates here investigated, likewise alkali metal carbamates,[4d,e] show a sharp band of variable intensity near 815 cm^{-1} assigned to the ω(OCN) out-of-plane bending.[20] This band is observed at 815 cm^{-1} in the spectrum of **2a** and is shifted to 790 cm^{-1} as a result of carbamic carbon isotopic labeling in **2a***. It is worth noting that none of the covalent transition metal carbamates studied by Chisholm were reported to show bands in the range 810 - 820 cm^{-1}.[21] Therefore, according to our results and to the data reported in the literature, we conclude that the amount of the isotopic shift of the band located around 1560-1650 cm^{-1} and the location of the band due to the out of plane vibration of the "NCO_2" group can be diagnostic of the nature of the bond of the carbamate group.

Ionic carbamates **2a-d** show quite a modest chemical stability in solution. As a matter of fact, the IR spectrum of a solution obtained by allowing a suspension of **2a** in THF to equilibrate overnight under a dinitrogen atmosphere shows, in addition to the absorptions assigned to $PhCH_2NHCO_2^-$ anion [3320 (br) and 1545 cm^{-1} (br)], also bands due to free amine **1a** [3390 and 3320 cm^{-1}] and carbon dioxide [2340 cm^{-1}], as well as absorptions at 1725 and 1685 cm^{-1} attributed to carboxylated species. These latter absorptions are shifted to 1678 and 1643 cm^{-1}, respectively, upon $^{13}CO_2$ isotopic labeling. Equations (2)[22], (3) and (4) can account for the conversion of alkylammonium carbamates **2** in solution.

$$\underset{\mathbf{2}}{[RNH_3][O_2CNHR]} = \underset{\mathbf{3}}{RNHC(O)OH} + \underset{\mathbf{1}}{RNH_2} \qquad (2)$$

$$\underset{\mathbf{3}}{RNHC(O)OH} \xrightleftharpoons{} \underset{\mathbf{1}}{RNH_2} + CO_2 \qquad (3)$$

$$2\ \underset{\mathbf{3}}{RNHC(O)OH} \xrightleftharpoons{} \underset{\mathbf{4}}{[RNHC(O)OH]_2} \qquad (4)$$

Therefore, carbamic acid **3** can undergo both decarboxylation and self-association leading, depending on its concentration and the temperature, to the formation of dimers **4** or more complex polymeric species. Intermolecular association phenomena are well documented in the literature for carboxylic acids and IR spectroscopy has been shown to be an useful tool to investigate these processes.[26] As a rule, in fact, both OH and C=O stretching frequency are shifted to lower wave numbers as a result of intermolecular self-association.[26] On this basis, we assign the absorption at 1725 cm^{-1} to monomeric N-benzylcarbamic acid, $PhCH_2NHC(O)OH$ **3a**, and the absorption at 1685 cm^{-1} to its dimeric form $[PhCH_2NHC(O)OH]_2$ **4a**. Further support for this attribution comes from the IR data reported for N,N-substituted carbamic acid $(NO)_2ClCo[PhP(OCH_2CH_2)_2NC(O)OH]$ recently characterized by X-ray.[27] This species,

that exists in the solid state as dimer $\{(NO_2)_2ClCo[PhP(OCH_2CH_2)_2NC(O)OH]\}_2$ owing to hydrogen bonding between the N-C(O)OH moieties of two molecules, shows a ν(CO) at 1665 cm^{-1}, while the IR spectrum of the monomer displays a band located at 1710 cm^{-1}.

Reactivity of Primary Amines towards Alkyl Halides in the Presence of Carbon Dioxide

When primary amines, RNH_2, were reacted with alkyl halides, R'X, in the presence of carbon dioxide the formation of organic carbamate RNHC(O)OR' was not observed at all or might occur only at a very low extent. The alkylammonium carbamate initially formed, eq. (1), reacts with R'X to give, mainly, N-alkylation products, eq. (5).

$$[RNH_3][O_2CNHR] + R'X \longrightarrow \underset{(R'RNH,\ R'_2RN,\ R'_3RNX)}{\text{N-alkylation products}} + CO_2 \qquad (5)$$

As an example, **2a** reacts with allylbromide (Table 2) affording essentially allylbenzylamine,[28] diallylbenzylamine[29] and alkylammonium salts. Analogous behaviour was shown by allylamine, cyclohexylamine, and *ter*-butylamine when treated with benzyl chloride or other alkyl halides under a CO_2 atmosphere.

