

## Mechanistic Studies on the Role of Carbon Dioxide in the Synthesis of Methylcarbamates from Amines and Dimethylcarbonate in the Presence of CO<sub>2</sub>.

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*Abstract:* *N*-alkylmethylcarbamates have been synthesized from amines and dimethylcarbonate (DMC) in the presence of carbon dioxide. The catalytic role of CO<sub>2</sub> in the overall process has been investigated and elucidated.

Organic carbamates<sup>1</sup> are compounds of growing interest because of their applications in pharmacology<sup>2</sup> as pharmaceuticals, in agriculture<sup>3</sup> as herbicides, fungicides and pesticides, and in chemical industry<sup>4</sup> as intermediates. Nowadays, the most common and versatile methods for the synthesis of carbamate esters use phosgene.<sup>5</sup> In spite of its cheapness and large availability, phosgene is a very toxic and harmful compound. For this reason, it is of interest to develop alternative effective carbamate synthetic routes which could use less dangerous starting materials.

Carbon dioxide itself and organic carbonates are good candidates in this sense. Utilization of carbon dioxide in the synthesis of carbamate esters has been investigated by several research groups.<sup>6</sup> We have shown that the reaction of amines and CO<sub>2</sub> in the presence of organic halides can be a useful method for the synthesis of organic carbamates in mild conditions.<sup>6d-f</sup> The reaction of amines with diesters of carbonic acid to give carbamates has been well known for a long time.<sup>7</sup> This reaction can also afford ureas, depending on the experimental conditions.<sup>8</sup> Nevertheless, very poor attention has been paid to the practical application of the synthesis of carbamate esters from amines and carbonates in the past and this can be explained considering that for a long time the most important way to the synthesis of carbonates has been

based on phosgene as a source of the carbonyl group.<sup>1,5</sup> Therefore, the use of phosgene turned out to be the most advantageous, from an economical point of view, also for the synthesis of carbamate esters.

In the last few years new synthetic routes to carbonates have been discovered. The oxidative carbonylation of methanol has been demonstrated as very interesting for obtaining DMC,<sup>9</sup> and other organic carbonates can be prepared by transesterification of DMC or diethylcarbonate with phenols<sup>10</sup> or long-chain alcohols.<sup>11</sup> So, owing to its cheapness, versatility and very low toxicity, DMC can be a suitable substitute for phosgene in the near future.

The reaction between primary or secondary amines and dialkylcarbonates needs a suitable catalyst in order to observe satisfactory conversion rates and high selectivities to carbamates. Strong bases,<sup>12</sup> such as alkali metal alkoxides, or Zn, Co, Sn, Al and Ti compounds<sup>13</sup> have been widely employed as catalysts in the carboalkoxylation of anilines and, more generally, of aromatic amines. Moreover, Lewis acids, such as AlCl<sub>3</sub>, SnCl<sub>2</sub>, ZnCl<sub>2</sub>, Zn(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, FeCl<sub>3</sub>, or metal (Rh, Ru) complexes have proved to be effective in promoting the conversion of n-propylamine and diethylcarbonate selectively to N-propylethylcarbamate.<sup>14</sup>

Our interest in CO<sub>2</sub> chemistry<sup>15</sup> and in the synthesis of carbamate esters via utilization of CO<sub>2</sub><sup>6d-f</sup> led us to investigate the reaction between aliphatic amines and dialkylcarbonates in the presence of carbon dioxide. Primary 1 or secondary aliphatic amines can react with carbon dioxide according to equilibrium (1) to give alkylammonium carbamates 2<sup>16</sup> that are a convenient source of the carbamate moiety in carbamate ester synthesis.<sup>6</sup>

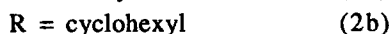


Furthermore, it is well known that dialkylcarbonates can show alkylating properties towards a large range of nucleophiles.<sup>9,17</sup> Moreover, although the reactivity of free or metal-bound RNHCO<sub>2</sub><sup>-</sup> anions towards many electrophiles has been studied,<sup>6,16f,18</sup> no information can be found in the literature about their reactivity towards dialkylcarbonates.

In this paper we describe the synthesis of a few N-alkylmethylcarbamates by reaction of aliphatic primary amines and DMC in the presence of carbon dioxide. This reaction has been studied also from a mechanistic point of view. <sup>13</sup>CO<sub>2</sub> labelling experiments have allowed us to get information on the reaction mechanism as well as to clarify the role of carbon dioxide in the overall process.

