

## Formation of Alkylurethanes from Carbon Dioxide by Regioselective *O*-Alkylation of Alkali-metal *N,N*-Diethylcarbamates in the Presence of Complexing Agents

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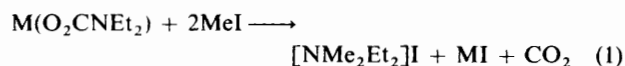
Alkali-metal *N,N*-diethylcarbamates [M(O<sub>2</sub>CNEt<sub>2</sub>); M = Li, Na, or K] undergo *N*-alkylation with MeI, giving tertiary amine and carbon dioxide, in addition to MI; however, *O*-alkylation with formation of alkylurethane occurs preferentially in the presence of a polyfunctional complexing agent.

One of the main goals in carbon dioxide chemistry is its incorporation into organic substrates.<sup>1</sup> This process may involve the formation of C-CO<sub>2</sub>,<sup>2</sup> O-CO<sub>2</sub>,<sup>3</sup> or N-CO<sub>2</sub><sup>4</sup> bonds. Prior co-ordination of carbon dioxide to a metal cation as the dialkylcarbamato group, [M(O<sub>2</sub>CNR<sub>2</sub>)<sub>n</sub>]<sub>m</sub><sup>5,6</sup> may accomplish the two-fold objective of stabilizing carbon dioxide as an O donor and promote its reactivity towards electrophiles. In several earlier papers<sup>5</sup> we dealt with the preparation of transition-metal carbamates, and we have recently shown<sup>6</sup> that this bonding situation may lead to electrophilic attack by acyl chlorides at the carbamato oxygen, with formation of the otherwise difficult to synthesize<sup>7</sup> mixed carboxylato-carbamato anhydrides.

The reaction of alkyl halides with metal carbamates may occur at the N or O end of the carbamato function, giving tertiary amine and CO<sub>2</sub> or alkylurethane, respectively. Alkylation of transition-metal carbamates leads to no reaction or to *N*-alkylation in all cases studied so far.<sup>5c,8</sup> On the other hand, the literature reports a few cases of *O*-alkylation, namely for solutions of ammonium<sup>9</sup> and copper(I)<sup>10</sup> carbamates. Also it is noted that an aluminium(III)-porphyrinato-carbamato complex<sup>4a</sup> catalyzes the addition of ethylene oxide to give an hydroxyurethane. In an attempt to understand this intriguing difference in reactivity, we have investigated the reaction of MeI with alkali-metal *N,N*-diethylcarbamates.

### Results and Discussion

Alkali-metal carbamates were found to be *N*-alkylated, see equation (1).



Following the idea that the nucleophilic activation of the carbamato group at its O terminus would be an essential

† Diethylcarbamates have been used in this study in order to compare our data with those reported in the literature,<sup>4a,9</sup> mostly dealing with the same type of product. Also it should be noted that the equilibrium  $2\text{NHEt}_2 + \text{CO}_2 \rightleftharpoons [\text{NH}_2\text{Et}_2]^+ [\text{O}_2\text{CNEt}_2]^-$  is almost completely shifted to the right.<sup>5b</sup>

**Table.** Reaction of alkali-metal carbamates M(O<sub>2</sub>CNEt<sub>2</sub>) with MeI, see reaction (2) in the text

M	Macrocycle	Solvent	Et <sub>2</sub> NCO <sub>2</sub> Me, yield (%)	
Li	None	n-Heptane	<i>b</i>	
		Toluene	<i>b</i>	
		Thf	<i>b</i>	
		MeOH	<i>b</i>	
Na	15-Crown-5 <sup>c</sup>	Thf	<i>b</i>	
		n-Heptane	<i>b</i>	
		Toluene	<i>b</i>	
K	None	Thf	<i>b</i>	
		n-Heptane	<i>b</i>	
	Dibenzo-18-crown-6 <sup>d</sup>	Toluene	<i>b</i>	
		Thf	<i>b</i>	
	Kryptofix 2.2.2 <sup>e</sup>	Toluene	30	
		Thf	81	
	Dibenzo-18-crown-6 <sup>d</sup>	None	n-Heptane	<i>b</i>
			Toluene	<i>b</i>
Kryptofix 2.2.2 <sup>e</sup>		Thf	<i>b</i>	
		Thf	81	
Kryptofix 2.2.2 <sup>e</sup>	None	Toluene	47	
		Thf	76	
Kryptofix 2.2.2 <sup>e</sup>	None	Toluene	81	
		Thf	86	

