Carbon Dioxide as a Phosgene Replacement: Synthesis and Mechanistic Studies of Urethanes from Amines, CO_2, and Alkyl Chlorides[1]

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Several carbamate esters were synthesized from amines, carbon dioxide, and alkyl chlorides. The effect of added base on the yield and selectivity of carbamate ester formation was found to be highly important with the use of sterically hindered guanidine bases giving the best results. Relative rate studies were carried out giving the following order of reactivity between carbamate anions in acetonitrile with benzyl chloride giving carbamate esters: $Et_2NCO_2^- = Bu_2NCO_2^- > t\text{-}BuNHCO_2^- = CyNHCO_2^- = s\text{-}BuNHCO_2^- > PhNHCO_2^- > CyCH_2NHCO_2^- = n\text{-}octylNHCO_2^- = n\text{-}BuNHCO_2^-$. Rate studies were carried out with the diethyl, *s*-butyl, phenyl, and *n*-butyl carbamates and activation parameters were determined to be $Et_2NCO_2^-$, $\Delta H^{\ddagger} = 11.8$ kcal/mol, $\Delta S^{\ddagger} = -33$ eu; $s\text{-}BuNHCO_2^-$, $\Delta H^{\ddagger} = 12.8$ kcal/mol, $\Delta S^{\ddagger} = -33$ eu; $PhNHCO_2^-$, $\Delta H^{\ddagger} = 14.3$ kcal/mol, $\Delta S^{\ddagger} = -28$ eu; $n\text{-}BuNHCO_2^-$, $\Delta H^{\ddagger} = 23.4$ kcal/mol, $\Delta S^{\ddagger} = -3$ eu. The unusual results obtained from the use of $n\text{-}BuNHCO_2^-$ prompted further studies which showed that the rate of reaction was inversely dependent on carbon dioxide pressure (20 psig CO_2, $k = 4.84 \times 10^{-4}$ M^{-1} s^{-1}; 120 psig CO_2, $k = 1.83 \times 10^{-4}$ M^{-1} s^{-1}). Nitrogen NMR spectroscopy indicated, via a labeling study with ^{15}N amines and ^{13}C enriched carbon dioxide, the formation of a doubly inserted product from the addition of two carbon dioxides to ethylamine in acetonitrile.

Introduction

More than a billion pounds a year of polyurethanes are sold annually in the U.S., and they are used in applications in foams, coatings, adhesives, plastics, and fibers. The most important route for the synthesis of these materials utilizes phosgene/isocyanate technology, eq. 1 and 2.[2]

$$RNH_2 + Cl_2CO \rightarrow RNCO + 2\ HCl \qquad (1)$$

$$RNCO + R'OH \rightarrow RNHCO_2R' \qquad (2)$$

Because of the toxicity of these materials a significant effort has been undertaken to find new methods for making polyurethane materials.

The use of amines, carbon dioxide, and electrophilic substrates in generating urethanes has been reported in the literature.[3] This approach lies on the production of the carbamate anion from the reaction of carbon dioxide with a primary or secondary amine.

$$2\ RR'NH + CO_2 \rightleftharpoons RR'NCO_2^-\ {}^+H_2NRR' \qquad (3)$$

Use of this anion as a nucleophile with various substrates can give urethanes (albeit in moderate to low yields); however, very few reports have appeared which have addressed the issue of utilizing the carbamate anion as a nucleophile in direct substitution reactions. In one of these reports, Yoshida et. al., found that the reaction of carbamate anions (base = RR'NH) with alkyl halides gave predominately nitrogen derived products and only poor yields of carbamate esters.[4] This result may be a reflection of the poor nucleophilicity of the oxygen of the carbamate over the reactivity of the nitrogen center or a result of unfavorable equilibrium concentration of carbamate in solution. Improvements in the yields and selectivities of urethane products over amine products were reported by Hori et al. by stabilizing the carbamate anion with the use of DBU as base.[5] In this case, however, only those reactions with highly reactive electrophiles, bromides and tosylates, gave acceptable amounts of urethanes. Calderazzo, et al. has also reported the use of the carbamate as a nucleophile in reactions with methyl iodide giving methyl carbamate esters.[6] These investigators found that the use of crown ethers and cryptands in combination with carbamate anion–potassium cation systems gave good yields of urethanes. A similar approach has been looked at by Aresta and Quaranta in a recent report.[7]

We have successfully constructed carbamate products in excellent yields with virtually 100% selectivity under mild conditions from amines, carbon dioxide, and alkyl chlorides using conditions which enhance the nucleophilic nature of the oxygen center of the carbamate anion. The key to this chemistry lies in the use of sterically hindered, powerful organic bases (i.e., pentaalkylguanidines, **I**) in driving the reaction depicted in eq. 3.

In this study we will discuss the factors which govern the reactivity of various carbamates in the S_N2 reaction

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(1) A preliminary account of this work has appeared: McGhee, W. D.; Pan, Y.; Riley, D. P. *J. Chem. Soc., Chem. Commun.* **1994**, 699–700. McGhee, W. D.; Parnas, B. L.; Riley, D. P.; Talley, J. J. U.S. Patent No. 5,223,638, June 29, 1993.

(2) See Oertel, G. *Polyurethane Handbook*; Hanser Publishers: Munich, 1985.

(3) See McGhee, W. D.; Pan, Y.; Riley, D. P. *J. Chem. Soc., Chem. Commun.* **1994**, 699–700, and references given therein.

(4) Yoshida, Y.; Ishii, S.; Watanabe, M.; Yamashita, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1534–1538.

(5) Hori, Y.; Nagano, Y.; Nakao, J.; Fukuoka, T.; Taniguchi, H. *Chem. Express* **1986**, *1*, 224–227.

(6) Belforte, A.; Calderazzo, F. *J. Chem. Soc. Dalton Trans.* **1989**, 1007–1009.