## RESULTS AND DISCUSSION

Alkylammonium N-alkylcarbamates, **2**, prepared at room temperature by saturating amine solutions with carbon dioxide ( $P_{CO_2} = 0.1$  MPa), Eq. (1), react with DMC to afford N-alkylmethylcarbamates **3**, Eq. (2).<sup>19</sup>



Reaction (2) is carried out in common organic solvents (aromatics, THF, dichloromethane) but, more easily, just the organic carbonate may be employed as the reaction solvent. Satisfactory reaction rates and good selectivities can be attained by heating the reaction mixture at temperatures higher than 343 K under a  $CO_2$  atmosphere ( $P_{CO_2} = 0.1 - 0.2$  MPa). Alkylammonium carbamates **2** do not need to be isolated for reaction (2) to occur as they can be prepared *in situ*, Eq. (1). After precipitation of **2**, the temperature of the reaction mixture can be raised to the required value.

Accordingly,  $(PhCH_2)NH_3^+ \cdot O_2CNH(CH_2Ph)$  **2a**,  $CyNH_3^+ \cdot O_2CNH(Cy)$  **2b** and  $(CH_2=CH-CH_2)NH_3^+ \cdot O_2CNH(CH_2-CH=CH_2)$  **2c** were converted respectively into N-benzyl- **3a**, N-cyclohexyl- **3b** and N-allylmethylcarbamate, **3c**, by heating their suspensions in DMC (see Table 1). **3a**, **3b** and **3c** were isolated in interesting yields and were completely characterized by elemental analyses, infrared and mass spectra and  $^1H$  and  $^{13}C$  nmr spectroscopy. Reaction (2) proceeds homogeneously at the temperatures reported in Table 1. However, after cooling to room temperature, some unreacted alkylammonium carbamate **2** may separate from the solution and can be recovered by filtration. Ureas, N,N-substituted carbamates, secondary and tertiary amines could be detected in the reaction mixture, but these by-products were always formed in very low yields (see Table 1).

Experiments were performed to shed light on the reaction mechanism for the synthesis of **3**.

Alkylammonium carbamate solutions show quite a modest chemical stability: as we have documented elsewhere,<sup>20</sup> ionic carbamates **2** can give back carbon dioxide and the free starting amine **1**, according to equilibrium (1), when they are dissolved or suspended in an organic solvent under an inert gas ( $N_2$ , Ar) atmosphere. These findings suggested that check-trials should be carried out in order to verify whether the direct reaction between DMC and free amine (present at the equilibrium) could be involved in the formation of organic carbamates from **2** and DMC.

Table 1. Synthesis of N-Alkylmethylcarbamates from Aliphatic Amines and DMC in the Presence of Carbon Dioxide ( $P_{CO_2} = 0.1$  MPa).

R	$RNH_2^a$ 1	DMC <sup>b</sup>	time(h)	T(K)	% yield of 3 <sup>c,d,e</sup>	% of 1 recovered as solid 2 <sup>d,f</sup>	Side-products
Benzyl	9.15	10	24	343 [363]	50:40 [92:71]	32%	g
Cyclohexyl	17.5	20	24	348 [363]	27:20 [45:35]	67% [50%]	h
Allyl	26.6	20	24	343 [363]	44:36 [70:55]	<1% [<1%] <sup>i</sup>	j

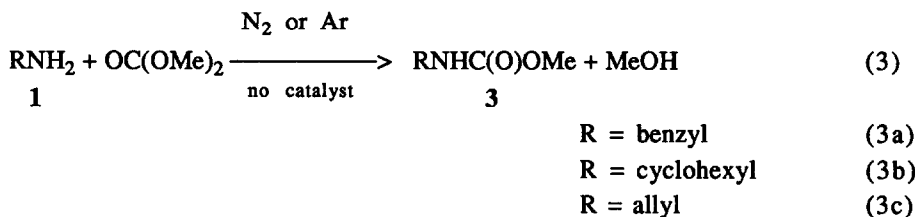
a) mmol. b) mL of DMC used as the solvent in all runs. c) Yields are based on 1. d) The values reported in square brackets are referred to the reaction temperature of 363 K. e) Gas-chromatographic, isolated (italic) yield of RNHC(O)OMe 3. f) By filtering out the reaction mixture (See Discussion). g)  $(PhCH_2)(Me)NH$  (max. 2%),  $(PhCH_2)(Me)_2N$  (<0.1%) and  $(PhCH_2)HNC(O)NH(CH_2Ph)$  (<0.1%) were formed as side-products. h)  $(Cy)(Me)NH$  (<0.1%),  $(Cy)(Me)_2N$  (max. 1%), N-cyclohexyl-N-methylmethylcarbamate (<0.2%). i) 10 mL of DMC and 13.3 mmol of 1c were used in this run. j)  $(C_3H_5)_3N$  (<2%) and N-allyl,N-methylmethylcarbamate (<0.5%) were detected in the reaction mixture.

Table 2. Synthesis of N-Alkylmethylcarbamates from Aliphatic Amines and DMC under a Dinitrogen Atmosphere ( $P_{N_2} = 0.1$  MPa).

