

# Alkali-metal-assisted Transfer of the Carbamate Group from Phosphocarbamates to Alkyl Halides: a New Easy Way to Alkali-metal Carbamates and to Carbamate Esters†

Michele Aresta\* and Eugenio Quaranta

Dipartimento di Chimica, Università di Bari, Campus Universitario, 70126 Bari, Italy, and Centro CNR-MISO, Via Amendola, 173, 70126 Bari, Italy

Phosphocarbamates  $P(O_2CNR_2)_x(NR_2)_{3-x}$  ( $R = \text{alkyl}$ ;  $x = 1$  or  $2$ ), easily obtainable by insertion of  $CO_2$  in the P–N bond of the corresponding aminophosphines  $P(NR_2)_3$ , have been used as a source of carbamate groups in the reaction with alkyl halides,  $R'X$ , to afford carbamate esters. The reaction is mediated by alkali-metal halides,  $MY$ , and requires the presence of a suitable macrocyclic polyether ( $L$ ). The overall reaction occurs in two steps: the carbamic group is first transferred to the alkali-metal cation to give a carbamate salt  $[ML][O_2CNR_2]$  which then reacts with the alkyl halide affording  $R_2NC(O)OR'$ . The yield and selectivity to the carbamate ester are remarkably influenced by the nature of  $MY$ . The influence of the nature of the alkali-metal salt in the overall process and the role of the macrocyclic ligand in modifying the reactivity of the  $R_2NCO_2^-$  anion in alkali-metal carbamates are discussed.

The interest in the synthesis of carbamate esters<sup>1</sup> remains very high owing to their wide utilization.<sup>2</sup> The synthesis of these compounds generally uses phosgene<sup>3</sup> or isocyanates<sup>4</sup> as the starting material. These are toxic, harmful compounds and, therefore, it is of interest to discover new synthetic routes to carbamate esters involving the use of less noxious starting materials.

Carbon dioxide is a good candidate as a substitute: its fixation by amines and other suitable organic substrates might be an attractive way to synthesize carbamate esters.

Direct interaction of amines with carbon dioxide leads to ionic carbamates  $RNH_3^+ \cdot O_2CNR$  **1**, equation (1).<sup>5</sup> In the



**1**  $R = \text{Alkyl}$

presence of metals,<sup>6</sup> metal salts,<sup>7</sup> metal amides,<sup>8</sup> or metal complexes,<sup>9</sup> metal carbamates  $[M(O_2CNR_2)_mL_n]$  **2** can be obtained. p-Block amides  $E(NR_2)_n$  ( $E = B,^{10e} Si,^{10a,b,c,i} Ge,^{10f,i} Sn,^{10d,g} As,^{10c} Sb,^{10b}, P^{10c}$ ) also react with  $CO_2$ : this reaction involves the formal insertion of the heterocumulene in the E–N bond and affords p-block carbamates  $E(NR_2)_{n-x}(O_2CNR_2)_x$  **3** ( $n = 3$  or  $4$ ).<sup>10</sup>

Compounds **1–3** can play an important role in the synthesis of carbamates as potential carriers or sources of the carbamic group  $O_2CNR_2$ .

The synthesis of carbamate esters from **1** and oxiranes,<sup>11</sup> alkynes<sup>12</sup> and activated olefins<sup>13</sup> has been reported by several workers. Direct reaction of amines and alkyl halides in the presence of  $CO_2$  has also been investigated.<sup>14</sup> Recently, we succeeded in setting up a new method of synthesis of carbamates from primary amines, carbon dioxide and alkyl halides.<sup>15,16</sup>

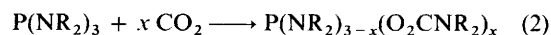
In spite of the great number of metal carbamates **2** isolated until now, attempts to transfer the carbamic group from a metal to suitable organic substrates to give carbamate esters have been successful in a few cases only. In the presence of carbon dioxide, titanium-<sup>17a</sup> or tungsten-amides<sup>17b</sup> react with oxiranes to afford, after hydrolysis, hydroxocarbamates. The transfer of

the carbamic group from metals to acylating systems to give mixed carbamic–carboxylic anhydrides,  $R_2NC(O)OC(O)R'$ , has been successfully accomplished by using both alkali- ( $Na$ ) and transition-metal [ $Cu^{II}$ ,  $Ti^{III}$ ,  $V^{III}$ ,  $Mn^{II}$  or  $Co^{II}$ ] carbamates and seems to be a general reaction little affected by the nature of the metal centre.<sup>18</sup> However, the analogous transfer to alkylating substrates such as alkyl halides or dialkyl sulfates has been documented only for metal carbamates of copper(I)<sup>19</sup> and zinc<sup>20</sup> respectively.

The role that p-block carbamates can play as carriers of the carbamic group still remains largely unknown. In a preliminary note<sup>21</sup> we have reported the results concerning the transfer of the carbamic group from phosphocarbamates to alkyl halides, a process of potential interest in organic synthesis. This reaction is, indeed, the first example of utilization of p-block carbamates as carriers of the carbamate group in the synthesis of carbamic esters.<sup>22</sup> In this paper we report details on the steps of the overall process and discuss and rationalize both the influence of the alkali-metal halides on the transfer reaction and the role played by the crown ether.

## Results and Discussion

*Insertion of  $CO_2$  into P–N Bonds and Characterization of Phosphocarbamates.*—Phosphocarbamates,  $P(O_2CNR_2)_x(NR_2)_{3-x}$  can be prepared by insertion of  $CO_2$  in the P–N bonds of the corresponding aminophosphines **4**, equation (2), a



long-known reaction which occurs under mild conditions (room temperature,  $p_{CO_2} = 0.1\text{--}0.2$  MPa).<sup>10c</sup>

Mono- or di-carbamates can be obtained according to the P/ $CO_2$  molar ratio and temperature. Our attempts to insert a third molecule of carbon dioxide in the P–N bond of aminophosphines  $P(NR_2)_3$  **4** [ $R = \text{Me}$  **4a**,  $R = \text{Et}$  **4b**] failed even when more drastic conditions ( $p_{CO_2} = 5$  MPa) were employed. In an attempt to extend the carbamate synthesis reaction described here to other systems containing P–N bonds, we studied the reaction of carbon dioxide with organo-

† Non-SI unit employed:  $eV \approx 1.6 \times 10^{-19}$  J.

**Table 1** Bond energy<sup>a</sup> and enthalpy change for the reaction:  $P(NR_2)_2(O_2CNR_2) + R'X \longrightarrow P(NR_2)_2X + R_2NC(O)OR'$  (4), (X = Cl, Br or I)

$D(P-O)$	$D(R'-X)$	$D(P-X)$	$D(O-R')$	$\Delta H_r^b$	X
kJ mol <sup>-1</sup>					
340 <sup>c</sup>	327	319	336	+12	Cl
	285	264		+25	Br
	213	184		+33	I

<sup>a</sup> Ref. 31a. <sup>b</sup> Calculated for reaction (4). <sup>c</sup> This value might be slightly underestimated. In  $P_4O_6$ ,  $E(P-O) = 360$  kJ mol<sup>-1</sup> and, in  $P(OR)_3$ ,  $D(P-O) = 381-385$  kJ mol<sup>-1</sup> (ref. 31b).

aminophosphines  $Ph_2P(NHR)$  (R = Bu<sup>l</sup> or Bu<sup>n</sup>), phosphoric amides  $O=P(NR_2)_3$  (R = Me or Et) and phosphonium salts  $[P(NR_2)_3R']X$  [X = halide; R = Me or Et; R' = allyl]. It is worth noting that, even under severe pressure conditions ( $p_{CO_2} = 5$  MPa), we have not obtained any experimental evidence of insertion of carbon dioxide in the P-N bonds of these systems. These results allow us to make a few comments about the insertion reaction of  $CO_2$  in P-N bonds. The experiments carried out with organoaminophosphines suggest that substituents at the phosphorus atom can considerably affect the rate of the insertion reaction. The substitution of  $NR_2$  with Ph groups in  $P(NR_2)_3$  both reduces the nucleophilic character of the nitrogen atoms and increases  $\pi$ -back donation from nitrogen to phosphorus.\* Thus, the reactivity of P-N systems towards carbon dioxide depends on the nucleophilicity at the nitrogen atom and the strength of the P-N bond.