(7) Aresta, M.; Quaranta, E. *J. Org. Chem.* **1988**, *53*, 4154–4156. Aresta, M.; Quaranta, E. *J. Chem. Soc., Dalton Trans.* **1992**, 1893–1899. Aresta, M.; Quaranta, E. *Tetrahedron* **1992**, *48*, 1515–1530.

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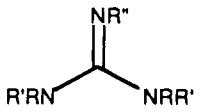
Table 1. Reaction of Carbamate Derived from RR'NH and CO_2 in the Presence of an Amidine or Guanidine Base with an Alkyl Chloride[a]

RR'NH	R''Cl	temp (°C)	% urethane GC yield	% urethane isolated yield[b]
Bu_2NH	$PhCH_2Cl$	40	95	64
Et_2NH	$PhCH_2Cl$	40	95	47
$BuNH_2$	$PhCH_2Cl$	55	95	64
s-$BuNH_2$	$PhCH_2Cl$	55	89	44
t-$BuNH_2$	$PhCH_2Cl$	55	90	41
n-$C_8H_{17}NH_2$	$PhCH_2Cl$	55	99.5	53
$CyNH_2$	$PhCH_2Cl$	55	97	50
$CyCH_2NH_2$	$PhCH_2Cl$	55	105	76
$PhNH_2$	$PhCH_2Cl$	55	90	64
Bu_2NH	BuCl	70	93.5	–
Et_2NH	BuCl	70	97	61
$BuNH_2$[c]	BuCl	85	82	71
$PhNH_2$[c]	BuCl	85	67	58
$PhNH_2$[c]	*i*-PrCl	85	54	20.5

[a] All reactions run in acetonitrile using CyTMG (*N*-cyclohexyl-*N',N',N'',N''*-tetramethylguanidine) as base under 80 psig carbon dioxide pressure with biphenyl as internal GC standard unless otherwise noted. [b] No attempt was made to optimize the isolation procedures. [c] DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) used as base.



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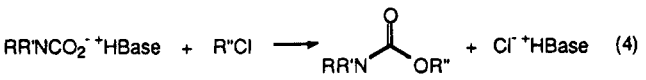
of such carbamate anions with alkyl chlorides.

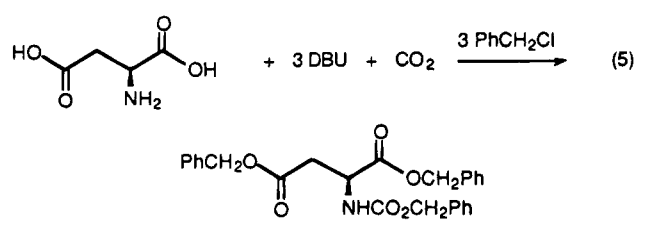


Results and Discussion

Synthesis of Carbamate Esters. We have generated several examples of carbamate esters from amines, carbon dioxide, and an alkyl chloride using amidines or most preferably guanidine bases. Examples are given showing that the reaction depicted in eq 4 is general to primary or secondary mono-, di-, or triamines and is general with a variety of alkyl chlorides giving mono-, di-, and tricarbamate esters.

Monourethanes. The results from the addition of various alkyl chlorides to carbamate anions are given in Table 1 and the details are given in the experimental section. Monourethanes produced (**1**–**14**) are unexceptional in themselves.

The use of the amino acid carbamate anion generated from aspartic acid gave the corresponding carbamate ester, **15**, in a 60% isolated yield (eq 5) with complete retention of configuration. Under the reaction conditions the carboxylate moieties were converted to their benzyl esters which was not unexpected.



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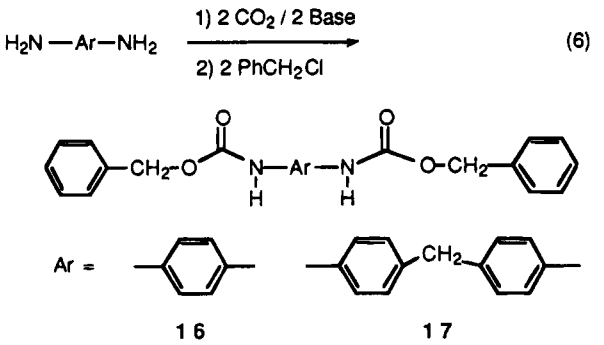
Di- and Triurethanes. O-Benzylic carbamates were generated from *p*-phenylenediamine and (methylenedi-*p*-phenylene)diamine by the addition of 2 equiv of benzyl chloride to a preformed dicarbamate salt solution (addition of 40 psig carbon dioxide to an acetonitrile solution of the diamine and CyTEG) and heating to 55 °C for 4 h (eq 6).



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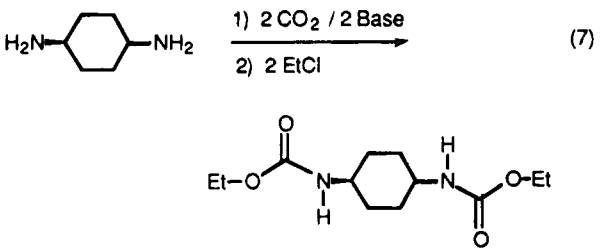
During the course of the reaction the dibenzyl carbamate precipitated from solution as a white solid. Filtration of the crude reaction mixture followed by washing the white precipitate gave dicarbamate products in good isolated yields (*p*-phenylenebis(benzyl carbamate), **16**, 70%, (methylenedi-*p*-phenylene)bis(benzyl carbamate), **17**, 50%). These compounds are high melting, sparingly soluble materials (soluble in DMSO).

Repeating the above experiment using ethyl chloride with *p*-phenylenediamine and heating to 85 °C gave the bis(ethyl carbamate) **18** in a 73% isolated yield (the bis(ethyl ester) was obtained from the crude reaction by precipitation from water, filtration, and air-drying).