R	$RNH_2^a$ 1	DMC <sup>b</sup>	time(h)	T(K)	% yield of 3 <sup>c,d,e,f</sup>	Side-products
Benzyl	18.3	20	24	343 [363]	4:3 [13:9]	g
Cyclohexyl	17.5	20	24	348 [363]	4:3 [6]	h
Allyl	26.6	20	24	343 [363]	13:9 [23] <sup>i</sup>	j

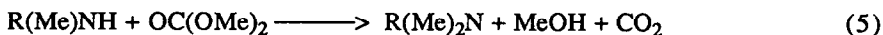
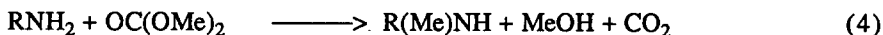
a) mmol. b) mL of DMC used as the solvent in all runs. c) Yields are based on 1. d) The values reported in square brackets are referred to the reaction temperature of 363 K. e) Gas-chromatographic, isolated (italic) yield of RNHC(O)OMe 3. f) All runs were carried out in a closed vessel [See text and Note 22]. g)  $(PhCH_2)(Me)NH$  (3%),  $(PhCH_2)(Me)_2N$  (0.5%) and a solid identified as 2a (0.115 g) were also formed as by-products.<sup>21</sup> h)  $(Cy)(Me)NH$  (4%) and 2b (0.14 g) were formed as by-products. i) 10 mL of DMC and 13.3 mmol of 1c were used in this run. j) N-allyl,N-methylmethylcarbamate (<0.5%) was detected in the reaction mixture.

Benzylamine **1a**, cyclohexylamine **1b** and allylamine **1c** were separately reacted with DMC under an inert gas ( $N_2$ , Ar) atmosphere, Eq. (3), and the results of reactions (3a), (3b) and (3c) were respectively compared with those of the corresponding reactions (2a), (2b) and (2c).



When reactions (2) and (3) were run under the same experimental conditions (temperature, time, amine concentration, DMC as the solvent, etc.), we found that reaction (2) affords **3** in higher yield and more selectively than reaction (3) (see Table 2).

Moreover, a careful investigation of the system has demonstrated that, starting from carefully purified DMC and amines **1**, Eq. (3), some carbon dioxide is formed in solution during the reaction, as evidenced by IR spectroscopy (band at  $2340 \text{ cm}^{-1}$ ), together with ammonium carbamates **2**. Eq. (4), (5) and (1) could offer a reasonable explanation for the formation of  $R(\text{Me})\text{NH}$ ,  $R(\text{Me})_2\text{N}$  and **2**.



The concentration of these species and the carbamate ester yield are dependent on the operative conditions.<sup>22</sup>

The formation of the alkylammonium carbamate **2** seems to be essential for the synthesis of **3**. In order to establish this in a clear way we have studied the kinetics of the following reaction systems (R = benzyl):

- a)  $\text{RNH}_3^+ \text{O}_2\text{CNHR}$  plus  $(\text{CH}_3\text{O})_2\text{C}=\text{O}$  or  $\text{RNH}_2$  plus  $\text{CO}_2$  in DMC;
- b)  $\text{RNH}_2$  plus  $(\text{CH}_3\text{O})_2\text{C}=\text{O}$ , under an inert gas ( $N_2$ ) atmosphere;
- c)  $\text{RNH}_2$  plus  $(\text{CH}_3\text{O})_2\text{C}=\text{O}$ , under an inert gas ( $N_2$ ) atmosphere and in the presence of a  $\text{RNH}_3\text{X}$  salt ( $X=\text{Cl}$ ).

Fig. 1 shows that system (a) does not present any induction time, while system (b) requires quite a long induction time. Moreover, we have ascertained that in the latter case, when the synthesis of carbamate **3** starts, alkylammonium carbamate **2** is present in the reaction medium. System (c) is quite interesting as its kinetics may