The co-ordination and oxidation state of phosphorus also can play an important role in the insertion reaction. Phosphonium salts and phosphoric amides have shown the poor reactivity of P-N bonds involving four-co-ordinated positively charged phosphorus atoms.

The phosphocarbamates considered in this work are  $P(NMe_2)(O_2CNMe_2)_2$  **5a** and  $P(NEt_2)(O_2CNEt_2)_2$  **5b**.<sup>10c</sup> The spectroscopic characterization of **5a** and of the corresponding monocarbamate  $P(NMe_2)(O_2CNMe_2)$  **6a** has been recently reported.<sup>23</sup> To our knowledge, no spectroscopic data are available in the literature for **5b** and  $P(NEt_2)(O_2CNEt_2)$  **6b**.

When  $P(NEt_2)_3$  **4b** was exposed to carbon dioxide ( $p_{CO_2} = 0.1$  MPa), the IR spectrum of the reaction mixture showed a decrease in the bands at 665 and 645 cm<sup>-1</sup>, assigned to P-N stretching in **4b**, and new strong absorptions to appear at 1685, 1275 and 1167 cm<sup>-1</sup>, assigned, respectively, to C=O, NCO<sub>2</sub> and P-O-C stretching modes in phosphocarbamates **5b** and **6b**. The appearance of these new bands can be considered as diagnostic of the insertion reaction of carbon dioxide into the P-N bond of aminophosphines, as confirmed also by <sup>13</sup>C NMR spectroscopy.

The <sup>13</sup>C spectra of **5b** and **6b** show carbamic carbon resonances at  $\delta$  153.4 and 154.38, respectively, as doublets [<sup>2</sup>J(CP) = 8.4 Hz, in both cases] owing to the coupling with the central phosphorus atom.† Moreover, the methylene carbon atoms in the carbamate groups of phosphocarbamates **5b** and **6b** lose the coupling with the phosphorus atom<sup>21</sup> and give downfield-shifted broadened singlets at  $\delta$  41.81 and 41.43, respectively. Broadening of these signals indicates that the rotation of the amino group around the N-CO<sub>2</sub> bond is relatively hindered in **5b** and **6b** owing to the double-bond character of the N-CO<sub>2</sub> bond and suggests that the delocalization of the carbamic nitrogen lone pair onto the carboxylic group is im-

portant. Accordingly, X-ray structural data for  $[CoCl(NO)_2-PhP(OCH_2CH_2)_2NC(O)OH]_2$  show the carbamic nitrogen to be planar with bond angles very close to 120° (sp<sup>2</sup> hybridization).‡<sup>24</sup>

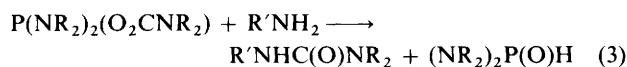
The <sup>31</sup>P-<sup>1</sup>H NMR spectra of **5b** and **6b** show single resonances at  $\delta$  125.85 and 127.15, respectively. This is the region wherein the chemical shifts of three-co-ordinate tetrahedral phosphorus atoms usually appear<sup>26</sup> and, therefore, monodentate carbamate co-ordination to phosphorus may be inferred both in **5b** and **6b**. Our results agree with the findings of other workers<sup>23</sup> that describe **5a** and **6a** as containing monodentate carbamate groups bonded to phosphorus(III). A bidentate co-ordination has been demonstrated by Cavell<sup>27</sup> for the *N,N*-dimethylcarbamato group in  $PMe(CF_3)_3(O_2CNMe_2)$ .

The <sup>31</sup>P NMR resonances for **5b** and **6b** are shifted to lower fields with respect to **4b** as would be expected when inductive as well as mesomeric effects exerted by  $NR_2$  and  $R_2NCO_2$  groups on the phosphorus atom are taken into account. However, the <sup>31</sup>P resonance upfield shift is higher in **5b** than in **6b**. This suggests that other factors, such as steric hindrance, can influence the <sup>31</sup>P chemical shift of phosphocarbamates. Indeed, it is well known that <sup>31</sup>P shifts depend on the size of the bond angles around phosphorus.<sup>28</sup>

The parent-ion peak is hardly observed in the mass spectra of **5b** and **6b** and no peak can be detected which accounts for the loss of CO<sub>2</sub> from the parent ion. In both compounds a base peak corresponding to the ion  $[Et_2NCO]^+$  appears at  $m/z$  100 and a strong peak is observed at  $m/z$  72 which is related with the presence of Et<sub>2</sub>N groups. The mass spectrum of **6b** also shows weak peaks at  $m/z$  219 and 175 which may be due to the loss of NEt<sub>2</sub> and Et<sub>2</sub>NCO<sub>2</sub> fragments from the  $[P(NEt_2)_2(O_2CNEt_2)]^+$  parent ion.

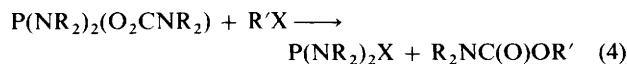
#### Reactivity of Phosphocarbamates towards Alkyl Halides.—

The chemistry of phosphocarbamates has not been previously widely investigated. The reactivity of phosphocarbamates co-ordinated to a metal centre was studied by Aresta *et al.*<sup>29</sup> Yamazaki *et al.*<sup>30</sup> described the reaction of phosphocarbamates with amines and observed the nucleophilic attack at the carbamic carbon to afford ureas, equation (3) (R = Me or Et).



To our knowledge, no data are available in the literature concerning the reactivity of phosphocarbamates with electrophiles.

The direct reaction of phosphocarbamates with alkyl halides does not lead to the formation of carbamate esters. In Table 1 we have reported the dissociation energy values for the bonds involved in reaction (4). Approximate  $\Delta H_r$  values estimated for



reaction (4) (X = Cl, Br or I) from data of Table 1 suggest that

‡ Further evidence of restricted rotation around the N-CO<sub>2</sub> bond of these systems comes from <sup>1</sup>H NMR spectroscopy. The carbamic group methylene protons of **5b**, which do not show resolvable coupling with the phosphorus atom, give two almost completely overlapping quadruplets at  $\delta$  2.81. In the <sup>1</sup>H spectrum of **5a** (CDCl<sub>3</sub>, 200 MHz) the non-equivalence of carbamic methyl groups is much more evident and two singlets, separated by 6.1 Hz at  $\delta$  2.85 (6 H) and 2.82 (6 H), can be observed for the methyl protons of the O<sub>2</sub>CNMe<sub>2</sub> groups;  $[P(NMe_2)(O_2CNMe_2)_2]$  protons give a doublet at  $\delta$  2.63 [6 H, *J*(HP) 9.77 Hz]. In a previous <sup>1</sup>H NMR study (100 MHz, neat) on **5a**, one broad resonance was observed for the carbamic group methyl protons.<sup>23</sup> The hampered rotation of  $NR_2$  groups around the N-CO<sub>2</sub> bond seems to be a general feature of carbamic systems and has also been documented both in organic carbamates  $R_2NC(O)OR'$ <sup>25</sup> and in metal carbamates.<sup>34</sup>

\* Experiments using aminoalkylphosphines or aminodialkylphosphines are in progress in order to evaluate the effects of the alkyl groups bonded at phosphorus on the carbon dioxide insertion reaction.