Several pathways can account for the formation of the N-alkylation products. As some free amine is present in the reaction mixture in equilibrium with **2**, the formation of N-alkylation products may be due to direct reaction of R'X with **1** (route a). On the other hand, the N-alkylation reaction may be the result of the electrophilic attack by the alkyl halide at the carbamic nitrogen atom of

Table 2. Reactivity of $[PhCH_2NH_3][O_2CNH(CH_2Ph)]$ **2a** towards Allyl Bromide in the Absence of 18-crown-6.

Entry	**2a**[a]	R'X[a,b]	S[c]	T(K)	t[d]	P_{CO_2}[e]	**5** (% yield[f])
1	1	2.5	THF	293	48	0.103	-
2	1	1	MeOH	"	18	"	-
3	1	1	"	"	60	"	<0.2
4[g]	1	1	[h]	353	24	"	<0.2

[a] mol of. [b] R'X is allyl bromide. [c] Solvent. [d] Reaction time in hours. [e] In MPa. [f] GC yield with respect to **1a**. [g] R'X conversion was 100% in this run. [h] A mixture dichloromethane/toluene (1:1 v/v) was used as solvent in this run.

$RNHCO_2^-$ (route b). This reaction has been reported to occur when alkyl halides were reacted with phosphocarbamates,[4d,e] or with a few transition metal carbamates,[30] or with alkali metal N,N-dialkylcarbamates.[4e,f] Finally, it cannot be ruled out that the formation of N-alkylation products might involve R'X attack at the nitrogen atom of species **3** or **4** present at the equilibrium (route c). In our opinion, the three routes may work simultaneously, although their relevance may remarkably depend on the experimental conditions.

The Role of Macrocyclic Polyethers in the Synthesis of Organic Carbamates from Primary Amines, CO_2 and Alkyl Halides

The synthesis of carbamate esters RNHC(O)OR' from primary amines, CO_2 and alkyl halides implies the O-alkylation of the intermediate ionic carbamate **2** and, therefore, requires that the reactivity of **2** towards R'X has to be modified with respect to that described so far.

We have elsewhere[4d,e] discussed the ambident nucleophile character of carbamate anions and rationalized the change of reactivity of alkali metal N,N-dialkylcarbamates towards alkyl halides upon alkali cation complexation by a suitable crown-ether.

Ionic association phenomena can be present in alkylammonium carbamates due to hydrogen bonding between the alkylammonium cation and the carbamate anion.[31] This interaction can lower the carbamate anion O-nucleophilicity and may be responsible for the poor aptitude of carbamates **2** to give O-alkylation when reacted with R'X. Thus, electrophilic attack by alkyl halides occurs preferentially at the carbamic nitrogen atom and, as we have already discussed above, this reaction can be one of the routes leading to the formation of the N-alkylation products.[32] Conversely, when alkylammonium carbamates **2** were reacted with alkyl halides in the presence of a macrocyclic polyether, organic carbamates were obtained in interesting yields. As an example, the reaction of **2a** with allylbromide in THF, in the presence of a stoichiometric amount of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane), afforded **5** (see Entry 1, Table 3). This result clearly shows that, under these conditions, the O-alkylation reaction can occur [eq.(6)] in competition with N-alkylation. We ascribe the change of reactivity to the formation

$$2\,RNH_2 + CO_2 + R'X + CE \longrightarrow RNHC(O)OR' + [RNH_3{\cdot}CE]X \qquad (6)$$

of a "host-guest" adduct between the crown-ether and the monoalkylammonium cation RNH_3^+ to give $[RNH_3{\cdot}CE][O_2CNHR]$.[33,34]

In our case, the crown-ether can both increase the solubility of the ionic carbamates **2**, usually poorly soluble in most organic solvents, and change the reactivity of the carbamate anion as ambident nucleophile. In fact, the complexation of RNH_3^+ ions by crown-ether molecules lowers the interaction between these

cations and the carbamate anion oxygen atoms whose nucleophilicity towards alkyl halides is, thus, enhanced, as already demonstrated for I Group metal carbamates.[4e]

The crown-ether can also influence the thermodynamic properties of alkylammonium cations,[35] and shift to left equilibria (2) and (3). This would repress the formation of N-alkylation products through route **a**.