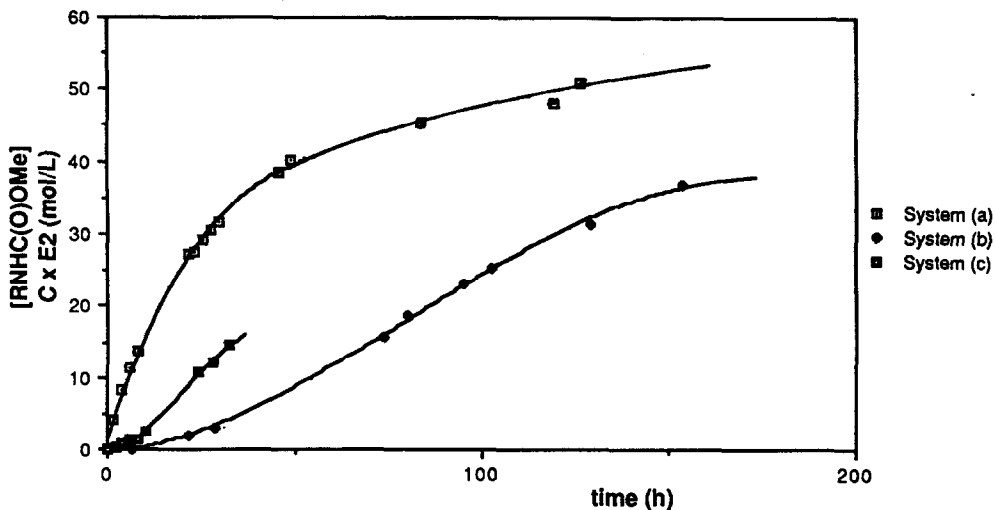


Fig.1. Kinetics of RNHC(O)OMe (R = benzyl) formation from: a)  $[(\text{PhCH}_2)_3\text{NH}][\text{O}_2\text{CNH}(\text{CH}_2\text{Ph})]$  **2a** (9.15 mmol) and DMC (20 mL), ( $P_{\text{CO}_2} = 0.1$  MPa, 343 K); b)  $\text{PhCH}_2\text{NH}_2$  (18.3 mmol) and DMC (20 mL), ( $P_{\text{N}_2} = 0.1$  MPa, 343 K); c)  $\text{PhCH}_2\text{NH}_2$  (18.3 mmol) and DMC (20 mL) in the presence of  $[(\text{PhCH}_2)_3\text{NH}_3]\text{Cl}$  (9.06 mmol), ( $P_{\text{N}_2} = 0.1$  MPa, 343 K).

suggest that the presence of a weak acid such as  $\text{RNH}_3^+$  can accelerate the reaction between the amine and DMC; nevertheless, an induction time, although shorter than for system (b), is observed also in this case.

Consequently, the possibility that formation of **3** involves, as the main reaction pathway, the reaction between DMC and the free amine present in the reaction medium can be excluded: more likely, it is formed from alkylammonium carbamate and DMC, Eq. (2).

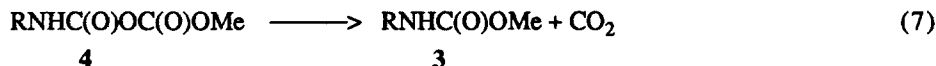
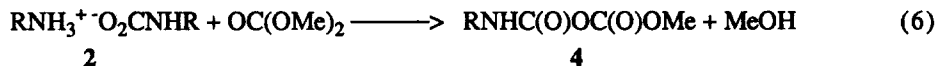
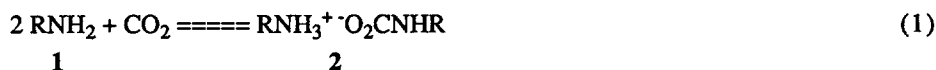
DMC shows two sites for interacting with nucleophilic reagents: a) the methyl  $\text{sp}^3$  carbon atoms; b) the carbonylic  $\text{sp}^2$  carbon. So, DMC and, more generally, dialkylcarbonates are interesting examples of ambident electrophilic substrates and the regioselectivity of the attack by nucleophiles is an important feature of the chemistry of these compounds. Accordingly, for the interaction of carbamate anion  $\text{RNHCO}_2^-$  with DMC two pathways can be envisaged:

- the nucleophilic attack by the carbamate anion  $\text{O}_2\text{CNHR}$  [oxygen atoms] to  $\text{sp}^3$  carbon atoms of DMC can result in its O-methylation and can afford **3**, [route (i)]. In this case, DMC will behave as an alkylating reagent.

- the carbamate anion may attack the DMC  $sp^2$  carbon, [route (ii)]. This interaction will result in the O-carbomethoxylation of the  ${}^-\text{O}_2\text{CNHR}$  anion with formation of mixed carbamic-carbonic anhydride  $\text{RNHC(O)OC(O)OMe}$  4.

In order to verify whether route (i) or (ii) is involved in reaction (2), we have reacted labelled  $(\text{PhCH}_2)\text{NH}_3^+ \text{}^-\text{O}_2^{13}\text{CNH}(\text{CH}_2\text{Ph})$  2a\* with DMC under a  ${}^{13}\text{CO}_2$  atmosphere at 343 K and monitored the products by gas-mass and IR techniques. N-benzylmethylcarbamate was formed, as the main product, after 2 h. The related mass spectrum showed the  $I(M+1)/I(M)$  isotope ratio to agree very well with the value expected for unlabelled carbamate 3a.<sup>23</sup> No labelled organic carbamate 3a\* was detected in solution or isolated at the end of the reaction. Moreover, the IR spectroscopy of the isolated organic carbamate confirmed that labelled  $\text{CO}_2$  was not incorporated into the organic carbamate. This allowed us to conclude that DMC does not behave as a methylation agent of  $\text{RNHCO}_2^-$  anion. Reaction (2) cannot be considered as a carbamation reaction involving carbon dioxide incorporation.