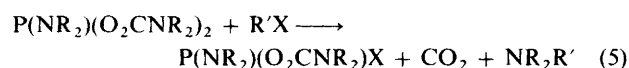
† No data were reported for the resonance of the carbamic carbon atom in **6a**.<sup>23</sup>

unfavourable thermodynamics may be responsible for the fact that reaction (4) does not occur.

The reactivity of phosphocarbamates towards alkyl halides is well illustrated by the reaction of **5b** with PhCH<sub>2</sub>Cl in CH<sub>2</sub>Cl<sub>2</sub>, at room temperature, under an inert gas (N<sub>2</sub>) atmosphere. The GC analyses of the gas phase in equilibrium with the solution and IR spectroscopy of the reaction mixture revealed the formation of free gaseous carbon dioxide (IR: 2340 cm<sup>-1</sup>). Gas-mass analyses of the reaction solution showed that Et<sub>2</sub>N(CH<sub>2</sub>Ph), P(NEt<sub>2</sub>)(O<sub>2</sub>CNEt<sub>2</sub>)Cl, Et<sub>2</sub>NC(O)Cl, O=P(CH<sub>2</sub>Ph)(NEt<sub>2</sub>)(O<sub>2</sub>CNEt<sub>2</sub>) and Et<sub>2</sub>NC(O)NEt<sub>2</sub> were formed.\* Phosphocarbamate **5a** reacts with PhCH<sub>2</sub>Cl to afford benzyl dimethylamine, *N,N*-dimethylcarbamoyl chloride and tetramethylurea.

These results point out that the reactivity of phosphocarbamates towards alkyl halides is quite complex.

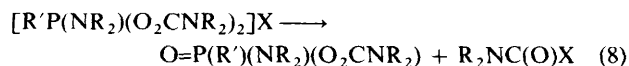
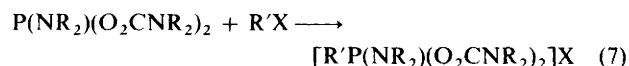
Electrophilic attack of alkyl halides onto the carbamic nitrogen atoms of phosphocarbamates results in the *N*-alkylation and decarboxylation of the carbamate groups to afford CO<sub>2</sub>, a tertiary amine, NR<sub>2</sub>R', and P(NR<sub>2</sub>)(O<sub>2</sub>CNR<sub>2</sub>)X [equation (5): R = Me or Et; R' = PhCH<sub>2</sub>; X = Cl]. This



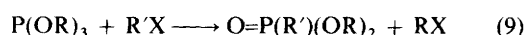
behaviour has also been encountered by other workers<sup>7b</sup> when metal carbamates were treated with alkyl halides, equation (6).



However, alkyl halides can also react at the phosphorus atom. This is clearly suggested by the presence of O=P(CH<sub>2</sub>Ph)(NEt<sub>2</sub>)(O<sub>2</sub>CNEt<sub>2</sub>) among the products of the reaction of **5b** with PhCH<sub>2</sub>Cl. Equations (7) and (8) (R = Et; R' =

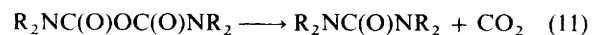
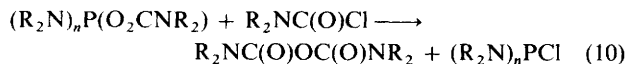


PhCH<sub>2</sub>, X = Cl), which are reminiscent of the steps involved in the well known Arbuzov reaction [equation (9)], are pro-



posed to explain the formation both of O=P(CH<sub>2</sub>Ph)(NEt<sub>2</sub>)(O<sub>2</sub>CNEt<sub>2</sub>) and Et<sub>2</sub>NC(O)Cl.

The formation of ureas R<sub>2</sub>NC(O)NR<sub>2</sub> (R = Me or Et) is more difficult to explain and, in our opinion, it might involve, as the initial step, the O-carbamoylation of one of the carbamate groups bonded to the phosphorus atom to give a carbamic anhydride R<sub>2</sub>NC(O)OC(O)NR<sub>2</sub> which undergoes fast decarboxylation to afford R<sub>2</sub>NC(O)NR<sub>2</sub> [equations (10) and (11)].

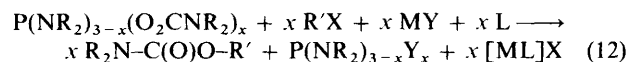


\* The formation of *N,N*-diethylcarbamoyl chloride and tetraethylurea was supported by the appearance of two strong absorptions at 1730 and 1640 cm<sup>-1</sup> respectively in the IR spectrum of the reaction solution. Mass spectra: diethylbenzylamine, *m/z* 163 (*M*<sup>+</sup>), 148, 91, 77, 65, 42, 30 and 29; P(NEt<sub>2</sub>)(O<sub>2</sub>CNEt<sub>2</sub>)Cl, *m/z* 212, 210 (*M*<sup>+</sup> - 44), 175, 140, 138, 104, 74, 72, 46, 44 and 29; Et<sub>2</sub>NC(O)Cl, *m/z* 137, 135 (*M*<sup>+</sup>), 122, 120, 100, 92, 90, 72, 58, 44, 30 and 29; O=P(CH<sub>2</sub>Ph)(NEt<sub>2</sub>)(O<sub>2</sub>CNEt<sub>2</sub>), *m/z* 282 (*M*<sup>+</sup> - 44), 211, 191, 163, 120, 91, 72 and 44; Et<sub>2</sub>NC(O)NEt<sub>2</sub>, *m/z* 172 (*M*<sup>+</sup>), 100, 72 and 29.

Indeed, it is known that metal carbamates are O-acylated under mild conditions to give mixed carbamic-carboxylic anhydrides.<sup>18</sup> Moreover, anhydrides of carbamic acids are known to undergo decarboxylation reactions very easily.<sup>18,32</sup>

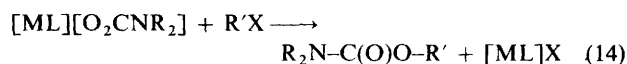
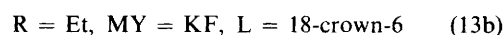
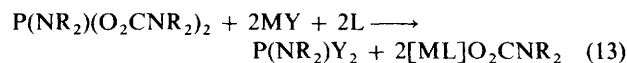
*Transfer of Carbamate Groups from Phosphocarbamates to Alkyl Halides.*—Alkyl halides thus usually react with phosphocarbamates at the phosphorus as well as at the carbamic nitrogen. However, it would be of great interest to address the electrophilic attack onto the oxygen atoms of the carbamate groups.

The transfer of carbamic groups from phosphocarbamates to alkyl halides to give organic carbamates can be successfully accomplished when phosphocarbamates are treated with alkyl halides in the presence of an alkali-metal halide, MY, and a suitable crown ether, L [L = 1,4,7,10-tetraoxacyclododecane (12-crown-4); 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5); or 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6)] [equation (12)]. Reaction (12) is usually carried out



in aprotic solvents such as tetrahydrofuran (thf); protic solvents cause the decomposition of phosphocarbamates.† Reaction (12) occurs at room temperature under a CO<sub>2</sub> or an inert gas atmosphere (*p* = 0.1 MPa). The yield depends on (i) the nature of the alkali-metal halide, MY [we have used several halides (M = Li, Na or K; Y = F, Cl, Br or I); the highest yields were obtained using KF]; (ii) the utilization of a crown ether, which co-ordinates to the alkali-metal cation. Carbamate esters were formed in very low amounts when unactivated aryl halides (e.g. 1-bromonaphthalene or chlorobenzene) were used.

Reaction (12) occurs in two steps, given by equations (13) and (14).