Addition of ethyl chloride to a mixture of cis/trans 1,4-diaminocyclohexane under 160 psig carbon dioxide pressure in acetonitrile using a stoichiometric amount of CyTEG gave after workup (ethyl acetate/water extraction) a 60.5% isolated yield of the bis(ethyl carbamate) **19** as a white solid (eq 7).



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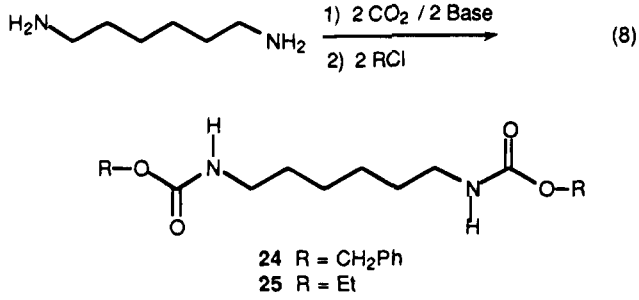
Addition of ethyl chloride to a mixture of cis/trans 1,2-diaminocyclohexane under 160 psig carbon dioxide pressure in acetonitrile using CyTEG gave after workup (ethyl acetate/water extraction) a 60% isolated yield of the bis(ethyl carbamate) **20** as a white solid.

Addition of a variety of alkyl chlorides to pregenerated solutions of the dicarbamate of 4,4'-methylenebis(cyclohexylamine) gave 70–89% isolated yields of carbamate esters **21**–**23** as white powders. Mixtures of various isomers gave rise to broad melting point ranges and complicated NMR spectra (NMR spectra included as supplementary data).

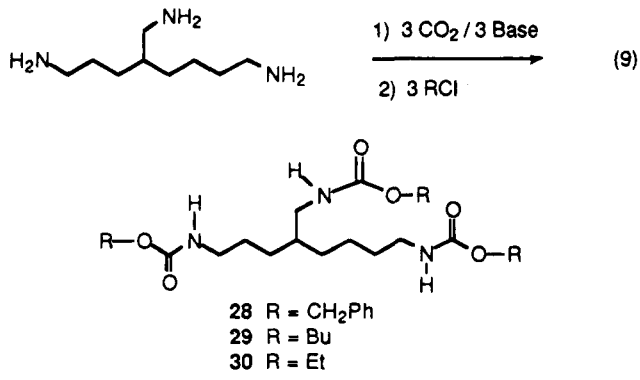
Addition of benzyl chloride (2 equiv) to an acetonitrile solution of a premade solution of the bis-carbamate of hexamethylenediamine using CyTEG as the base and heating to 59 °C gave a 63.5% yield of highly crystalline 1,6-hexamethylenebis(benzyl carbamate) (**24**) (eq 8). This material was isolated by filtration of the product from the crude reaction mixture at room temperature

(virtually insoluble in acetonitrile at room temperature). Replacement of benzyl chloride with ethyl chloride and heating to 85 °C gave a 57% isolated yield of the bis-(ethyl carbamate) **25**.



Two other primary diamines, 2-methyl-1,5-pentanediamine and 1,2-ethylenediamine were converted to their corresponding bis(benzyl carbamates) (**26** and **27**) in 67 and 55% isolated yields, respectively.

Addition of 3 equiv of benzyl chloride to an acetonitrile solution of a carbamate salt generated from 4-(aminomethyl)-1,8-diaminooctane, CyTEG, and carbon dioxide and heating to 55 °C gave 60−70% isolated yields of the corresponding tris(benzyl carbamate) **28**. This material has been successfully generated on a several pound scale with good base recovery (CyTEG, 93−95%).



The tris-butyl, **29**, and tris-ethyl, **30**, carbamate derivatives have also been generated in good isolated yields (85.5 and 60%, respectively).[8]

Dicarbamate esters were also generated by the addition of monocarbamate anions to dichloroalkanes and the results are given in the Experimental Section.

$$2\ RR'NCO_2^-\ ^+HBase + Cl\text{-}R''\text{-}Cl \rightarrow RR'NCO_2\text{-}R''\text{-}O_2NRR' + 2\ Cl^-\ ^+HBase$$

Oligo and Polycarbamate Esters. Use of dicarbamate anions with dialkyl chlorides gave oligo- and polycarbamate esters. Control of the stoichiometry of the reagents made it possible to construct oligocarbamate ester materials which had predominately chloro end groups or amine end groups. These oligocarbamate ester materials were used as prepolymers in the synthesis of segmented polyurethanes.

Mechanistic Considerations

Base Effects. Critical to the successful generation of urethanes vs amine products was found in the choice of added base. The results of the nature of added base vs yield and selectivity of urethane are shown in Table 2. It is clear that there are three distinct regimes: zero to poor yields, moderate yields and selectivities, and excellent yields and selectivities. The use of simple tertiary amines (i.e., triethylamine) gave poor conversions to urethanes which is in line with the results reported by Yoshida et al.[9] A significant increase in yield can be achieved by the use of the commercially available amidine base, DBU. Such amidine bases are well known in the organic literature as powerful organic bases yet have reportedly little nucleophilic nature. The use of DBU in increasing the yields of carbamate esters has been reported in one literature account. In this report the authors found that the use of DBU gave good yields of urethane products when relatively reactive electrophiles were used (i.e., alkyl tosylates and alkyl bromides). They reported only poor yields of urethanes, however, when alkyl chlorides were used.[10]

We have found that the greatest improvement in selectivity and yields was found by using guanidine bases.