The N,N-dialkylcarbamate ester (RR'NC(O)OR') is also formed in reaction (6), in very low amount [< 2-3% vs **1**]. We have ruled out the possibility that this compound is formed by N-alkylation of the corrisponding N-monoalkylcarbamate RNHC(O)OR', although a similar reaction has been described in the literature for urethan.[36] However, we have not observed the formation of N-benzyl,N-allyl,allylcarbamate when N-benzyl,allylcarbamate (**5**) was reacted with allyl bromide under the same experimental conditions used for reaction (6). RR'NC(O)OR' is most probably formed by reaction of the secondary amine RR'NH (one of the N-alkylation products) with carbon dioxide and R'X. However, it is worth noting that when CE was not used [see Entries 1-3, Table 2], the formation of RR'NC(O)OR' was not observed.[37]

Influence of Experimental Parameters.

In order to improve the selectivity of the process leading to the formation of the organic carbamate RNHC(O)OR', we have studied the influence of parameters such as the nature of solvent (Table 3), the temperature (Table 4) and CO_2 pressure on reaction (6) [R = benzyl; R'X = allyl bromide; CE = 18-crown-6].

Best selectivity in organic carbamate was obtained when reaction (6) was carried out in pure chlorinated solvents such as CH_2Cl_2, $CHCl_3$ or in mixtures with aromatic solvents.

The influence of the solvent on the selectivity of reaction (6) can be rationalized by taking into account that solvents can influence the thermodynamic stability of the $(RNH_3{\cdot}CE)^+$ adducts with respect to dissociation, eq. (7).[39] The

Table 3. Influence of the Solvent on the Reaction of $[PhCH_2NH_3][O_2CNH(CH_2Ph)]$ **2a** with Allyl Bromide in the Presence of 18-crown-6.

Entry	**2a**[a]	CE[a,b]	R'X[a,c]	S[d]	T(K)	t[e]	P_{CO_2}[f]	**5** (% yield[g])
1	1	1	2	THF	293	7	0.103	6
2	1	1	1	MeOH	"	2.5	"	<0.2
3	1	1.1	1.1	CH_2Cl_2	283	2	"	57

[a] mol of. [b] CE is 18-crown-6. [c] R'X is allyl bromide. [d] Solvent. [e] Reaction time in days. [f] In MPa. [g] For isolated carbamates. Yield is calculated with respect to **1a**.

Table 4. Influence of the Temperature on the Reaction of $[PhCH_2NH_3][O_2CNH(CH_2Ph)]$ **2a** with Allyl Bromide in the Presence of 18-crown-6.

Entry	2a[a]	CE[a,b]	R'X[a,c]	S[d]	T(K)	t[e]	P_{CO_2}[f]	5(% yield[g])	R'X Conversion
1	1	1.1	1.1	*h*	243	24	0.103	-	-
2	1	1.1	1.1	"	273	24	"	1	1%
3	1	1.1	1.1	"	283	40	"	57	>70%
4	1	2[i]	1	*j*	363	28	0.206	30	100%

[a] mol of. [b] CE is 18-crown-6. [c] R'X is allyl bromide. [d] Solvent. [e] Reaction time in hours. [f] In MPa. [g] For isolated carbamates. Yield is calculated with respect to **1a**. [h] CH_2Cl_2 was used as solvent. [i] An excess of CE was used in this run to limit the dissociation of $(RNH_3 \cdot CE)^+$ complex. [j] A mixture $CH_2Cl_2/PhCH_3$ (1:1 v/v) was used as solvent in this run.

formation of organic carbamates is, thus, related to the stability of alkylammonium cation-polyether complex.

$$(RNH_3 \cdot CE)^+ \text{ ====== } (RNH_3)^+ + CE \qquad (7)$$

In methanol, both in presence and in absence of CE, the formation of the carbamate ester RNHC(O)OR' was always observed to occur in very low yield, the main reaction being the alkylation of primary amines [compare Entry 3, Table 2 with Entry 2, Table 3].