The first step, equation (13), is the formation of the alkali-metal carbamate salt [ML][O<sub>2</sub>CNR<sub>2</sub>]. Alkali-metal carbamates **7a** [R = Me, M = K] and **7b** [R = Et, M = K] have been isolated when **5a** or **5b** was treated (room temperature, *p*<sub>CO<sub>2</sub></sub> or *p*<sub>N<sub>2</sub></sub> = 0.1 MPa) with KF and 18-crown-6 in the absence of R'X [equations (13a) and (13b), respectively]. Both (13a) and (13b) are complete, very selective reactions (100% yield). Moreover, as previously pointed out, reaction (13) represents a new economically advantageous way to alkali-metal carbamates that are usually prepared by treating an amine with alkali metals under a carbon dioxide atmosphere.

The second step of the overall process is the reaction of **7** with the alkyl halide to give the carbamate ester, equation (14); this suggests that metal carbamates prepared in whatever manner can be used in the synthesis of carbamate esters under the conditions described.‡

† The IR spectrum of P(NR<sub>2</sub>)<sub>3-x</sub>(O<sub>2</sub>CNR<sub>2</sub>)<sub>x</sub> (R = Me or Et) solutions in methanol shows the fast disappearance of the strong band at 1700 cm<sup>-1</sup>, typical of the carbamic group in phosphocarbamates.

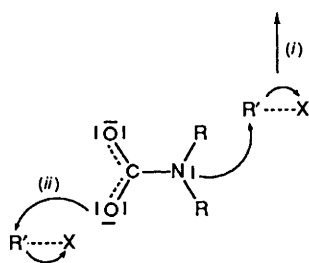
‡ After issuing the preliminary results concerning this work,<sup>21</sup> it has been reported, independently, by Belforte and Calderazzo<sup>33</sup> that alkali-metal carbamates prepared from the alkali metal, Et<sub>2</sub>NH and CO<sub>2</sub> upon treatment with methyl iodide, in the presence of a macrocyclic polyether, gave methyl *N,N*-diethylcarbamate.



**Table 2** Influence of alkali-metal salt MY in the carbamate group transfer reaction

P(NR <sub>2</sub> )(O <sub>2</sub> CNR <sub>2</sub> ) <sub>2</sub> R	R'X	MY	L	Solvent	Yield R <sub>2</sub> NC(O)OR' <sup>a</sup> (%)
Et	C <sub>10</sub> H <sub>21</sub> Br	KF	18-crown-6	thf	91
Me	PhCH <sub>2</sub> Cl	KF	18-crown-6	thf	90
Me	CH <sub>2</sub> =CHCH <sub>2</sub> Br	KF	18-crown-6	thf	89
Me	CH <sub>2</sub> =CHCH <sub>2</sub> Br	KCl	18-crown-6	thf	<i>b</i>
Me	CH <sub>2</sub> =CHCH <sub>2</sub> Br	KBr	18-crown-6	thf	<i>b</i>
Me	CH <sub>2</sub> =CHCH <sub>2</sub> Br	KI	18-crown-6	thf	<i>b</i>
Me	CH <sub>2</sub> =CHCH <sub>2</sub> Br	NaF	15-crown-5	thf	<i>b</i>
Me	CH <sub>2</sub> =CHCH <sub>2</sub> Br	NaCl	15-crown-5	thf	<i>b</i>
Me	CH <sub>2</sub> =CHCH <sub>2</sub> Br	LiF	12-crown-4	thf	<i>b</i>
Me	CH <sub>2</sub> =CHCH <sub>2</sub> Br	LiCl	12-crown-4	thf	<i>b</i>

<sup>a</sup> Isolated yield from column chromatography. <sup>b</sup> Yield generally lower than 5–10%.



**Fig. 1** Reactivity of the carbamate anion towards alkyl halides (i) N-alkylation  $\longrightarrow$  tertiary amines or ammonium salts (ii) O-alkylation  $\longrightarrow$  organic carbamates

#### Influence of MY in the Carbamate Group Transfer Reaction.—

The yield of reaction (12) strongly depends on the nature of the alkali-metal halide MY. Very high yields were obtained by using KF; other alkali-metal halides, in the presence of a suitable crown ether, did not lead to formation of organic carbamates (Table 2) in high yields; therefore K<sup>+</sup> and F<sup>-</sup> ions seem to play a very specific role in reaction (12).

When MY is a potassium halide, the formation of **7** from **5a** or **5b** was observed in very high yield only for the fluoride. Reaction (13) involves the breaking of a P–O bond and the formation of a P–Y bond. Comparison between dissociation energies of P–O and P–Y bonds [ $D(\text{P–F}) = 490 \text{ kJ mol}^{-1}$ ;<sup>31a</sup> see also Table 1] suggests that the formation of a strong P–Y bond might be the driving force of reaction (13).<sup>\*</sup> Indeed, KF affords the best yields despite its high lattice energy.<sup>34</sup>

The nature of the alkali-metal cation can influence reaction (13). In the presence of 12-crown-4 and 15-crown-5, LiF and NaF respectively did not afford **7** in good yield. The ionic association between  $[\text{M}\cdot\text{L}]^+$  and F<sup>-</sup>, the relative thermodynamic stabilities of  $[\text{M}\cdot\text{L}]\text{F}$  and  $[\text{M}\cdot\text{L}][\text{O}_2\text{CNR}_2]$  (M = Li, Na or K) might be responsible for this fact. It should be noted that LiF and NaF show higher lattice energies than KF;<sup>34</sup> moreover, the stronger binding properties of thf towards Li<sup>+</sup> and Na<sup>+</sup> (when compared with K<sup>+</sup>) are well known.<sup>35</sup> Our findings match the fact that potassium ions are implicated in biological systems related to the synthesis<sup>36</sup> and transfer<sup>37</sup> of the carbamate group.

*The Role of the Macrocyclic Polyether. Reactivity of the R<sub>2</sub>NCO<sub>2</sub><sup>-</sup> Anion towards Alkyl Halides.*—The presence of a suitable macrocyclic polyether is essential for phosphocarbam-

ates to react with alkyl halides in the presence of alkali-metal salts to afford organic carbamates.

The properties of crown ethers in complexing metal cations, in particular alkali-metal cations, are well documented in the literature.<sup>38</sup> The effects of complexation both on the solubility of inorganic salts and on the basicity and nucleophilicity of anions have been investigated extensively.<sup>39</sup>

The role of the macrocyclic ligand is not confined to the first step of the overall process, equation (13), but is relevant also for the transfer reaction of the carbamate group to the organic halide. Indeed, the reactivity of carbamate R<sub>2</sub>NCO<sub>2</sub><sup>-</sup> anion in alkali-metal carbamates is remarkably affected by the presence of a macrocyclic ligand: when K(O<sub>2</sub>CNR<sub>2</sub>) (R = Me or Et), prepared by different routes<sup>6</sup> was treated with an alkyl halide in the absence of a suitable crown ether, tertiary amines, NR<sub>2</sub>R' tetraalkylammonium salts,  $[\text{NR}_2\text{R}'_2]\text{X}$ , and carbon dioxide were formed as the only reaction products.