We have shown that the best results are obtained with the use of pentaalkylguanidine bases which are relatively hindered in nature. These pentaalkylguanidines are also considerably more basic than the amidine bases and additionally they are capable of greater charge delocalization. It is this charge delocalization, we feel, that is responsible for the greater selectivity of urethane products. The use of highly polarizable counterions has been shown to increase the reactivity of various nucleophiles. The use of highly polarizable counterions is believed to

Table 2. Effect of Base on Carbamate Formation from *n*-Butylamine, Carbon Dioxide, and Benzyl Chloride[a]

base[b]	% urethane GC yield	% nitrogen derived products[c]
Proton Sponge	0	63
$BuNH_2$	2	77
PMP	7	92.5
n-BuTEG	45	24
t-BuDEF	48	34
TEG	50	17
TMG	62	22
DBU	69	18
MTDB	86	14
t-BuDMA	87	18
CyTEG	92	14
t-BuTEG	92	13
CyTMG	94	9
CyTBG	97	6

[a] All reactions run at 55 °C under 80 psig carbon dioxide pressure and run to completion based on butylamine. GC yields determined using biphenyl as internal standard. [b] Proton Sponge = *N,N,N',N'*-tetramethyl-1,8-naphthalenediamine; PMP = 1,2,2,6,6-pentamethylpiperidine; *n*-BuTEG = *N*-butyl-*N',N',N'',N''*-tetraethylguanidine; *t*-BuDEF = *N-tert*-butyl-*N',N'*-diethylformamidine; TEG = *N,N,N',N'*-tetraethylguanidine; TMG = *N,N,N',N'*-tetramethylguanidine; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; MTDB = 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene; *t*-BuDMA = *N-tert*-butyl-*N',N'*-dimethylacetamidine; CyTEG = *N*-cyclohexyl-*N',N',N'',N''*-tetraethylguanidine; *t*-BuTEG = *N-tert*-butyl-*N',N',N'',N''*-tetraethylguanidine; CyTMG = *N*-cyclohexyl-*N',N',N'',N''*-tetramethylguanidine; CyTBG = *N*-cyclohexyl-*N',N',N'',N''*-tetrabutylguanidine. [c] Nitrogen derived products include, *N*-butyl-*N*-benzylamine; *N*-butyl-*N,N*-dibenzylamine and benzyl *N*-butyl-*N*-benzylcarbamate (secondary product derived from the *N*-butyl-*N*-benzylamine generated).

(8) *Chem. Abstr.* **1981**, *95*, 188072p. JP 81 61,341 (May 26, 1981 to Toray Ind., Inc.). U.S. Patent 4,314,048 (Feb. 2, 1982 to Asahi).

(9) See ref 2. In this paper typical yields of carbamate esters were reported to be 0−53%.

(10) See ref 5. In this paper the authors report a yield of 17% of butyl *N,N*-dibutylcarbamate from the reaction of dibutylamine, carbon dioxide, and DBU with butyl chloride.

Table 3. Conductance of Various Triethylammonium and *N*-Cyclohexyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidinium Ions in CH_3CN

$RR'NCO_2^-$ $BaseH^+$	$[RR'NCO_2^-]$	$[RR'NCO_2^-]^{1/2}$	conductance (μmho)	*K/c*
$Et_2NCO_2^-$ CyTMGH$^+$	0.0075	0.087	438	58.4
	0.075	0.274	1235	16.5
	0.1875	0.433	2140	11.4
	0.375	0.612	3300	8.8
	0.75	0.866	4600	6.1
$CH_3CO_2^-$ CyTMGH$^+$	0.0075	0.087	365	48.7
	0.075	0.274	1600	21.3
	0.1875	0.433	3200	17.1
	0.375	0.612	5050	13.1
	0.75	0.866	7600	10.1
n-$BuNHCO_2^-$ CyTMGH$^+$	0.0075	0.087	670	89.3
	0.075	0.274	4060	54.1
	0.1875	0.433	7010	37.4
	0.375	0.612	10170	27.1
	0.75	0.866	12230	16.3
n-$BuNHCO_2^-$ Et_3NH^+	0.0075	0.087	45	6.0
	0.075	0.274	305	4.1
	0.15	0.387	520	3.5
	0.75	0.866	1600	2.1

increase ionic separation in solution giving "naked" anions. The concept of "naked" anions is not new and has been used to increase the nucleophilic nature of the acetate anion and of the fluoride anion primarily by the use of crown ethers and cryptands.[11] In solvents such as acetonitrile (highly polar aprotic solvent capable of good cation solvation and poor interaction with anions) high rates of substitution reactions have been observed.[12]

In the present case of the carbamate anion greater ionic separation frees the oxygen center of the carbamate anion for reactions with electrophiles. The guanidinium ion is ideal as it is capable of distributing the positive charge through four atoms.

This ionic separation, therefore, lowers the cation's coulombic interaction with the anionic carbamate. This interaction is further reduced by introducing steric hindrance into the guanidinium ion. In terms of a ground state energy argument this increased charge separation raises the ground state energy of the anion; therefore, increasing its reactivity. In systems with poor ionic separation (use of simple trialkylamines) the reactivity of the oxygen center is tempered. Again in terms of ground state energies the tight ion pair lowers the ground state energy of the ion pair and therefore lowers the reactivity of the anion. The reactivity of the nitrogen center (neutral) is not affected to a great extent by the nature of the counterion (assuming steric effects are negligible) and its reactivity, and therefore selectivity is based on relative differences between its ground state energy and that of the oxygen center (as a tight ion pair or solvent separated). The choice of a pentaalkylguanidine therefore serves several purposes: the high basicity[13] of the guanidine drives the equilibrium reaction of the amine with carbon dioxide toward formation of the carbamate anion; the high polarizability and steric hindrance of the resultant guanidinium cation increases ionic separation in solution thereby making the oxygen center of the carbamate more reactive, and the pentaalkyl system increases the solubility of the carbamate salt in aprotic solvents.