The stability of alkyl- or aryl-ammonium cation complexes with macrocyclic ligands also depends on the temperature and it has been shown to increase when the temperature is lowered.[39] We have investigated the influence of temperature on the O-alkylation reaction (Table 4). Reaction (6) occurs selectively, although slowly, at temperatures lower than room temperature. Higher temperatures favour the complete conversion of the alkyl halide but lead to less satisfactory selectivity towards organic carbamates.

In order to suppress the decarboxylation of **2** [eq. (2) and (3)], reaction (6) was carried out under CO_2 (0.103-0.206 MPa). However, the utilization of higher CO_2 pressures does not improve the yield of organic carbamate. In fact, when **2a** [1 eq] was reacted with allyl bromide [1 eq] and 18-crown-6 [1 eq] in a toluene/CH_2Cl_2 (1:1 v/v) mixture, at 283 K, under 3.09 MPa of CO_2, **5** was observed with 15% yield (determined by GC), also after a long time (5 days).[40]

Synthesis of Carbamate Esters and Crown-Ether Recovering

Reaction (6) has been utilized for the synthesis of a few carbamates of formula RNHC(O)OR', where R and R' are alkyl or cycloalkyl groups. In Table 5 we have listed a few of the organic carbamates synthesized according reaction (6) and the related yield vs **1**.

Alkylammonium carbamates **2** do not need to be isolated: they can be prepared *in situ* by reaction of **1** with CO_2 and, then, treated with the crown-ether and the alkyl halide. We have also found an easy and cheap procedure which allows to recover the pure macrocyclic ligand from $(RNH_3{\cdot}CE)X$ in almost quantitative yield. This is of interest in a cyclic process of synthesis of carbamates.

Table 5. RNHC(O)OR' Carbamate Esters Synthesized through Reaction (6).

RNHC(O)OR'	T(K)	t(h)	% yield[a]
$(PhCH_2)NHC(O)OCH_2CH{=}CH_2$[b]	283	40	57[c]
$(PhCH_2)NHC(O)OMe$[d,e]	298	28	42
$(CH_2{=}CHCH_2)NHC(O)OCH_2Ph$[b]	293	70	55[c]
(Cy)NHC(O)OMe[d,e]	293	36	41
(Cy)NHC(O)OCH_2Ph[d,f]	298	72	35
(*t*-Bu)NHC(O)OMe[d,g]	293	28	9

[a] GC yield, unless otherwise indicated. [b] See also Experimental Section. [c] Isolated. [d] (1): 2 eq; R'X: 1 eq; 18-crown-6: 1 eq. Solvent was dichloromethane and P_{CO_2}= 0.103 MPa, in this run. [e] See ref. (41). [f] See Note (42). [g] See Note (43).

CONCLUSIONS

The utilization of transition metal complexes or strong proton acceptors in the synthesis of carbamate esters from amines, CO_2 and alkyl halides has been documented by Saegusa[4a] and Hori,[4g] respectively. We have shown that N-alkylcarbamate esters RNHC(O)OR' can be easily prepared by direct reaction of primary amines, carbon dioxide and alkyl halides in the presence of a suitable macrocyclic polyether able to form a stable "host-guest" adduct with monoalkylammonium cations, $(RNH_3{\cdot}CE)^+$. In these conditions, the O-alkylation of $RNHCO_2^-$ can compete with the N-alkylation reaction and the synthesis of N-alkylcarbamate esters RNHC(O)OR' can be accomplished in mild conditions and in interesting yields.

In the reactions investigated up to now, we have always used the 18-crown-6 polyether. However, as the stability of the complex $(RNH_3 \cdot CE)^+$ seems to be of crucial importance in controlling the yield and selectivity of reaction (6), we have under investigation the utilization of other macrocyclic ligands able to bind $(RNH_3)^+$ cations in order to discover whether the nature of the polyether can further improve yields and selectivity.

EXPERIMENTAL SECTION

IR spectra were obtained with a Perkin Elmer 883 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with a Varian XL-200 spectrometer. GC and GC-MS analyses were carried out with a DANI HR 3800 gas-chromatograph and a HP 5890 gas-chromatograph equipped with a HP 5970 mass-selective detector.