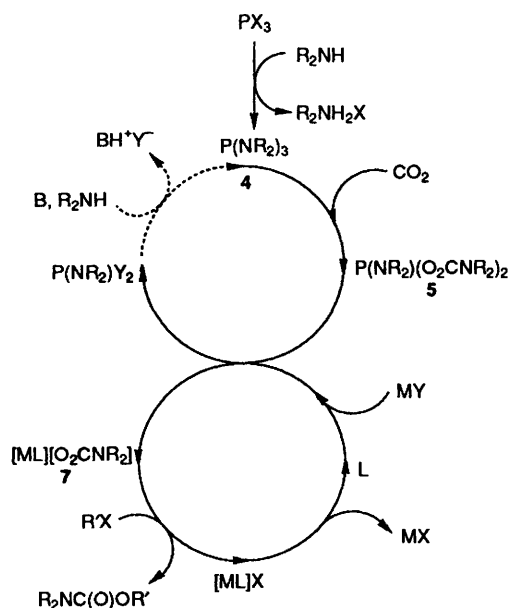
As illustrated in Fig. 1, the carbamate anion shows two sites for the interaction with electrophilic reagents such as alkyl halides, *i.e.* the nitrogen and oxygen atoms. Attack onto the nitrogen atom gives N-alkylation products and carbon dioxide evolution, whereas attack onto the terminal oxygens leads to carbamate esters with incorporation of CO<sub>2</sub>. The carbamate anions are, therefore, an example of an ambidentate nucleophile.

Our findings show that the utilization of a crown ether allows control of the alkylation site in carbamate anions. An analogous behaviour has been found by other workers for other ambidentate anions.<sup>40</sup> This change of reactivity may be due to the interaction of between the carbamate anion and the alkali-metal cation. In the absence of a complexing agent, the interaction between the cation and one or both of the carbamate oxygen atoms can depress the oxygen nucleophilicity so that R'X reacts with the nitrogen atom, in spite of the delocalization of the nitrogen lone pair onto the CO<sub>2</sub> functional group.<sup>7b,c</sup> On the other hand, in the presence of a macrocyclic ligand, which interacts with the alkali-metal cation, much more loose coulombic interaction would be expected between the cation and the oxygen atoms of the carbamate anion as the polyether shields the cationic charge. Consequently, the oxygen nucleophilicity will be increased.<sup>38</sup>

The anion–cation interaction can thus play a key role in the transfer reaction. Indeed, to our knowledge, carbamate transfer from a transition metal to an alkyl halide is documented in the literature by only one example. Copper(I) carbamates have been reported to transfer the carbamate group to methyl iodide<sup>19</sup> only when a strong  $\sigma$ -donor ligand is present in the coordination sphere of the metal, so labilizing the carbamate group.

It may also be of interest to compare our findings with the results concerning the reactivity of metal carbamates towards other classes of electrophiles. Alkali- and transition-metal carbamates  $[\text{Ti}^{\text{III}}, \text{V}^{\text{III}}, \text{Co}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Na}^+]$  regioselectively

\* The behaviour observed using different potassium halides cannot be ascribed to unfavourable kinetic factors. Sodium iodide in acetone reacts with **5a** to give Na(O<sub>2</sub>CNMe<sub>2</sub>) (IR: 1565 and 1375 cm<sup>-1</sup>). The poor solubility of the ionic carbamate Na(O<sub>2</sub>CNMe<sub>2</sub>) in the reaction solvent might be the driving force in this case.



**Scheme 1** Synthesis of carbamate esters *via* alkali-metal-assisted transfer of the carbamic group from phosphocarbamates to alkyl halides R'X (X = Cl, Br or I); M = Li, Na or K; L = crown ether; Y = Cl, Br or I; B = base

undergo O-acylation when treated with acyl chlorides.<sup>18</sup> O-Functionalization has been observed also when alkylammonium or alkali-metal carbamates are treated with  $\text{SiMe}_3\text{Cl}$ ,<sup>41</sup>  $\text{ClC(O)OMe}$ ,<sup>42,43</sup> or dimethyl carbonate.<sup>43</sup> This behaviour is in contrast with the reactivity of alkylammonium or metal carbamates towards alkyl halides. The reagents  $\text{RC(O)Cl}$ ,  $\text{SiMe}_3\text{Cl}$ ,  $\text{ClC(O)OMe}$  and  $(\text{MeO})_2\text{CO}$  show a quite hard electrophilic character and their observed reactivity could express the trend of the carbamate anion to react more easily at the oxygen atom sites with hard electrophiles.<sup>44</sup>

**Synthesis of Carbamate Esters  $\text{R}_2\text{NC(O)OR}'$ .**—Reaction (12) [ $\text{MY} = \text{KF}$ ; L = 18-crown-6] has been utilized for the synthesis, in high yields (>85%) of several carbamate esters. We report here as examples the synthesis and the isolation of  $\text{Me}_2\text{NC(O)OCH}_2\text{Ph}$  **8**,  $\text{Me}_2\text{NC(O)OCH}_2\text{CH}=\text{CH}_2$  **9** and  $\text{Et}_2\text{NC(O)OCH}_2(\text{CH}_2)_8\text{CH}_3$  **10**. Compounds **8–10** were identified and characterized by means of elemental analyses, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra,<sup>21</sup> and mass spectrometry. The same reaction has been used also for the synthesis of other carbamates of general formula  $\text{R}_2\text{NC(O)OR}'$ , where R = Et or Me and R' = alkyl or cycloalkyl.

Potassium carbamates **7a** and **7b** do not need to be isolated and can be treated with the alkyl halide *in situ*.

If **7a** or **7b** is not isolated, the alkyl halide should be added after most of the phosphocarbamate has reacted with  $[\text{KL}]\text{F}$ : reaction (13) can be easily monitored by IR spectroscopy, by following the disappearance of the absorption at  $1700\text{ cm}^{-1}$ , which is characteristic of phosphocarbamates.

We have developed a procedure to recover, in very high yields, pure 18-crown-6 from  $[\text{K}(18\text{-crown-6})]\text{X}$ , but, until now, we have not succeeded in complete recycling of  $(\text{R}_2\text{N})\text{PF}_2$  to obtain the starting tris(dialkylamino)phosphine. The accomplishment of this step in 100% yield is of great interest, as it would allow the overall synthetic process according to Scheme 1 to be made cyclic.

## Conclusion

The transfer of the carbamic group from phosphorus of phosphocarbamates to an alkyl halide to afford carbamic esters is mediated by alkali-metal halides in the presence of a suitable macrocyclic ligand whose role is to complex the alkali-metal

cation. A carbamate salt  $[\text{ML}][\text{O}_2\text{CNR}_2]$  **7** is formed as an isolable intermediate species which reacts with the alkyl halide to afford  $\text{R}_2\text{NC(O)OR}'$ . The transfer reaction is strongly influenced by the nature of the alkali-metal halide and best yields and selectivity to carbamate esters are obtained by using KF. Comparative experiments performed in the absence of macrocyclic polyethers have shown that the reactivity of alkali-metal carbamates towards alkyl halides can be remarkably modified by the presence of the macrocyclic ligand.

Phosphocarbamates can be easily obtained by insertion of carbon dioxide in the P–N bond of corresponding amino-phosphines; as shown in Scheme 1, aminophosphines can be prepared by reaction of  $\text{PCl}_3$  with amines. Therefore, reaction (12) is a new method for the synthesis of carbamate esters, in high yield and selectivity, from amines and alkyl halides *via* incorporation of carbon dioxide.

## Experimental

**Materials.**—Solvents were dried and distilled from sodium-benzophenone and stored under dinitrogen;  $\text{CO}_2$  (99.99% pure) and  $^{13}\text{CO}_2$  (99%  $^{13}\text{C}$ ) were from SIO SpA and CIL, respectively. Aminophosphines  $\text{P}(\text{NR}_2)_3$  (R = Me or Et),<sup>45</sup>  $\text{P}(\text{NHR})\text{Ph}_2$  (R = Bu<sup>n</sup> or Bu<sup>t</sup>)\*,<sup>46</sup> and phosphocarbamates  $\text{P}(\text{NR}_2)_{3-x}(\text{O}_2\text{CNR}_2)_x$  (R = Me or Et)<sup>10c,23,29</sup> were prepared as reported in the literature; crown ethers, benzyl chloride, allyl and *n*-decyl bromides and other alkyl or cycloalkyl halides were all Aldrich products; KF was from Fluka.