Nevertheless,  $\text{CO}_2$  plays a role in this reaction, as we have shown before. Eq. (1), (6) and (7) summarize the reaction mechanism we suggest for the carbamate ester formation from amines and DMC in the presence of carbon dioxide.



O-carbomethoxylation of carbamate anion is the first step, Eq.(6), to give a mixed carbamic-carbonic anhydride,  $\text{RNHC(O)OC(O)OMe}$  4. This step could be catalyzed by acidic species, such as  $\text{RNH}_3^+$  or  $\text{RNHC(O)OH}$ , present at the equilibrium. Selective decarboxylation of 4 through expulsion of a  $\text{CO}_2$  molecule from its carbamic moiety leads to the formation of 3. Molecular models of mixed anhydrides 4 (R = benzyl, cyclohexyl, allyl) show that there exist the conditions for an intramolecular transfer of the "NHR" group onto the carbonylic carbon of the methylcarbonic moiety to give 3. This mechanism can rationalize satisfactorily why incorporation of  ${}^{13}\text{CO}_2$  in the organic carbamate is not observed when  $\text{RNH}_3^+ \text{}^-\text{O}_2^{13}\text{CNHR}$  was utilized as the starting reactant.<sup>24</sup>

Carbamic-carbonic anhydrides are described in the literature. The synthesis of  $\text{Ph(Me)NC(O)OC(O)OBu}^t$  5 from N-methylaniline and di-ter-butyltricarboxylate has been reported by Tarbell and Dean.<sup>25</sup>

We have failed both to isolate **4** by reaction of **2** with DMC at 298 K and to detect it in the reaction mixture, in order to support the proposed reaction mechanism. Indeed, the reaction to afford **4** has a very low rate at room temperature while the conversion of **4** into **3** is a very fast process (see below). This fact can be explained assuming that the formation of carbamic-carbonic anhydrides from **2** and dialkylcarbonates has a high activation energy and, thus, requires temperatures at which the mixed anhydride undergoes a fast decarboxylation reaction. In order to prove this hypothesis, we prepared the mixed anhydride  $(\text{PhCH}_2)\text{NHC}(\text{O})\text{OC}(\text{O})\text{OMe}$  **4a** by reaction of **2a** with  $\text{ClC}(\text{O})\text{OMe}$ , at 233 K. The IR spectrum of **4a** shows characteristic IR bands at 3360 (s, br), 1805 (s) and 1740  $\text{cm}^{-1}$  (s, br) that agree with IR data reported by Tarbell for **5** [1795 and 1735  $\text{cm}^{-1}$ ]. **4a** is extremely unstable at room temperature. In fact, when a solid sample of **4a** was kept at room temperature, the carbonylic bands at 1805 and 1740  $\text{cm}^{-1}$  disappeared almost completely within 10 min and a new strong broad band appeared at 1700  $\text{cm}^{-1}$ . A similar behaviour was observed when cooled (233 K) ethereal solutions of **4a** [IR: 1815 and 1758  $\text{cm}^{-1}$ ] were warmed up to room temperature [IR: 1730  $\text{cm}^{-1}$ ]. The gas-mass analysis of this solution showed the presence of **3a**. This result proves that **4a** can convert into **3a** even at room temperature and allows us to rationalize the spectroscopic changes observed in the IR spectra of **4a**.<sup>26</sup>

Therefore, the assumption of mixed anhydrides **4** as intermediates in reaction (2) seems to be correct. In accordance with our findings, Tarbell reported that **5** is a thermally labile species which can convert by heating into *N*-methyl,*N*-phenyl-*tert*-butylcarbamate and  $\text{CO}_2$ .<sup>25</sup> Moreover, intramolecular decomposition of carbamic-carbonic-anhydrides was suggested to be an intermediate step also in the synthesis of methylcarbamates  $\text{R}^1\text{R}^2\text{NC}(\text{O})\text{OMe}$  from  $\text{R}^1\text{R}^2\text{NCO}_2\text{Li}$  and  $\text{ClC}(\text{O})\text{OMe}$ .<sup>18c</sup>

## CONCLUSIONS

Scheme 1 summarizes the overall process we have discussed. A few comments are worthwhile.

As shown by the labeled  $^{13}\text{CO}_2$  experiments, the  $\text{CO}_2$  molecule fixed by the starting amine into **2** is not incorporated in the final product, but is released when the organic carbamate is formed. Nevertheless, carbon dioxide acts as a catalyst generating carbamic acid,  $\text{RNHC}(\text{O})\text{OH}$ , and/or ionic carbamate **2**.