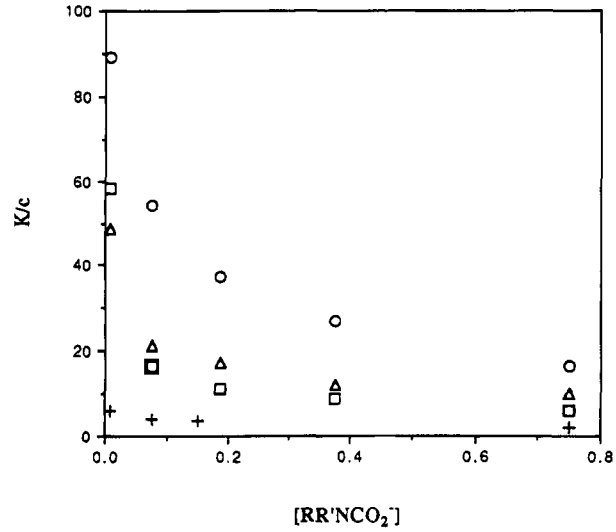


Figure 1. Results of conductance study of various carbamate salts generated *in situ*: (○) *n*-$BuNHCO_2^-$ $^+$HCyTMG; (□) $Et_2NCO_2^-$ $^+$HCyTMG; (△) $CH_3CO_2^-$ $^+$HCyTMG; (+) *n*-$BuNHCO_2^-$ $^+$HEt$_3$N.

Conductivity studies over the range of concentrations used in our studies clearly shows the difference in ionic separation between those anions generated from trialkylamines and guanidines which is in agreement with the above arguments. The results of the conductivity studies are given in Table 3 and Figure 1.

Relative Rates. During the course of our studies we recognized that the time required to convert primary amines to their corresponding carbamate esters differed significantly from that required for secondary amines. For this reason we undertook a study of the relative rates of reaction of various carbamate anions in direct competition studies with benzyl chloride as the electrophile. We chose to set up the competition studies under conditions where the carbamate nucleophiles were equal in concentration and in large excess over the concentration of benzyl chloride. All comparative results are based on calculated GC yields and yields of carbamate esters were >95% in all cases. The results of these studies are given in Figure 2. The difference in reactivity between carbamates derived from amines such as diethylamine and cyclohexylamine are not unexpected. Surprisingly, we saw a large difference in reactivity between primary amines attached to secondary alkyl groups (i.e., cyclo-

(11) See Liotta, C. L.; Grisdale, E. E.; Hopkins, H. P. *Tetrahedron Lett.* **1975**, *48*, 4205–4208 and references given therein.

(12) An excellent description of solvent effects in S_N2 type reactions is given in: Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH, New York, 1988.

(13) See Schwesinger, R. *Chimia* **1985**, *39*, 269. Leffek, K. T.; Pruszynski, R.; Thanapaalasingham, K. *Can. J. Chem.* **1989**, *67*, 590–595. Boyle, P. H.; Convery, M. A.; Davis, A. P.; Hosken, G. D.; Murray, B. A. *J. Chem. Soc., Chem. Commun.* **1992**, 239–242.

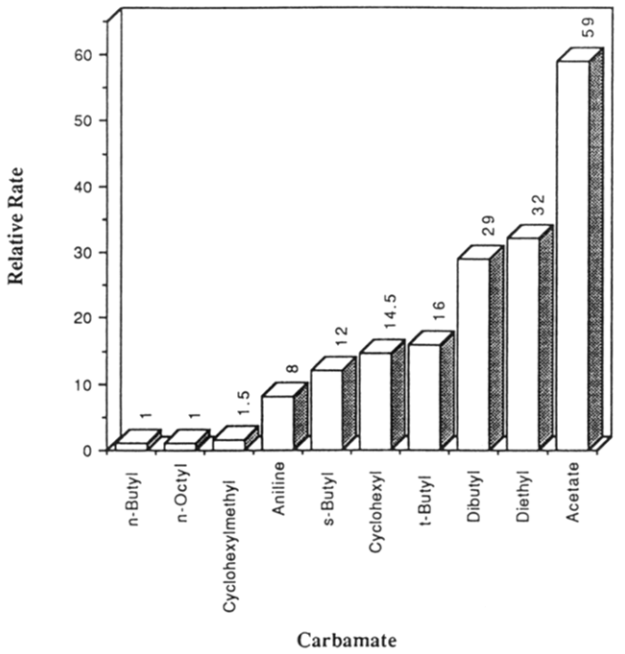


Figure 2. Relative rate between various carbamate anions in reaction with benzyl chloride in acetonitrile.

Table 4. Effect of Concentration of Carbamate Anion on Rate of Reaction with Benzyl Chloride in Acetonitrile[a]

$[RR'NCO_2^-]$	$Et_2NCO_2^- \times 10^4$	$s\text{-}BuNHCO_2^- \times 10^4$	$n\text{-}BuNHCO_2^- \times 10^4$
0.75	33.5	8.33	1.83
0.375	17	4.13	0.87
0.1875	7.55	1.95	0.51
0.0938	3.98	1.02	0.25

[a] All reactions run under 80 psig carbon dioxide pressure at 50 °C using biphenyl as internal GC standard.

hexyl and *sec*-butyl) and those attached to primary centers (i.e. *n*-butyl- and *n*-octylamine). In light of this surprising difference and its implications in the synthesis of materials based on feedstocks such as 1,6-hexamethylenediamine, we took a more detailed look at the rate of reaction of several carbamate anions.

Rate Studies. For three model systems (representing three distinct types of carbamates) diethyl, *sec*-butyl, and *n*-butyl we first determined that the reaction was first order in carbamate anion, and the results are given in Table 4 and Figure 3. In all cases excellent first order decay of benzyl chloride was observed (all reactions run under pseudo first order conditions with an excess of carbamate anion) along with good first order appearance of carbamate esters. The difference in calculated second order rates between these carbamates is in reasonable agreement with the relative rate results given above.

For each of these three systems and for the reaction with the carbamate derived from aniline we experimentally determined the activation parameters by the standard Arrhenius plot method. The results of this study are shown in Tables 5 and 6 and Figure 4. The results from the reactions with the diethyl, aniline, and *sec*-butyl carbamates are not unexpected for S_N2 type reactions.[14] Large negative entropy values are indicative of a transition state containing more order than the reactants in the ground state. This increase in order is consistent with a S_N2 transition state where two molecules come

(14) See ref 12, Chapter 5, for a detailed discussion of transition state theory.