**Physical Measurements and Instrumentation.**—IR spectra were obtained with a Perkin-Elmer 883 spectrophotometer;  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{19}\text{F}$  NMR spectra were recorded with a Varian XL-200 spectrometer. Chemical shifts are reported in ppm *vs.*  $\text{SiMe}_4$  for  $^1\text{H}$  and  $^{13}\text{C}$ ; *vs.*  $\text{H}_3\text{PO}_4$  and  $\text{O}=\text{C}(\text{CF}_3)_2 \cdot 6\text{H}_2\text{O}$  for  $^{31}\text{P}$  and  $^{19}\text{F}$ , respectively. The GC and GC-MS analyses were carried out with a DANI HR 3800 gas chromatograph and a HP 5890 gas chromatograph connected to a HP 5970 selective mass detector and equipped with a 30 m SE-30 (0.25 mm i.d.; 0.25  $\mu\text{m}$  film thickness) capillary column. The mass spectra of the carbamate esters were recorded with a MS 80 Kratos instrument.

**Spectroscopic Characterization.**— $\text{P}(\text{NEt}_2)(\text{O}_2\text{CNEt}_2)_2$  **5b**. IR (neat): 1675s, 1275s, 1167s  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.64 [12 H, t,  $^3J(\text{HH})$  7.08,  $(\text{CH}_3\text{CH}_2)_2\text{NCO}_2$ ], 0.67 [6 H, t,  $^3J(\text{HH})$  7.15,  $(\text{CH}_3\text{CH}_2)_2\text{N}$ ], 2.70 [4 H, m,  $^3J(\text{HP})$  9.92,  $(\text{CH}_3\text{CH}_2)_2\text{N}$ ] and 2.81 [8 H, br q,  $(\text{CH}_3\text{CH}_2)_2\text{NCO}_2$ ];  $\delta_{\text{C}}(\text{CDCl}_3)$ , sample enriched with  $^{13}\text{CO}_2$  13.18 and 13.88 [two singlets,  $(\text{CH}_3\text{CH}_2)_2\text{NCO}_2$  and  $(\text{CH}_3\text{CH}_2)_2\text{N}$ ], 38.81 [d,  $^2J(\text{CP})$  23.2,  $(\text{CH}_3\text{CH}_2)_2\text{N}$ ], 41.81 [br s,  $(\text{CH}_3\text{CH}_2)_2\text{NCO}_2$ ] and 153.42 [d,  $^2J(\text{CP})$  8.4 Hz,  $\text{NCO}_2$ ];  $\delta_{\text{P}}(\text{CDCl}_3)$  125.85;  $m/z$  335 ( $M^+$ ), 264, 218, 171, 118, 100, 72, 44 and 29.

$\text{P}(\text{NEt}_2)_2(\text{O}_2\text{CNEt}_2)$  **6b**.  $\delta_{\text{C}}(\text{CDCl}_3)$ , sample enriched with  $^{13}\text{CO}_2$  14.50 and 14.57 [two singlets,  $(\text{CH}_3\text{CH}_2)_2\text{NCO}_2$  and  $(\text{CH}_3\text{CH}_2)_2\text{N}$ ], 39.67 [d,  $^2J(\text{CP})$  20.2 Hz,  $(\text{CH}_3\text{CH}_2)_2\text{N}$ ], 41.43 [br s,  $(\text{CH}_3\text{CH}_2)_2\text{NCO}_2$ ] and 154.38 [d,  $^2J(\text{CP})$  8.4 Hz,  $\text{NCO}_2$ ];  $\delta_{\text{P}}(\text{CDCl}_3)$  127.15;  $m/z$  291 ( $M^+$ ), 219, 175, 100, 72, 44 and 29.

**Reaction of  $\text{P}(\text{NR}_2)(\text{O}_2\text{CNR}_2)_2$  with KF in the Presence of 18-crown-6.**—**Synthesis of  $[\text{K}(18\text{-crown-6})][\text{O}_2\text{CNMe}_2]$  **7a**.** Finely powdered KF (0.639 g,  $1.10 \times 10^{-2}$  mol) and 18-crown-6 (2.908 g,  $1.10 \times 10^{-2}$  mol) were introduced into a flask flushed with  $\text{CO}_2$  and warmed for about 30 min under vigorous stirring. After cooling to room temperature, solvent (thf, 13  $\text{cm}^3$ ) was

\* Spectroscopic data for  $\text{P}(\text{NHBu}^n)\text{Ph}_2$ . IR (neat): 3400m (br), 3080m, 3060m, 2960s, 2930s, 2865ms, 1580m, 1485ms, 1440s, 1120ms (br), 1095vs, 745vs and 700vs  $\text{cm}^{-1}$ ;  $\delta_{\text{H}}(\text{C}_6\text{D}_6)$ : 7.49 (4 H, t,  $H_{\text{meta}}$ ), 7.16 (6 H, m,  $H_{\text{ortho}}$  and  $H_{\text{para}}$ ), 2.83 [2 H, m,  $^3J(\text{HCCH}) = ^3J(\text{HCNH})$  6.86,  $^3J(\text{HP})$  8.38,  $\text{CH}_2\text{N}$ ], 1.71 [1 H, q,  $^2J(\text{HP}) = ^3J(\text{HCNH})$  6.46, NH], 1.19 (4 H, m,  $\text{CH}_2\text{CH}_2$ ), 0.76 [3 H, t,  $^3J(\text{HH})$  7.06 Hz,  $\text{CH}_3$ ].

added and the resulting suspension was treated with a solution of  $P(NMe_2)(O_2CNMe_2)_2$  ( $5.50 \times 10^{-3}$  mol) in thf ( $5 \text{ cm}^3$ ). The reaction mixture was stirred for 15 h at room temperature and then distilled at this temperature *in vacuo*. A white microcrystalline solid was obtained as the residue which correctly analysed for **7a** (4.300 g, 99.8%) (Found: C, 46.2; H, 7.8; N, 3.7.  $C_{15}H_{30}KNO_8$  requires C, 46.0; H, 7.7; N, 3.6%). IR (Nujol): 1580s, 1345s, 1110vs, 965s and 840ms  $\text{cm}^{-1}$ .

The distilled fraction was collected in a liquid-nitrogen bath. After warming up to room temperature, it was analysed by means of IR,  $^{31}\text{P}$  and  $^{19}\text{F}$  NMR spectroscopic techniques and shown to contain  $PF_2(NMe_2)$ .<sup>21,47</sup>

**Synthesis of [K(18-crown-6)][O<sub>2</sub>CNEt<sub>2</sub>]**7b**.** Salt **7b** was prepared in a manner analogous to **7a** (yield 99.7%) (Found: C, 48.7; H, 8.3; N, 3.5.  $C_{17}H_{34}KNO_8$  requires C, 48.7; H, 8.2; N, 3.3%). IR (Nujol): 1565s, 1297s, 1110vs, 965s and 845  $\text{cm}^{-1}$ .