Solvents were dried and distilled as described in the literature and stored under dinitrogen. CO_2 (99.99% pure) and carbon-^{13}C dioxide (^{13}C 99%) were from SIO Spa and CIL, respectively. 18-crown-6, benzyl chloride, methyl iodide and allyl bromide were all Aldrich products. Benzylamine, cyclohexylamine and allylamine were from Fluka, *ter*-butylamine was from Janssen Chimica.

I. Synthesis of Alkylammonium N-Alkylcarbamates $[RNH_3][O_2CNHR]$ **2** [*R=benzyl* **2a**, *allyl* **2b**, ter-*butyl* **2c**, *cyclohexyl* **2d**]

A solution of RNH_2 **1** [10 mL] in THF (100 mL) was saturated at 293 K with CO_2 (0.103 MPa). The carbamate salt that precipitated from the solution was filtered out, washed with diethyl ether (3x30 mL) and dried in vacuo.

A) $[(PhCH_2)NH_3][O_2CNH(CH_2Ph)]$ **2a**. Yield = 90%.
Elemental analysis. Calculated for $C_{15}H_{18}N_2O_2$: C, 69.68; H, 6.97; N, 10.84. Found: C, 69.40; H, 6.89; N, 10.77.

2a* was prepared as **2a**.

B) $[(CH_2{=}CHCH_2)NH_3][O_2CNH(CH_2CH{=}CH_2)]$ **2b**. Yield = 80%. More carbamate was isolated from the mother solution upon addition of pentane (total yield 90%).
Elemental analysis. Calculated for $C_7H_{14}N_2O_2$: C, 53.15; H, 8.93; N, 17.70. Found: C, 52.97; H, 9.00; N, 17.60.

C) $[(t\text{-}Bu)NH_3][O_2CNH(t\text{-}Bu)]$ **2c**. Yield = 60%. More carbamate was isolated from the mother solution upon addition of n-hexane (overall yield 89%).
Elemental analysis. Calculated for $C_9H_{22}N_2O_2$: C, 56.81; H, 11.65; N, 14.72. Found: C, 56.57; H, 11.73; N, 14.64.

D) $[(Cy)NH_3][O_2CNH(Cy)]$ **2d**. Yield = 75%. More carbamate was isolated from the mother solution upon addition of n-hexane (overall yield 90%).
Elemental analysis. Calculated for $C_{13}H_{26}N_2O_2$: C, 64.43; H, 10.81; N, 11.55. Found: C, 64.15; H, 10.77; N = 11.48.

II. Synthesis of Carbamate Esters RNHC(O)OR'

As examples we report in detail the synthesis of N-benzyl,allylcarbamate and N-allyl,benzylcarbamate.