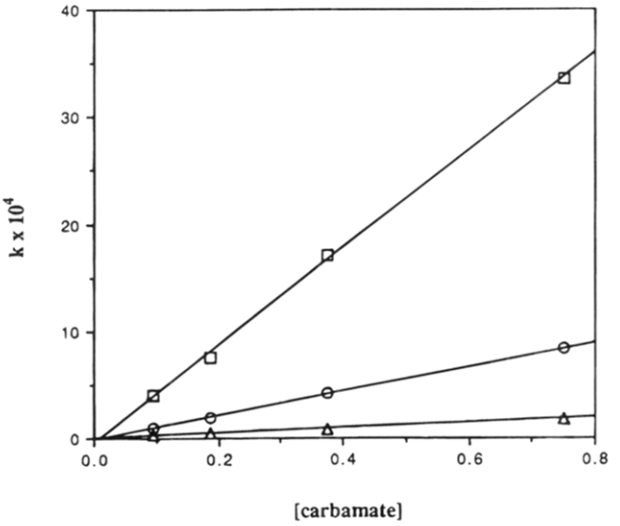
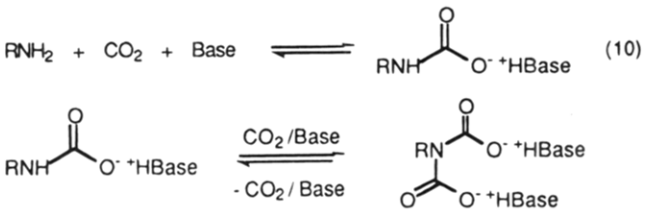


Figure 3. Rate dependence of [carbamate anion] in reaction with benzyl chloride in acetonitrile: (□) $Et_2NCO_2^-$ $^+$HCyTMG; (○) $s\text{-}BuNHCO_2^-$ $^+$HCyTMG; (△) $n\text{-}BuNHCO_2^-$ $^+$HCyTMG.

together to form a single complex. The results for the *n*-butyl carbamate are not consistent with this concept ($\Delta H^\ddagger = 23.4$ kcal/mol; $\Delta S^\ddagger = -3$ eu). The small entropy effect is more consistent with no change in order and is not in line with the results obtained with the other carbamate anions.

Further insight into this unusual difference in reactivity was gained by an investigation of the dependence of rate on carbon dioxide pressure, see Table 7. The results of this study were also somewhat surprising. With *n*-butyl carbamate the rate of reaction significantly decreased with an increase of carbon dioxide pressure (20 psig, $k = 4.84 \times 10^{-4}$ M^{-1} s^{-1}; 120 psig, $k = 1.83 \times 10^{-4}$ M^{-1} s^{-1}). We postulate that this affect is due to the involvement of a second equivalent of carbon dioxide with the carbamate which lowers the reactivity of the oxygen of the carbamate anion. One possible explanation which would account for this effect may involve a reversible insertion of a second equivalent of carbon dioxide into the remaining N−H giving a dianion as shown below in eq 10.



This carbon dioxide experiment is consistent with the experimentally obtained activation parameters. The involvement of an extra mole of carbon dioxide, which must be expelled at some point along the reaction profile, could explain the entropy term obtained from the Arrhenius plot.

NMR Experiments. We probed the possibility of the interaction of a second equivalent of carbon dioxide by a spectroscopic investigation of the nature of various carbamates generated *in situ*. In order to determine the viability of possible double carbon dioxide insertion, eq 10, we looked at the ^{15}N NMR of the result of the addition of $^{13}CO_2$ to $Et^{15}NH_2$, $Cy^{15}NH_2$, $Ph^{15}NH_2$, and $Et_2{}^{15}NH$. The spectra obtained (at −30 °C in CD_3CN with CD_3CN used as internal reference) for the $Et^{15}NH_2/^{13}CO_2$ experiment

Table 5. Calculated Second Order Rate Constants for the Reaction of Amines, Carbon Dioxide, and CyTMG with Benzyl Chloride[a]

temp (K)	$Et_2NCO_2^-$ × 10^4	s-$BuNHCO_2^-$ × 10^4	n-$BuNHCO_2^-$ × 10^4	$PhNHCO_2^-$ × 10^4
303	12.5	2.94	–	–
308	17.3	3.6	–	–
313	22.9	5.60	0.747	4.98
318	32.6	7.64	1.39	7.2
323	45.2	11.0	2.32	10.2
328	–	15.1	–	15.1
330	–	–	5.82	–
333	–	20.6	–	21.1
339	–	–	14.1	–

[a] All reactions run in acetonitrile under 80 psig carbon dioxide.

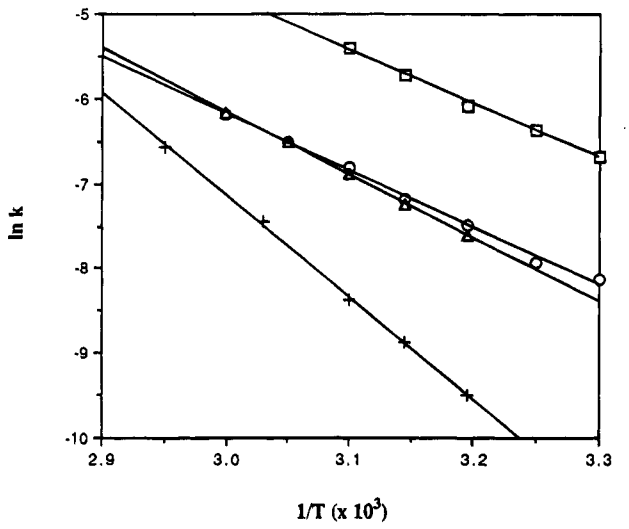


Figure 4. Arrhenius plot for reaction of carbamate anion with benzyl chloride in acetonitrile: (□) $Et_2NCO_2^-$ $^+$HCyTMG; (○) s-$BuNHCO_2^-$ $^+$HCyTMG; (△) $PhNHCO_2^-$ $^+$HCyTMG; (+) n-$BuNHCO_2^-$ $^+$HCyTMG.