The infrared spectrum of the reaction solution showed absorptions typical of  $PF_2(NEt_2)$ .<sup>47</sup>

**Synthesis of R<sub>2</sub>NC(O)OR' (R = Me, R' = CH<sub>2</sub>Ph, CH<sub>2</sub>=CH-CH<sub>2</sub>; R = Et, R' = C<sub>10</sub>H<sub>21</sub>)-Me<sub>2</sub>NC(O)OCH<sub>2</sub>Ph **8**.** Benzyl chloride (2.54 cm<sup>3</sup>, 2.785 g,  $2.20 \times 10^{-2}$  mol) previously dissolved in thf ( $20 \text{ cm}^3$ ) was added to a suspension of **7a**, prepared as described above and directly employed without isolation of the ionic carbamate [ $P(NMe_2)(O_2CNMe_2)_2$  1.10  $\times 10^{-2}$  mol; KF 1.279 g,  $2.20 \times 10^{-2}$  mol; 18-crown-6 5.819 g,  $2.20 \times 10^{-2}$  mol; thf  $30 \text{ cm}^3$ ]. The reaction mixture was stirred at room temperature for 24 h under a CO<sub>2</sub> atmosphere and then filtered. The mother-liquor and washing solutions were collected together and evaporated *in vacuo*. The residue was fractionated on a silica gel column [2.4 cm (i.d.)  $\times$  120 cm] with diethyl ether-hexane (1:1 v/v) as the eluent mixture. Evaporation of solvent from the eluted fractions afforded pure **8** (3.54 g, 90%) (Found: C, 67.1; H, 7.4; N, 7.7. Calc. for  $C_{10}H_{13}NO_2$ : C, 67.0; H, 7.3; N, 7.8%). Mass spectrum (10 eV):  $m/z$  179 ( $M^+$ ), 134, 107 ( $R'O^+$ ), 91 ( $R'^+$ ), 72 ( $Me_2NCO^+$ ) and 44.

**Me<sub>2</sub>NC(O)OCH<sub>2</sub>CH=CH<sub>2</sub> **9**.** The reaction mixture [ $CH_2=CH-CH_2Br$  1.9 cm<sup>3</sup>, 2.656 g,  $2.20 \times 10^{-2}$  mol;  $P(NMe_2)(O_2CNMe_2)_2$  1.10  $\times 10^{-2}$  mol; KF 1.279 g,  $2.20 \times 10^{-2}$  mol; 18-crown-6 5.820 g,  $2.20 \times 10^{-2}$  mol; thf  $30 \text{ cm}^3$ ] was stirred at room temperature for 24 h under a CO<sub>2</sub> atmosphere and then filtered. The mother-liquor and washing solutions were collected together and evaporated *in vacuo*. The residual oil was chromatographed on a silica gel column [2.4 cm (i.d.)  $\times$  120 cm] using a diethyl ether-pentane mixture (1:1 v/v) as eluent. Evaporation of solvent (*in vacuo*) from the eluted fractions afforded pure **9** (2.37 g, 89%) (Found: C, 55.9; H, 8.6; N, 10.9. Calc. for  $C_6H_{11}NO_2$ : C, 55.8; H, 8.6; N, 10.8%). Mass spectrum (70 eV):  $m/z$  129 ( $M^+$ ), 85 ( $M^+ - 44$ ), 72 ( $Me_2NCO^+$ ), 57 ( $R'O^+$ ), 41 ( $R'^+$ ) and 28.

**Et<sub>2</sub>NC(O)OCH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub> **10**.** *n*-Decyl bromide (3.0 cm<sup>3</sup>, 3.229 g,  $1.46 \times 10^{-2}$  mol) was dissolved in thf ( $20 \text{ cm}^3$ ) and this solution was added to a thf ( $50 \text{ cm}^3$ ) suspension of **7b** (6.120 g,  $1.46 \times 10^{-2}$  mol). The reaction mixture was stirred at room temperature for 24 h under an inert gas atmosphere and then filtered. The mother-liquor and washing solutions, after collection, were evaporated *in vacuo* to give a residue from which, by fractionating on a silica gel column [2.4 cm (i.d.)  $\times$  120 cm] with light petroleum (b.p. 40–70 °C)-diethyl ether (1:1 v/v), **10** was recovered (3.41 g, 91%) (Found: C, 70.1; H, 12.2; N, 5.5. Calc. for  $C_{15}H_{31}NO_2$ : C, 70.0; H, 12.1; N, 5.4%). Mass spectrum (70 eV):  $m/z$  257 ( $M^+$ ), 242 ( $M^+ - CH_3$ ), 118 [ $Et_2NC(OH)_2^+$ ], 102 ( $Et_2NCO^+$ ), 85, 73 ( $Et_2NH^+$ ), 58, 43 and 29.

In a similar way other carbamates, such as  $Et_2NC(O)OME$  (87% yield),  $Me_2NC(O)OME$  (85% yield),  $Me_2NC(O)OEt$  (90% yield) and  $Me_2NC(O)OC_6H_{11}$  (90% yield) were synthesized.

**Recovery of 18-crown-6 from K(18-crown-6)X (X = Cl, Br or I).**—An aqueous solution of NaF (1 mol dm<sup>-3</sup>) was percolated through an Amberlite IRA 400 (Cl) column [1.7 cm (i.d.)  $\times$  70

cm] until chloride assay was negative or only moderately positive. After washing with water until neutral pH to eliminate excess of fluoride salt, methanol (1 l) was passed through the resin.

The salt K(18-crown-6)Br (3.40 g,  $8.87 \times 10^{-3}$  mol) was dissolved in methanol ( $100 \text{ cm}^3$ ) and this solution was charged in the column and eluted with methanol until fluoride negative assay was observed. The eluted fractions were collected and evaporated *in vacuo*. The residue was extracted with diethyl ether ( $6 \times 10 \text{ cm}^3$ ) to give pure KF, insoluble in the solvent used, and an ethereal solution which was concentrated under vacuum to  $10 \text{ cm}^3$ . By cooling to 233 K, pure crystalline 18-crown-6 was obtained which was filtered off, washed with cold pentane and dried *in vacuo*. The mother-liquors and washing solutions were concentrated again and cooled to 233 K. More crown ether was obtained (0.3 g), so that the overall mass of recovered polyether was 2.3 g, corresponding to 98% of the amount present in the starting material.

### Acknowledgements

This work was supported by Progetto Chimica Fine II, Consiglio Nazionale delle Ricerche Rome (Grant no. 212306/72/8903623 and 104308/72/8903624). Financial support from MURST (40%, 60%) and the EEC [Contract SC1.0227.C(JR)] is also acknowledged.