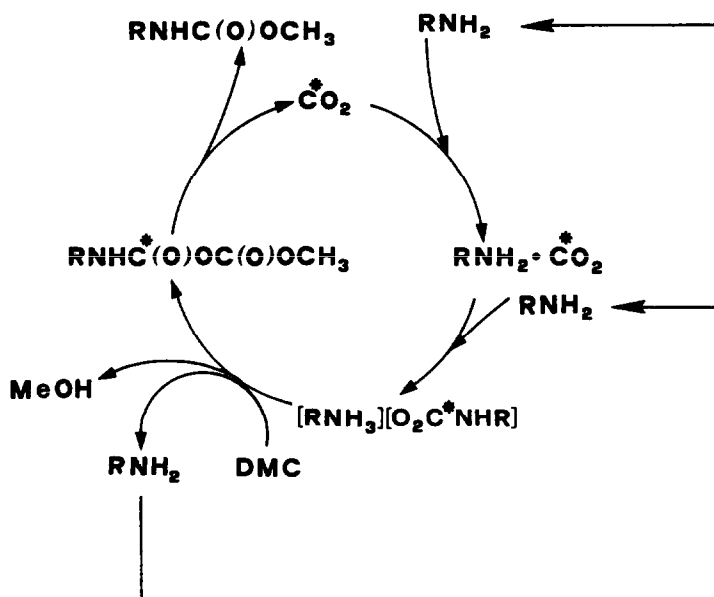
The utilization of Lewis bases or acids as catalysts in the synthesis of carbamates from amines and organic carbonates has been discussed.<sup>13,14</sup> Our findings show that a catalytic role can be also played by carbon dioxide itself (Eq. 8), a cheap abundant non-toxic species which does not present regeneration and recycling problems.





As we have demonstrated, the alkylammonium carbamate formation plays a key-role in the overall reaction (8) that can be considered as an interesting new method of synthesis of carbamates from amines and organic carbonates via carbon dioxide activation.

Scheme 1



## EXPERIMENTAL SECTION

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

Solvents were dried and distilled as described in the literature and stored under dinitrogen. CO<sub>2</sub> (99.99% pure) and Carbon-<sup>13</sup>C Dioxide (<sup>13</sup>C 99%) were from SIO S.p.A. and CIL, respectively. Benzylamine, allylamine and cyclohexylamine were Fluka products. Methylchloroformate was from Janssen Chimica. DMC was an EniChem Synthesis loan gift.

*I. Synthesis of RNHC(O)OCH<sub>3</sub> 3 from a primary amine RNH<sub>2</sub> 1 and DMC in the presence of CO<sub>2</sub>.*

The experimental procedures for the synthesis of 3a, 3b and 3c according to reaction (8) are very similar. As an illustrative example, we will describe in greater detail only the synthesis of 3a.

*A) Synthesis of N-benzylmethylcarbamate (3a).* - A solution of (PhCH<sub>2</sub>)NH<sub>2</sub> (1.0 mL, 0.981 g, 9.15·10<sup>-3</sup> mol) in DMC (10 mL) was prepared under dinitrogen in an appropriate flask and, then, saturated with CO<sub>2</sub> (P<sub>CO<sub>2</sub></sub> = 0.1 MPa) to give 2a as a white microcrystalline solid which was poorly soluble in the reaction solvent. The vessel was placed in a pressure vessel flushed with CO<sub>2</sub> and, after assembling, the system was heated to 343 K and kept at that temperature for 24 h. After cooling to room temperature, the reaction mixture was filtered out. A white solid was isolated which was washed with more DMC (2x5 mL), dried in vacuo and identified as unreacted 2a (m = 0.378 g) by elemental analysis and IR spectroscopy.<sup>20</sup> Mother liquor and washing solutions were collected and evaporated in vacuo. The residue was fractionated on a silica gel column with a diethyl ether/hexane (2:1 v/v) eluent mixture. Solvent was evaporated from the eluted fractions and 0.604 g of pure 3a were obtained [Yield = 40% vs 1a].

By heating the reaction mixture at 363 K for 24 h and processing it as above described, 1.07 g of 3a were obtained [Yield = 71% vs 1a].

Elemental analysis. Calculated for C<sub>9</sub>H<sub>11</sub>NO<sub>2</sub>: C = 65.45%, H = 6.67%, N = 8.48%; Found: C = 65.70%, H = 6.87%, N = 8.37%.

MS: 165, 150, 133, 121, 106, 91, 79, 77, 28 m/e.

IR (nujol): 3374 (ms), 3350 (m, sh), 1715 (ms, sh), 1690 (vs), 1527 (vs), 1274 cm<sup>-1</sup> (vs).