Table 6. Calculated Activation Parameters for Reaction of Carbamate Anions with Benzyl Chloride in Acetonitrile

nucleophile	E_a (kcal/mol)	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (eu)
$Et_2NCO_2^-$	12.4	11.8	−33
s-$BuNHCO_2^-$	13.4	12.8	−33
n-$BuNHCO_2^-$	24	23.4	−3
$PhNHCO_2^-$	14.9	14.3	−28

is shown in Figure 5 and a summary of all the results is given in Table 8.

The appearance of a triplet centered at δ 129.1 ppm in the ^{15}N NMR of the product of the addition of $^{13}CO_2$ to $Et^{15}NH_2$ with 2 equiv of CyTMG suggests the formation of $Et^{15}N(^{13}CO_2)_2^{2-}$ $(^+HCyTMG)_2$ with J_{N-C} = 15.2 ppm. The appearance of a doublet at δ 87.6 ppm and 109.1 for the addition of $^{13}CO_2$ to $Et_2{}^{15}NH$ and $Ph^{15}NH_2$, respectively, with CyTMG as base indicates the generation of $Et_2{}^{15}N^{13}CO_2^-$ $^+$HCyTMG with J_{N-C} = 19.3 Hz and $Ph^{15}NH^{13}CO_2^-$ $^+$HCyTMG with J_{N-C} = 17.1 Hz (with aniline there is no observable evidence for the generation of the doublely inserted product; $Ph^{15}N(^{13}CO_2)_2^{2-}$.) With $Cy^{15}NH_2$ both species, $Cy^{15}NH^{13}CO_2^-$ $^+$HCyTMG and $Cy^{15}N(^{13}CO_2)_2^{2-}$ are observable, and the ratio of the two is highly dependent on the temperature at which the spectra were obtained.

Conclusions and Implications

The results of the rate studies with benzyl chloride as the electrophile and the NMR evidence for the *in situ* generation of the dianion resulting from the addition of carbon dioxide to primary amines with primary alkyl substituents (i.e. ethyl amine, n-butylamine) using strong non-nucleophilic bases such as CyTMG indicate a strong effect in the ability of these carbamates to act as nucleophiles in substitution reactions.

With regard to the practical use of this technology in the synthesis of urethane materials from various amine feed stocks certain factors must be considered. The nature of the amine, i.e. a primary amine attached to a primary alkyl center, a primary amine attached to a secondary or tertiary alkyl center, a secondary amine, or an aromatic amine, must be looked at with caution and the results described in the present study on model systems must be taken into account.

Experimental Section

Materials. Amines used in this account were obtained either from Aldrich Chemical Co. or Kodak Chemical Co. and were used as received or distilled from KOH prior to use. Anhydrous solvents under nitrogen were purchased from Aldrich Chemical Co.; pentaalkylguanidines were synthesized according to literature procedure.[15] Carbon dioxide was supplied from Acetylene Gas Co. (welding grade) and used without any further purification. $^{13}CO_2$ was supplied by Isotec Inc. $Et_2{}^{15}NH$·HCl, $Et^{15}NH_2$·HCl, and $Ph^{15}NH_2$ were supplied by MSD Isotopes. $Cy^{15}NH_2$ was obtained by catalytic reduction of $Ph^{15}NH_2$.[16]

Analytical. Gas chromatographic analysis was performed on a Varian Model 3400 gas chromatograph with a Model 8000 auto sampler using a 30 m Megabore DB-1 (3 μm) J & W Scientific column. Nuclear magnetic resonance spectra were obtained on Varian VXR-300, VXR-400, or UNITY-400 spectrometers. Infrared spectra were obtained on a Nicolet FT-IR. Conductivity results were obtained using a Model 31A conductance bridge and a Model 3403 (cell constant = 1.0/cm) cell obtained from YSI. Elemental analysis was performed by Galbraith Laboratories Inc.

Phenylmethyl Dibutylcarbamate (1). A Fischer-Porter bottle was charged with 2.58 g (0.02 mol) dibutylamine, 3.94 g (0.02 mol) *N*-cyclohexyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidine, 154 mg (0.001 mol) of biphenyl as internal GC standard, and 20 mL of CH_3CN. The Fischer-Porter bottle was attached to a pressure head and at room temperature with stirring was added 80 psig carbon dioxide. Addition of CO_2 resulted in an exothermic reaction with a rise in temperature to ca. 40 °C. Into a second Fischer-Porter bottle was added 10.12 g (0.08 mol) of benzyl chloride in 10 mL of CH_3CN. This mixture was attached to a pressure head, and 80 psig carbon dioxide was added above the solution. After 1 h the benzyl chloride solution was added all at once under 80 psig CO_2 to the preformed carbamate anion solution generated in the first Fischer-Porter bottle. After addition the reaction mixture was warmed to 40 °C for 3 h. After this time the reaction mixture was allowed to cool to room temperature and then the pressure was released. An aliquot was taken and diluted with diethyl ether, Cl^- $^+$HCyTMG precipitated from solution and was

(15) Bredereck, H.; Bredereck, K. *Chem Ber.* **1961**, *94*, 2278–2295.
(16) Catalytic reduction carried out by Dr. Thomas Waldman.

Table 7. Rate Dependence on Carbon Dioxide Pressure for Reaction of Amine, CO_2, and CyTMG with Benzyl Chloride in CH_3CN[a]

CO_2 (psig)	$Et_2NCO_2^-$ × 10^3	s-$BuNHCO_2^-$ × 10^3	n-$BuNHCO_2^-$ × 10^3	$PhNHCO_2^-$ × 10^3
120	3.97	0.92	0.183	1.02
80	4.53	1.10	0.232	1.28
50	5.38	1.42	0.393	–
20	4.89	1.54	0.484	1.04
20/120	1.23	1.67	2.64	1.02

[a] All reactions run at 50 °C, and rate constants are calculated second order rates from pseudo first order decay of benzyl chloride.