### References

- 1 P. Adams and F. A. Baron, *Chem. Rev.*, 1965, **65**, 567.
- 2 P. Piccardi, *Chem. Ind. (Milan)*, 1986, **68**, 108; T. Teh Wu, J. Huang, N. D. Arrington and G. M. Dill, *J. Agric. Food. Chem.*, 1987, **35**, 817; F. Rivetti, U. Romano and M. Sasselli, *US Pat.*, 4 514 339, 1985 (to ECS).
- 3 H. Babad and A. G. Zeiler, *Chem. Rev.*, 1973, **73**, 75.
- 4 W. Lorenz and I. Hamman, *Ger. Pat.*, 2258805, 1972 (to Bayer AG) (*Chem. Abstr.*, 1974, **81**, 77701); B. A. Teicher and A. C. Sartorelli, *J. Med. Chem.*, 1980, **23**, 955; F. Maurer, I. Hamman, B. Homeyer and W. Behrenz, *Eur. Pat.*, 23326, 1979 (to Bayer AG) (*Chem. Abstr.*, 1985, **95**, 43096q).
- 5 T. Hayashi, *Bull. Inst. Phys. Chem. Res. (Tokyo)*, 1932, **11**, 133; H. B. Wright and M. B. Moore, *J. Am. Chem. Soc.*, 1948, **70**, 3865; J. K. Wolfe and K. L. Temple, *J. Am. Chem. Soc.*, 1948, **70**, 1414; K. R. Zahradnich, *Chem. Tech.*, 1959, **11**, 546; J. B. Lallau, J. Masson, H. Guerin and M. F. Roger, *Bull. Soc. Chim. Fr.*, 1972, 1311; S. Theodoropoulos, *Eur. Pat.*, 62161, 1981 (to Union Carbide Corp.) (*Chem. Abstr.*, 1983, **98**, 88842h).
- 6 T. W. Martinek, *US Pat.* 3 061 637, 1958 (to The Pure Oil Co.) (*Chem. Abstr.*, 1963, **58**, 6700g).
- 7 (a) M. A. Bernard and M. M. Borel, *Bull. Soc. Chim. Fr.*, 1968, 2362; (b) D. Belli Dell'Amico, F. Calderazzo, B. Giovannitti and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1984, 647; (c) F. Calderazzo, S. Ianelli, G. Pampaloni, G. Pelizzi and M. Sperrle, *J. Chem. Soc., Dalton Trans.*, 1991, 693.
- 8 (a) J. V. Noltes, *Recl. Trav. Chim. Pays-Bas*, 1965, **84**, 126; (b) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, 1974, **96**, 6214; (c) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, 1977, **99**, 782; (d) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, 1977, **99**, 792; (e) H. Noth and D. Schlosser, *Chem. Ber.*, 1988, **121**, 1715.
- 9 H. Ito and T. Ito, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 1755; R. L. Cowan and W. C. Troglor, *Organometallics*, 1987, **6**, 2451.
- 10 (a) R. H. Cragg and M. F. Lappert, *J. Chem. Soc.*, 1962, 82; (b) H. Brederweld, *Recl. Trav. Chim. Pays-Bas*, 1962, **81**, 276; (c) G. Oertel, H. Malz and H. Holtschmidt, *Chem. Ber.*, 1963, **97**, 891; (d) T. A. Georges, K. Jones and M. F. Lappert, *J. Chem. Soc.* 1965, 2157; (e) M. F. Lappert and B. Prokay, *Adv. Organomet. Chem.*, 1967, **5**, 225; (f) M. R. Baudet and J. Sotge, *Bull. Soc. Chim. Fr.*, 1969, 1356; (g) R. F. Dalton and K. Jones, *J. Chem. Soc. A*, 1970, 590; (h) J. Koretsu and Y. Ishii, *J. Chem. Soc. C*, 1971, 511; (i) L. K. Peterson and K. I. Thé, *Can. J. Chem.*, 1972, **50**, 562.
- 11 Y. Yoshida and S. Inoue, *J. Chem. Soc., Perkins Trans 1*, 1979, 3146; F. Kojima, T. Aida and S. Inoue, *J. Am. Chem. Soc.*, 1986, **108**, 391.
- 12 Y. Sasaki and P. H. Dixneuf, *J. Org. Chem.*, 1987, **52**, 314; R. Mahé, Y. Sasaki, C. Bruneau and P. H. Dixneuf, *J. Org. Chem.*, 1989, **54**, 1518; T. J. Kim, K. H. Kwon, S. C. Kwon, J. O. Baeg and S. C. Shim, *J. Organomet. Chem.*, 1990, **389**, 205.

- 13 Y. Yoshida and S. Inoue, *Chem. Lett.*, 1977, 1375.
- 14 Y. Yoshida, S. Ishii and T. Yamashita, *Chem. Lett.*, 1984, 1571; Y. Hori, T. Nagano, S. Nakao, T. Fukuhara and H. Taniguchi, *Chem. Express*, 1986, 1, 224.
- 15 M. Aresta and E. Quaranta, *Ital. Pat., Appl.*, 22 740 A, 1989.
- 16 M. Aresta and E. Quaranta, *Tetrahedron*, 1992, 48, 1515.
- 17 (a) Y. Yoshida and S. Inoue, *Bull. Chem. Soc. Jpn.*, 1978, 51, 559; (b) Y. Yoshida and S. Inoue, *Polym. J.*, 1980, 12, 763.
- 18 D. Belli Dell'Amico, F. Calderazzo and U. Giurlani, *J. Chem. Soc., Chem. Commun.*, 1986, 1000.
- 19 T. Tsuda, K. Watanabe, K. Miyata, H. Yamamoto and T. Saegusa, *Inorg. Chem.*, 1981, 20, 2728.
- 20 Y. Yoshida, S. Ishii, A. Kawato, T. Yamashita, M. Yano and S. Inoue, *Bull. Chem. Soc. Jpn.*, 1988, 61, 2913.
- 21 M. Aresta and E. Quaranta, *J. Org. Chem.*, 1988, 53, 4153.
- 22 M. Aresta and E. Quaranta, *Ital. Pat.*, 1 198 206, 1988.
- 23 R. W. Light, R. T. Hutchins, R. T. Paine and C. F. Campana, *Inorg. Chem.*, 1980, 19, 3597.
- 24 M. Aresta, D. Ballivet-Tkatchenko, M. C. Bonnet, R. Faure and H. Loiseleur, presented at the NATO-ASI Summer School on Carbon Dioxide, Pugnochiuso (Italy), 1986.
- 25 M. Oki and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, 1971, 44, 3148; S. Yamagami, T. Say and N. Takao, *Aust. J. Chem.*, 1987, 40, 2005.
- 26 M. G. Thomas, C. W. Schultz and R. W. Pory, *Inorg. Chem.*, 1977, 16, 994.
- 27 K. I. Thé, L. Vande Griend, W. A. Whitla and R. G. Cavell, *J. Am. Chem. Soc.*, 1977, 99, 7379; R. G. Cavell and L. Vande Griend, *Inorg. Chem.*, 1983, 22, 2066.
- 28 D. G. Gorenstein, *Prog. Magn. Reson.*, 1983, 16, 1.
- 29 M. Aresta, M. De Fazio and P. Bruno, *Inorg. Chem.*, 1982, 21, 441.
- 30 N. Yamazaki, T. Tomioka and F. Higashi, *Synthesis*, 1975, 6, 384.
- 31 (a) F. A. Cotton and G. W. Wilkinson, *Chimica Inorganica*, Ambrosiana, Milan, 2nd Ital. edn., 1974, p. 121; (b) S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole and J. C. McCoubrey, *Q. Rev. Chem. Soc.*, 1963, 17, 213.
- 32 C. S. Dean and D. S. Tarbell, *J. Org. Chem.*, 1971, 36, 1180.
- 33 A. Belforte and F. Calderazzo, *J. Chem. Soc., Dalton Trans.*, 1989, 1007.
- 34 *Handbook of Chemistry and Physics*, ed. R. C. Weast, The Chemical Rubber Co., Cleveland, 49th edn., 1968-1969, p. F-165.
- 35 K. H. Wong, G. Konizer and J. Smid, *J. Am. Chem. Soc.*, 1970, 92, 666.
- 36 V. Rubio and S. Grisolia, *Enzyme*, 1981, 26, 233.
- 37 P. McIntire and M. Hoogenraad, *FEBS Lett.*, 1981, 135, 65.
- 38 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, 89, 7017.
- 39 J.-M. Lehn, J. P. Sauvage and B. Dietrich, *J. Am. Chem. Soc.*, 1970, 92, 2916; J.-M. Lehn, J. P. Sauvage and B. Dietrich, *Chem. Commun.*, 1971, 440.
- 40 J. G. Smith and M. H. Hanson, *J. Org. Chem.*, 1971, 36, 1931.
- 41 D. Knausz, A. Meszticzky, L. Szakács, B. Csákvári and K. Ujszászy, *J. Organomet. Chem.*, 1983, 256, 11.
- 42 S. Ram and R. E. Ehrenkauf, *Tetrahedron Lett.*, 1985, 26, 5367.
- 43 M. Aresta and E. Quaranta, *Tetrahedron*, 1991, 47, 9489.
- 44 R. G. Pearson (Editor), *Hard and Soft Acids and Bases*, Hutchinson and Ross, Inc., Dowden, 1973.
- 45 G. Schrader, in *Methoden der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, 1963, XII/2, p. 808.
- 46 H. H. Sisler and N. L. Smith, *J. Org. Chem.*, 1961, 26, 611.
- 47 R. Schmutzler, *Inorg. Chem.*, 1964, 3, 415.

Received 16th December 1991; Paper 1/06286G