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NOTE

CO_2-catalysed carbamation of aminofunctional silanes†

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Under mild conditions (348 K), carbon dioxide ($P_{CO_2} = 0.1$ MPa) catalytically promotes the carbamation of the following industrially relevant aminofunctional silanes: $H_2N(CH_2)_3Si(OMe)_3$, $H_2N(CH_2)_3Si(OEt)_3$ and $H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3$. These, upon reaction with dimethylcarbonate, are selectively converted into the methyl carbamate esters $MeO(O)CNH(CH_2)_3Si(OMe)_3$, $MeO(O)CNH(CH_2)_3Si(OEt)_3$ and $MeO(O)CNH(CH_2)_2NH(CH_2)_3Si(OMe)_3$ respectively. Carbamate $MeO(O)CNH(CH_2)_3Si(OEt)_3$ is accompanied by $MeO(O)CNH(CH_2)_3Si(OMe)_x(OEt)_{3-x}$ formed *via* transesterification of the triethoxysilyl group by the co-produced methanol. The carbamation process is very selective and *N*-methylated species are formed in trace amounts. Conversely, the ureidofunctional silane $H_2NC(O)NH(CH_2)_2NH(CH_2)_3Si(OMe)_3$ shows a poor reactivity towards carbamation, and, under the above conditions, *N*-methyl derivatives are preferably formed. Copyright © 2000 John Wiley & Sons, Ltd.

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1 RESULTS AND DISCUSSION

The methods of synthesis of organic carbamates[1] are mostly based on the use of phosgene. Much effort is currently devoted to the development of new clean synthetic methodologies that employ less harmful starting materials. Both carbon dioxide and organic carbonates are good candidates as substitutes for phosgene.[2]

Aminolysis of carbonic acid diesters represents a very interesting synthetic route to carbamates as non-phosgene routes to organic carbonates are now available.[3] However, a suitable catalyst is usually required in order to observe a good conversion rate and selectivity to carbamate ester.[4–7]

CO_2 itself can act as catalyst in the aminolysis of dimethylcarbonate (DMC) by aliphatic amines (Eqn [1]).[8,9]

$$RNH_2 + (MeO)_2C{=}O \xrightarrow{CO_2} RNHC(O)OMe + MeOH \qquad [1]$$

$$R = \text{alkyl}$$

In this process, the carbamate salt, $RNH_3^{+}\,{}^{-}O_2CNHR$, formed upon reaction of the amine with CO_2, reacts with DMC to afford a mixed carbamic–carbonic anhydride, RNHC(O)OC(O)OMe,[8] that converts into the carbamate ester, RNHC(O)OMe, by decarboxylation (Eqns. [2]–[4]).

$$2RNH_2 + CO_2 \;{=}{=}{=}{=}{=}\; RNH_3^{+-}O_2CNHR \qquad [2]$$

$$RNH_3^{+-}O_2CNHR + OC(OMe)_2 \rightarrow RNHC(O)OC(O)OMe + RNH_2 + MeOH \qquad [3]$$

$$RNHC(O)OC(O)OMe \longrightarrow RNHC(O)OMe + CO_2 \qquad [4]$$

As this synthetic approach requires quite mild reaction conditions (343–363 K, $P_{CO_2} = 0.1$ MPa),

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we have studied the possibility of applying it to amines bearing other functionalities in the molecule. We have focused our attention on a few industrially relevant aminofunctional silanes,[10] such as $H_2N(CH_2)_3Si(OMe)_3$ (**1**), $H_2N(CH_2)_3Si(OEt)_3$ (**2**), $H_2N(CH_2)_2NH(CH_2)_3Si(OMe)_3$ (**3**) and $H_2NC(O)NH(CH_2)_2NH(CH_2)_3Si(OMe)_3$ (**4**), in view of the potential that their methyl carbamate derivatives have both as new silane coupling agents and as a ready source of isocyanates,[11] largely used in the chemical industry as modulators of the physico-mechanical properties of polymeric materials.[12]

We have found that under mild conditions (348 K) and in the presence of CO_2 (0.1 MPa), aminofunctional silanes **1–3** react with DMC to give the corresponding methyl carbamate esters $MeO(O)CNH(CH_2)_3Si(OMe)_3$ (**5**), $MeO(O)CNH(CH_2)_3Si(OEt)_3$ (**6**), $MeO(O)CNH(CH_2)_2NH(CH_2)_3Si(OMe)_3$ (**7**) respectively. The carbamation reaction is very selective and no, or very minor, amounts of *N*-mono- or *N*,*N*′-di-methylated derivatives are formed as side-products.

In this way, both amines **1** and **2** are converted into methyl carbamate esters with gas chromatographic (GC) yields higher than 70–80%. Carbamate **6** is accompanied by $MeO(O)CNH(CH_2)_3Si(OMe)(OEt)_2$ (**6**′), $MeO(O)CNH(CH_2)_3Si(OMe)_2(OEt)$ (**6**″) [**6**:**6**′:**6**″ molar ratio ≃1:1:0.4] and minor amounts of **5**. The formation of $MeO(O)CNH(CH_2)_3Si(OMe)_x(OEt)_{3-x}$ species can be rationalized considering that methanol co-produced according to Eqn [1] [R = —$(CH_2)_3Si(OEt)_3$] can be involved in progressive transesterification of the triethoxysilyl group as described in Eqn [5].

$$RNH(CH_2)_3Si(OEt)_3 + x\,MeOH \rightarrow RNH(CH_2)_3Si(OMe)_x(OEt)_{3-x} + x\,EtOH \quad [5]$$

$$x = 1\text{–}3;\ R = H,\ C(O)OMe$$

However, the formation of $MeO(O)CNH(CH_2)_3Si(OMe)_x(OEt)_{3-x}$ carbamates can also take place through the direct carbamation of the corresponding amine $H_2N(CH_2)_3Si(OMe)_x(OEt)_{3-x}$ (Eqn [5]; R = H) according to reaction [6].