<sup>1</sup>H nmr (CDCl<sub>3</sub>): 7.27 ppm (m, 5H, H<sub>aromatic</sub>), 5.44 ppm (br, 1H, NH), 4.31 ppm (d, 2H, CH<sub>2</sub>; <sup>3</sup>J<sub>H<sub>C</sub>NH</sub> = 5.32 Hz), 3.64 ppm (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C nmr (CDCl<sub>3</sub>): 127.43 (dm), 127.41 (dm), 128.61 (dm) and 138.60 ppm (m), (aromatic carbon atoms); 45.07 ppm (t, br, CH<sub>2</sub>; <sup>1</sup>J<sub>CH</sub> = 137 Hz); 157.16 ppm (sest, C(O)O; <sup>3</sup>J<sub>COCH</sub> = <sup>3</sup>J<sub>CNCH</sub> = 3.8 Hz); 52.20 ppm (q, CH<sub>3</sub>; <sup>1</sup>J<sub>CH</sub> = 146.58 Hz).

*B) Synthesis of N-cyclohexylmethylcarbamate (3b).* - 2b, prepared in situ from 1b [2.0 mL, 1.734 g, 1.75·10<sup>-2</sup> mol] and CO<sub>2</sub> (P<sub>CO<sub>2</sub></sub> = 0.1 MPa), was reacted with DMC (20 mL) at 363 K for 24 h under 0.1 MPa of CO<sub>2</sub>. By filtration of the reaction mixture,

some unreacted **2b** ( $m = 1.06$  g) was recovered. Mother liquor and washing solutions were collected together and worked up as above described for **3a**. 0.962 g of pure **3b** were obtained [Yield = 35% vs **1b**].

Elemental analysis. Calculated for  $C_8H_{15}NO_2$ : C = 61.12%, H = 9.62%, N = 8.90%; Found: C = 61.25%, H = 9.70%, N = 8.85%.

MS: 157, 142, 114, 101, 82, 76, 59, 28 m/e.

IR (nujol): 3350 (s), 3320 (ms, sh), 1710 (s, sh), 1685 (vs), 1529 (vs), 1450 (s), 1317 (s), 1275 (s), 1250 (s), 1228 (s), 1052  $cm^{-1}$  (vs).

$^1H$  nmr ( $CDCl_3$ ): 4.61 ppm (br, 1H,  $NH$ ), 3.62 ppm (s, 3H,  $CH_3$ ), 3.44 ppm [m, br, 1H,  $>C(H)NH-$ ]. The cyclohexyl group remaining protons, which rightly integrate as 10H, give overlapping multiplets between 0.9 and 2.0 ppm. No attempts were made to assign these signals.

$^{13}C$  nmr ( $CDCl_3$ ): 49.67 (d, br;  $^1J_{CH}=136$  Hz), 33.25 (t, br;  $^1J_{CH}=127$  Hz), 24.67 (t, br;  $^1J_{CH}=127$  Hz) and 25.24 ppm (t, br;  $^1J_{CH}=129$  Hz) (cyclohexyl carbon atoms); 156.18 ppm [m, br,  $C(O)O$ ]; 51.65 ppm (q,  $CH_3$ ;  $^1J_{CH}=146.1$  Hz).

C) *Synthesis of N-allylmethylcarbamate (3c)*. - A DMC (20 mL) suspension of **2c**, prepared as previously described for **2a** [**1c**: 2.0 mL, 1.52 g,  $2.66 \cdot 10^{-2}$  mol;  $P_{CO_2} = 0.1$  MPa] was heated at 343 K for 36 h under a  $CO_2$  atmosphere. After cooling to room temperature, the reaction mixture was distilled in vacuo at 273 K. A residue was obtained, which was chromatographed on a silica gel column with diethyl ether/n-pentane (1:1 v/v) as eluent mixture. Solvent was evaporated in vacuo (at 273 K) from the eluted fractions and 1.37 g of pure **3c** were obtained [Yield = 45% vs **1c**].

Elemental analysis. Calculated for  $C_5H_9NO_2$ : C = 52.16%, H = 7.88%, N = 12.16%; Found: C = 52.20%, H = 7.95%, N = 12.10%.

MS: 115, 100, 88, 83, 70, 56, 41, 28 m/e.

IR (neat): 3390 (ms, br, sh), 3344 (s, br), 1710 (vs), 1644 (ms), 1528 (vs), 1261 (vs), 1194 (ms), 1142 (ms), 1073 (ms), 996 (s), 924 (s), 780  $cm^{-1}$  (s).