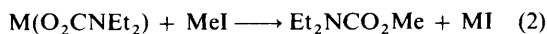
<sup>a</sup> All runs were carried out at room temperature; yields are spectroscopic; thf = tetrahydrofuran. <sup>b</sup> In this case the ammonium salt was isolated, see equation (1), and identified by i.r. and <sup>1</sup>H n.m.r. spectra. No diethylurethane was detected spectroscopically. <sup>c</sup> 15-Crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane. <sup>d</sup> Dibenzo-18-crown-6 = 6,7,9,10,17,18,20,21-octahydrodibenzo[*b,k*]-1,4,7,10,13,16-hexaoxa-cyclo-octadecane. <sup>e</sup> Kryptofix 2.2.2 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

prerequisite for yielding alkylurethanes, we have investigated the effect of a complexing agent on the reaction of alkali-metal diethylcarbamates with MeI.†

In the presence of a crown ether or a cryptand a striking change in reactivity was found, with predominant formation of alkylurethanes, see equation (2) and the Table.‡ The complexing agent, by spreading the positive charge, decreases the charge

‡ While this work was in progress, we learned that carbamato group transfer from phosphorus in (R<sub>2</sub>N)P(O<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub> to alkyl halides is assisted by an alkali metal cation and a crown ether. We thank Professor Michele Aresta for a copy of his paper prior to publication.<sup>11</sup>

density of the alkali-metal cation and its polarizing power, thus enhancing the nucleophilicity of the carbamate group.\*



The present results may help in developing a general pattern for the reactions of metal carbamates with electrophiles. Reaction (1) is presumably thermodynamically favoured with respect to (2);† however, *N*-alkylation has always been found to be slow,<sup>8</sup> presumably due to lone pair delocalization, as evidenced by the substantially planar arrangement of the O<sub>2</sub>CN system.<sup>5</sup> Reaction (1) can become relatively unimportant by localizing negative charge on the *O*-ending of the carbamate group.

### Experimental

All the operations concerning the preparation and reactivity of metal carbamates were performed under carbon dioxide or dinitrogen atmospheres. Solvents were dried by conventional methods; diethylamine was distilled from sodium and stored over sodium sand; methyl iodide was distilled from P<sub>4</sub>O<sub>10</sub>. The complexing agents used in this work were Fluka products vacuum dried before use.

*Synthesis of Alkali-metal N,N-Diethylcarbamates.*—These products were prepared by reacting the metal with a toluene solution containing an excess of diethylamine and saturated with CO<sub>2</sub>.<sup>17</sup> The reaction flask was heated to 50 °C until all the metal had disappeared, and the carbamate was obtained as a colourless, hygroscopic solid after evaporation of the solvent and drying *in vacuo*. The products are insoluble in ethers or hydrocarbons but soluble in the presence of excess amine or in strongly polar solvents such as methanol or dimethylformamide. Percentage yields and analytical data (CO<sub>2</sub> content as determined by the amount of gas evolved after decomposition with 20% H<sub>2</sub>SO<sub>4</sub>) are as follows (calculated values for C<sub>5</sub>H<sub>10</sub>MNO<sub>2</sub> in parentheses): Li, 49, 35.1 (35.8); Na, 62, 31.5 (31.5); K, 90, 26.9 (28.4). All these compounds showed the characteristic i.r. absorptions (Nujol) between 1 600 and 1 400 cm<sup>-1</sup> due to the carbamate group.