A) Synthesis of $(PhCH_2)NHC(O)OCH_2CH=CH_2$. A suspension of **2a** in CH_2Cl_2 (40 mL), prepared by saturating at 293 K a solution of **1a** [4.04 mL, 3.965 g, $3.70 \cdot 10^{-2}$ mol] with CO_2 (0.103 MPa) was treated with 18-crown-6 [5.44 g, $2.06 \cdot 10^{-2}$ mol]. A clear solution was obtained which was allowed to react with allyl bromide [1.80 mL, 2.516 g, $2.08 \cdot 10^{-2}$ mol] for 40 h at 283 K. The reaction mixture was, then, concentrated in vacuo to about 10 mL. By adding diethyl ether (40 mL) and cooling at 253 K a white solid (alkylammonium salts) was obtained which was separated from the solution by filtration. The mother liquor and the washing solutions were collected together and evaporated in vacuo. The residual oil was chromatographed on a silica gel column. n-Hexane/diethyl ether (2:1 v/v) was used as eluent as long as tertiary amine R'_2RN [R = benzyl, R' = allyl] was eluted and, then, a n-hexane/diethyl ether (1:1 v/v) mixture. After evaporation of the solvent 2.015 g of pure **5** were obtained (Yield = 57% vs **1a**).
Elemental analysis. Calculated for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.95; H, 6.80; N, 7.28%.
MS: 191 (M^+), 150 (base peak, M-allyl), 133 ($RNCO^+$), 117, 106 (RNH^+), 91 (R^+), 79, 65, 51, 41 (allylic ion), 39 (propargylium ion), 28 *m/e* . The intensity of the parent peak is very low.
IR (neat, KBr plates): 3415 (shoulder) and 3335 (s, br) (N-H stretching), 1705 (vs, br, C=O stretching), 1525 (vs, br, N-H bending), 1250 (vs, br, N-CO_2 group stretching), 1140 (s) and 1045 cm^{-1} (s) (C-O-C stretchings).
^1H NMR ($CDCl_3$): 4.35 (d, 2, $^3J_{HCNH}$ = 5.97 Hz, $H_{benzylic}$), 4.58 (dd, slightly broad, 2, $^3J_{HCCH}$ = 5.59 Hz, $H_{allylic}$), 5.20 (dq, 1, $^3J_{cis}$ = 10.41 Hz, $^2J_{HCH} = {}^4J_{HCCCH}$ = 1.3 Hz, $CH=C\underline{H}_2$), 5.2-5.3 (br, 1, N<u>H</u>), 5.30 (dd,1, $^3J_{trans}$ = 17.30 Hz, $CH=C\underline{H}_2$), 5.91 (ddt,1, $C\underline{H}=CH_2$), 7.29 ppm (m, 5, $H_{aromatic}$). N<u>H</u> proton gives exchange with D_2O. ^1H-decoupling and D_2O exchange experiments have shown that the amidic proton is coupled with the benzylic protons.
^{13}C NMR ($CDCl_3$): 44.98 (t, $^1J_{CH}$ = 138.44 Hz, $C_{benzylic}$), 65.60 (tm, $^1J_{CH}$ = 147.12 Hz, $^2J_{CCH}$ = 5.07 Hz, $^3J_{CCCH}$ = 13.17 Hz, $^3J_{CCCH}$ = 7.77 Hz, $C_{allylic}$), 117.56 (ddtd, $^1J_{CH}$ = 159.37 Hz, $^1J_{CH}$ = 154.31 Hz, $^3J_{CCCH}$ = 5.24 Hz, $^2J_{CCH}$ = 1.5 Hz, $CH=\underline{C}H_2$), 127.40 (dm) 128.58 (dm) and 138.73 (m) (aromatic carbons), 133.0 (dm, br, $^1J_{CH}$ = 155.4 Hz, $^2J_{C\text{-}CH}$ = 4.1 Hz, $\underline{C}H=CH_2$), 156.50 ppm [quint, $^3J_{CNCH} = {}^3J_{COCH}$ = 3.4 Hz, $\underline{C}(O)O$].[44]