$^1H$  nmr ( $CDCl_3$ ): 3.39 ppm (s, 3H,  $CH_3$ ), 3.51 ppm (t, 2H,  $H_{allylic}$ ;  $^3J_{HCNH} = 5.71$  Hz), 4.82 ppm (dq, 1H,  $CH_2=CH$ ;  $^3J_{cis} = 10.22$  Hz,  $^4J_{HCCCH} = 1.48$  Hz,  $^2J_{HCH} = 1.52$  Hz), 4.92 ppm (dq, 1H,  $CH_2=CH$ ;  $^3J_{trans} = 17.19$  Hz,  $^4J_{HCCCH} = 1.65$  Hz), 5.58 ppm (ddt, 1H,  $CH_2=CH$ ;  $^3J_{HCCCH} = 5.42$  Hz), 5.63-5.64 ppm (br, 1H,  $NH$ ; this signal overlaps with the signal at 5.58 ppm).

$^{13}C$  nmr ( $CDCl_3$ ): 156.92 ppm (sest,  $C(O)O$ ;  $^3J_{COCH} = ^3J_{CNCH} = 3.7$  Hz), 134.40 ppm (dtd,  $CH_2=CH$ ;  $^1J_{CH} = 154.9$  Hz,  $^2J_{CCH} = 5.3$  Hz,  $^2J_{C=CH} = 2.2$  Hz), 115.46 ppm (ddtd,  $CH_2=CH$ ;  $^1J_{CH} = 153.8$  Hz,  $^1J_{CH} = 159.0$  Hz,  $^3J_{CCCH} = 5.5$  Hz,  $^2J_{CCH} < 1$  Hz), 43.20 ppm (tm, br,  $C_{allylic}$ ;  $^1J_{CH} = 138.0$  Hz), 51.81 ppm (q,  $CH_3$ ;  $^1J_{CH} = 146.3$  Hz).

## II. Reaction of $RNH_2$ ( $R = benzyl, cyclohexyl, allyl$ ) with DMC (under dinitrogen).

An appropriate glass-vessel containing a solution of **1** in DMC was placed in an autoclave flushed with dinitrogen. After assembling, the autoclave was heated to

343 K and kept at that temperature for 24 h. A suspension was obtained which was worked up as described above, to give pure 3.

### III. Reaction of $(\text{PhCH}_2)\text{NH}_3^+ \cdot \text{O}_2\text{CNH}(\text{CH}_2\text{Ph})$ with $\text{ClC}(\text{O})\text{OMe}$ .

An ethereal suspension of 2a, prepared at room temperature by saturating with  $\text{CO}_2$  a solution of  $(\text{PhCH}_2)\text{NH}_2$  (1.0 mL, 0.981 g,  $9.15 \cdot 10^{-3}$  mol) in diethyl ether (40 mL), was cooled to 233 K. A solution of  $\text{ClC}(\text{O})\text{OMe}$  (0.35 mL, 0.432 g,  $4.57 \cdot 10^{-3}$  mol) was added dropwise to the suspension and the system was stirred at 233 K for 4 h under a  $\text{CO}_2$  atmosphere. The reaction mixture was filtered out at low temperature. The mother liquor and washing ethereal solutions were collected in a cold bath and evaporated in vacuo. A white solid residue was obtained which showed IR bands at 3360, 1805 and 1740  $\text{cm}^{-1}$ . This compound was found to be very unstable and no further purification of this material was attempted.

Elemental analysis. Calculated for  $\text{C}_{10}\text{H}_{11}\text{NO}_4$ : C = 57.41%, H = 5.30%, N = 6.69%; Found: C = 58.00%, H = 5.78%, N = 7.01%.

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21. Ureas were not found under these experimental conditions. As a rule, formation of ureas from amines and dialkylcarbonates is favoured by higher temperatures.<sup>5,8</sup>
22. Lower yields in **3** were obtained when reaction (3) was carried out by heating **1** in DMC under a dinitrogen atmosphere, in a vessel open to the atmosphere. In a closed vessel, CO<sub>2</sub> generated according to Eq. (4) and (5) accumulates in the vessel and causes the increase of the yield of formation of the organic carbamate with respect to the case in which the same reaction is carried out in a vessel that allows the formed CO<sub>2</sub> to escape into the atmosphere.
23.  $[I(M+1)/I(M)] \cdot 100 = 10.14$  vs. 10.26 calculated for **3a**.
24. It cannot be escluded, however, that, depending on bulkiness of groups bonded to the carbamic nitrogen atom, the decarboxylation of the mixed carbamic-carbonic anhydride might occur through selective CO<sub>2</sub> elimination from the methylcarbonic moiety.<sup>18c</sup>
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26. The IR spectrum (nujol) of **3a** shows a strong absorption at 1700 cm<sup>-1</sup> due to carbonyl stretching vibration (see the Experimental Section). This band is shifted to 1730 cm<sup>-1</sup> in an ethereal solution and to 1725 cm<sup>-1</sup> in dichloromethane.