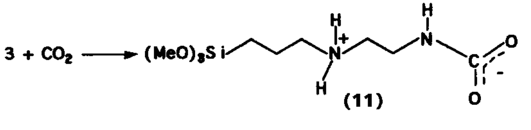
$$H_2N(CH_2)_3Si(OMe)_x(OEt)_{3-x}) + DMC \xrightarrow{CO_2} MeO(O)CNH(CH_2)_3Si(OMe)_x(OEt)_{3-x} + MeOH \quad [6]$$

Di-amine **3** shows a higher reactivity with respect to **1** and **2** and, in the presence of CO_2, at 348 K, easily reacts with DMC to give **7**, with high selectivity and in a practically quantitative yield. The conversion of **3** into **7** is complete in less than 7 h. The carbamation reaction involves selectively the primary amino-group as only traces of monocarbamate $(Me)HN(CH_2)_2N(CO_2Me)(CH_2)_3Si(OMe)_3$ (**8**) or dicarbamate $MeO(O)CNH(CH_2)_2N(CO_2Me)(CH_2)_3Si(OMe)_3$ (**9**) are formed under the working conditions. Allowing **7** to react further with DMC under CO_2 at 363 K, a slow but not selective conversion into $MeO(O)CNH(CH_2)_2N(Me)(CH_2)_3Si(OMe)_3$ (**10**) and **9** has been observed [by GC–mass spectrometry (MS)]. Minor amounts of $MeO(O)CN(Me)(CH_2)_2N(CO_2Me)(CH_2)_3Si(OMe)_3$ are also found in the reaction solution, probably formed by carbomethoxylation of **8**.

Under similar conditions (348 K, $P_{CO_2} = 0.1$ MPa), ureido-amine **4** shows a very poor reactivity towards DMC. After 11 h at 348 K, the conversion of **4** is very low and *N*-methyl derivatives, instead of carbamate methyl esters, are preferentially formed. This result further confirms the scarce tendency of the secondary amino-group to take part in the carbamation process and also emphasizes the low reactivity of the ureido-nitrogen atoms towards the carbamation reaction.

The reactivity of amines **1–3** towards DMC has been investigated, at 348 K, under a dinitrogen atmosphere, in the absence of any catalyst. Under these conditions, both amines **1** and **2** react slowly with DMC with very low conversion yield and the formation of *N*-methylated species is the most favoured process. Di-amine **3** behaves in an analogous way. At 348 K, under dinitrogen, the carbamation of **3** by DMC takes place in a non-selective way. After 7 h at 348 K, the GC–MS analysis of the reaction mixture shows the presence of unreacted **3** and its *N*-methyl derivatives (*m/z* 236) and the formation of **7** together with minor amounts of *N*-methyl carbamate species.

The results reported above, and comparative kinetic experiments carried out in the absence and presence of CO_2 (0.1 MPa), clearly demonstrate that CO_2 plays a key role in the carbamation of amines **1–3** as it acts as an active catalyst of the carbomethoxylation reaction (see Section 2). The first step of the carbamation process is clearly the reaction of CO_2 with the amine to afford an ionic carbamate $RNH_3{}^{+-}O_2CNHR$ (Eqn [2]; R = $(CH_2)_3Si(OMe)_3$ or $(CH_2)_3Si(OEt)_3$), or the zwitterion **11** (eqn [7]).



(11) [7]

Once formed, the carbamate moiety can give a nucleophilic attack to DMC, generating, thus, the mixed anhydride RNHC(O)OC(O)OMe (R = $(CH_2)_3Si(OMe)_3$, $(CH_2)_3Si(OEt)_3$, $(CH_2)_2NH(CH_2)_3Si(OMe)_3$) that easily undergoes decarboxylation[8] to afford the organic carbamate (Eqn [4]). This mechanism has been proved for primary amines by the isolation of the intermediate at low temperature[8] and recording its spontaneous decarboxylation.

2 EXPERIMENTAL

In a typical experiment, a DMC (30 ml) solution of the amine (4 ml), previously saturated with carbon dioxide (0.1 MPa), was heated, under vigorous stirring, at 348 K until conversion of the starting amine (monitored by GC–MS) was complete (as for **3**) or taking place at rate negligible from the synthetic point of view (amines **1–2**). After cooling to room temperature (293 K), the solvent was evaporated *in vacuo* and the residue distilled at reduced pressure to give the pure carbamate (**5** or **7**) that was fully characterized by elemental analysis, IR, GC–MS, ^1H and ^{13}C NMR.

As described in Section 1, starting from **2**, a mixture of carbamates (**6**, **6′**, **6″** and **5**) was formed. In this case, no attempt to isolate **6** from this mixture was carried out. Nevertheless, the formation of carbamates **6**, **6′**, **6″** and **5** was confirmed by analysing the crude product by GC–MS, IR and ^1H and ^{13}C NMR.

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