*Reactions with MeI.*—All reactions were carried out in a similar manner; allowing the metal carbamate to react with a

\* One of the referees suggested that, in the absence of added complexing agent, *O* alkylation may be hampered by the formation of polynuclear aggregates. High nuclearity has indeed been observed both in crystals and in solutions of transition-metal carbamates,<sup>5</sup> and can reasonably be suggested for the alkali-metal derivatives also. The drift of electron density from the oxygen to the metal (and the corresponding lower nucleophilicity) will, however, take place regardless of the aggregation state.

† By considering that the enthalpy change for reaction (1) is the sum of the enthalpy changes for reactions (2) and (3), there is little doubt that



alkylurethanes are kinetically controlled products. An approximate calculation for the reaction  $H_2NCO_2Me_{(l)} + MeI_{(l)} \longrightarrow NH_2Me_2I_{(s)} + CO_{2(g)}$  gives an enthalpy change  $\Delta H^\ddagger = -8.8$  kcal/mol<sup>-1</sup>. [ $\Delta H^\ddagger = \Delta H^\ddagger_f(CO_2)^{12} + \Delta H^\ddagger_f(NH_2Me_2I) - \Delta H^\ddagger_f(H_2NCO_2Me) - \Delta H^\ddagger_f(MeI)^{12} \cong (-94.0 - 37.1 + 119 + 3.3)$  kcal/mol<sup>-1</sup>.  $\Delta H^\ddagger_f(NH_2Me_2I) \cong \Delta H^\ddagger_f(NHMe_2)^{12} + \Delta H^\ddagger_f(HI)^{12} + d.e.(HI)^{13} + i.p.(H)^{13} + e.a.(I)^{13} + p.a.(NHMe_2)^{14} + U_0(NMe_2I)^{13} = (-4.5 + 6.3 + 71.4 + 313.5 - 70.8 - 223 - 130)$  kcal/mol<sup>-1</sup>. (d.e. = dissociation energy; i.p. = ionization potential; e.a. = electron affinity; p.a. = proton affinity; U<sub>0</sub> = lattice energy). The  $\Delta H^\ddagger_f(H_2NCO_2Me)$  value was estimated from the reported value for the corresponding ethyl derivative,<sup>12</sup> corrected for the group contribution.<sup>15</sup> To the best of our knowledge, the reaction of alkylurethanes with RX has not been reported, and alkylurethanes react with the strong electrophiles RCOX only at high temperature.<sup>16</sup>

five- to ten-fold excess of MeI at room temperature. A typical example is described below.

A Schlenk tube containing Kryptofix 2.2.2 (161 mg, 0.42 mmol) was carefully evacuated and filled with dinitrogen. Then K(O<sub>2</sub>CNEt<sub>2</sub>) (66 mg, 0.42 mmol) and tetrahydrofuran (15 cm<sup>3</sup>) were added, and the mixture stirred until all the solid had dissolved. Then MeI (0.3 cm<sup>3</sup>, 4.82 mmol) was added, and the ready formation of a colourless precipitate was observed. After 15 h the i.r. spectrum of the reaction mixture showed, in the region 2 500—1 500 cm<sup>-1</sup>, only the band at 1 710 cm<sup>-1</sup> due to Et<sub>2</sub>NCO<sub>2</sub>Me. No variations were detected after 24 h. From the intensity of this absorption ( $\epsilon = 1\,350$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) the amount of urethane present in solution was calculated, see the Table. The colourless solid was collected by filtration, washed with *n*-pentane and dried. It was then dissolved in D<sub>2</sub>O and its <sup>1</sup>H n.m.r. spectrum showed the presence of the K c 2.2.2 cryptate.<sup>18</sup>

### Acknowledgements

The authors wish to thank the Consiglio Nazionale della Ricerche (C.N.R.), Roma Progetto Finalizzato Energetica II and Ente Nazionale Idrocarburi (E.N.I., Roma) for a post-doctoral fellowship at Scuola Normale Superiore of Pisa to A. B.; and Dr. Ugo Giurlani for carrying out some preliminary experiments.

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*Received 15th March 1988; Paper 8/01077C*