B) Synthesis of $(CH_2{=}CHCH_2)NHC(O)OCH_2Ph$. A suspension of **2b** in CH_2Cl_2 (20 mL) was prepared as described in (IIA) [**1b**: 3.18 mL, 2.421 g, $4.24{\cdot}10^{-2}$ mol] and, then, treated with 18-crown-6 [5.97 g, $2.26{\cdot}10^{-2}$ mol]. After complete dissolution of **2b**, $PhCH_2Cl$ [2.70 mL, 2.970 g, $2.35{\cdot}10^{-2}$ mol] was added to the solution and the reaction mixture was stirred at room temperature, under a CO_2 atmosphere (0.206 MPa) for 3 days. The solvent was eliminated in vacuo and the residual white solid was whashed with THF (4x10 mL). Evaporation in vacuo of the collected washing solutions afforded a colourless oil which was fractionated on a silica gel column using n-hexane/diethyl ether (2:1 v/v) as eluent as long as RR'_2N (R= allyl, R'= benzyl) was eluted, and then n-hexane/diethyl ether (1:1 v/v) as long as elution of N-allyl,N-benzyl,benzylcarbamate was complete and, finally, n-hexane/diethyl ether (1:3 v/v) until complete elution of **6**. The eluted fractions were worked up as described in (IIA) and 2.227 g of pure **6** were isolated (Yield = 55% vs **1b**).
Elemental analysis. Calculated for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.00; H, 6.79; N, 7.27.
MS: 191 (M^+), 130, 108 (ROH^+), 100, 91 (base peak, tropilium ion), 79, 56 (RNH^+), 41 (R^+), 39 (propargilium ion), 28 *m/e* . The intensity of the parent peak is very low.
IR (neat, KBr): 3415 (shoulder) and 3340 (s, br) (N-H stretching), 1710 (vs, br, C=O stretching), 1525 (vs, br, N-H bending), 1250 (vs, br, $N\text{-}CO_2$ group stretching), 1135 cm^{-1} (s, C-O-C stretching).
^1H NMR ($CDCl_3$): 3.81 (t, br, 2, $^3J_{HCNH}$ = 5.7 Hz, $H_{allylic}$), 4.91 (br, 1, N<u>H</u>), 5.11 (s, 2, $H_{benzylic}$), 5.12 (dm, 1, $^3J_{cis}$ = 10.18 Hz, CH=C<u>H</u>$_2$), 5.19 (dq, 1, $^3J_{trans}$ = 17.19 Hz, $^2J_{HCH}$ = $^4J_{HCCCH}$ = 1.35 Hz, CH=C<u>H</u>$_2$), 5.84 (ddt,1, $^3J_{HCCH}$ = 5.40 Hz, C<u>H</u>=CH$_2$), 7.35 ppm (m, 5, $H_{aromatic}$). ^1H-decoupling experiments have shown that the amidic proton is coupled with the allylic protons.
^{13}C NMR ($CDCl_3$): 43.47 (tm, br, $^1J_{CH}$ = 137.76 Hz, $C_{allylic}$), 66.68 ppm (t, $^1J_{CH}$ = 147.18 Hz, $C_{benzylic}$), 115.84 (dddt, $^1J_{CH}$ = 158.99 Hz, $^1J_{CH}$ = 153.55 Hz, $^3J_{CCCH}$ = 5.49 Hz, $^2J_{CCH}$ = 1.42 Hz, CH=<u>C</u>H$_2$), 128.49 (dm) 128.07 (dm) and 136.64 (m) (aromatic carbons), 134.63 (dtdd, $^1J_{CH}$ = 154.6Hz, $^2J_{C\text{-}CH}$ = 5.30 Hz, $^2J_{C=CH}$ = 2 Hz, $^2J_{C=CH}$ < 1 Hz, <u>C</u>H=CH$_2$), 156.47 ppm [quint, $^3J_{CNCH}$ = $^3J_{COCH}$ = 3.49 Hz <u>C</u>(O)O].[44]

Following an analogous procedure other carbamate esters of general formula RNHC(O)OR', where R and R' are alkyl groups, were prepared (Table 5).

III. Crown-ether Recovering from $[RNH_3{\cdot}CE]X$ [*CE = 18-crown-6; X = Cl, Br*]

The alkylammonium salts recovered from the reaction mixture [see (II)] were collected together and, then, treated with an aqueous suspension (20 mL) of CaO (excess). The mixture was stirred for 2-3 h and, then, filtered out. The aqueous solution was extracted with small volumes of dichloromethane (7x10 mL) and the organic phase was evaporated in vacuo to give a residue which was washed with diethyl ether (20 mL). The ethereal solution was cooled to 253 K and pure crown-

ether precipitated which was isolated by filtration. More crown-ether could be isolated from the concentrated ethereal mother solution by adding n-hexane and cooling to 253 K.

This procedure allowed us to recover up to 80% of crown-ether used for the synthesis of the organic carbamate RNHC(O)OR'. More crown-ether could be recovered from the residual oil after extraction of the organic carbamate by crystallization from diethyl ether/n-hexane (overall yield: 95 %).

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22. It should be noted that the pK_a value of aliphatic primary amine alkylammonium cations is, approximately, 10, while the pK_a for primary amine carbamic acids may be close to 5.[23] As examples, pK_a= 9.37 for $PhCH_2NH_3^+$,[24] the pK_a values for (p-NO_2Ph)NHC(O)OH and $H_2NC(O)OH$ are 4.2 and 5.25, respectively.[25]
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43. IR (neat, KBr): 1712 cm^{-1} (C=O). MS (relative intensity, fragment): 131 (<1, M^+), 116 (100, M^+-15), 100 (1, M^+- OMe), 84 (22), 73 (27), 72 [32, (*t*-Bu)NH^+], 57 [31, $(t\text{-Bu})^+$], 42 *m/e* (30).
44. No evidence for resolvable coupling with the amidic proton can be observed in the spectra.