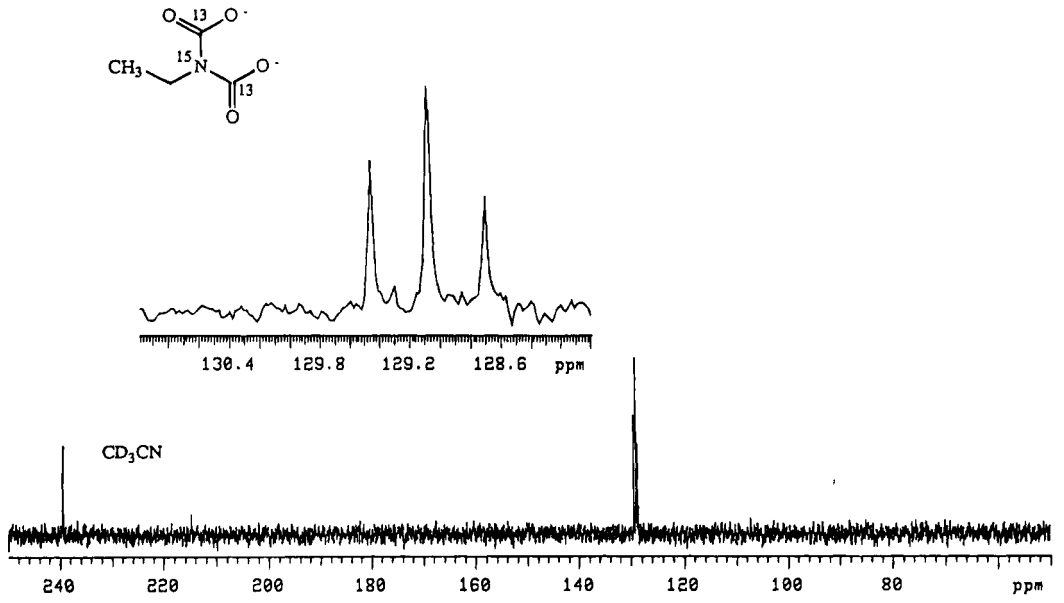


Figure 5. ^{15}N NMR of $Et^{15}NH_2/^{13}CO_2$/CyTMG in CD_3CN at −30 °C.

Table 8. NMR Results of Addition of $^{13}CO_2$ to RR'^{15}NH and CyTMG[a]

RR'^{15}N H	temp (°C)	^{15}N (ppm)	J_{N-C} (Hz)	$^{13}C\{^1H\}$ (ppm)	J_{C-N} (Hz)
diethyl	−30	87.6	19.3 (d)	161.5	19.9 (d)
aniline	−30	109.1	17.1 (d)	158.8	17.0 (d)
cyclohexyl	−30	137.1	14.5 (t)	158.5	broad
		97.5	broad	162.1	18.5 (d)
cyclohexyl	25	–	–	159.0	14.8 (d)
		95.3	18.6 (d)	162.1	18.5 (d)
ethyl	−30	129.1	15.2 (t)	158.6	15.2 (d)

[a] ^{15}N NMR chemical shifts referenced to CD_3CN at δ 239.5 ppm based on $^{15}NH_3$ δ = 0 ppm.

filtered off, and by GC analysis a 95% yield of urethane was calculated. The crude material was poured into 100 mL of ethyl acetate and extracted with 2 × 100 mL of 0.5 M aqueous HCl followed by 100 mL of brine. The organic layer was dried over Na_2CO_3, filtered, and concentrated leaving a light yellow oil. This oil was chromatographed on silica gel using first 100% hexane (to remove excess benzyl chloride and internal GC standard) and then with 100% CH_2Cl_2. The *O*-benzyl carbamate product, **1**, was isolated as a clear oil (3.38 g, 64%): oil, ^1H NMR ($CDCl_3$) δ 7.39−7.30 (overlapping m, 5H), 5.17 (s, 2H), 3.27 (br, 4H), 1.55 (br, 4H), 1.33 (br m, 4H), 0.94 (br, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.7, 137.7, 128.9, 128.3, 128.2, 67.2, (47.8, 47.2),[17] (31.4, 30.8), 20.5, 14.4; IR (film) 1703; MS (FAB) *m*/*z* = 264 (MH^+). Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.97; H, 9.57; N, 5.32. Found: C, 73.22; H, 9.35; N, 5.45.

Phenylmethyl Diethylcarbamate (2). Procedures as described in synthesis of **1**. A GC yield of 95% was calculated and a 47% isolated yield of benzyl *N*,*N*-diethyl carbamate (**2**) resulted: oil; ^1H NMR ($CDCl_3$) δ 7.35−7.25 (overlapping m, 5H), 5.12 (s, 2H), 3.29 (br q, *J* = 6.4 Hz, 4H), 1.15 (t, *J* = 6.9 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.7, 137.1, 128.4, 127.7, 127.6, 66.7, 41.6 (br), 13.8 (br); IR (film) 1700; MS (EI) *m*/*z* = 207 (M^+).

(17) Hindered rotation gives broadening of some resonances in the NMR spectra and in some cases two resolvable peaks result.

Phenylmethyl Butylcarbamate (3). Procedures as in the synthesis of **1** with the exception that the reaction was carried out at 55°C for 18 h. The *O*-benzyl carbamate product, **3**, was isolated as a clear oil (2.64 g, 64%): oil; ^1H NMR ($CDCl_3$) δ 7.40−7.34 (overlapping m, 5H), 5.14 (s, 2H), 4.9 (br s, NH), 3.21 (br q, *J* = 5.1 Hz, 2H), 1.51 (m, 2H), 1.38 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.4, 136.6, 128.4, 128.2, 127.9, 66.4, 40.7, 31.9, 19.7, 13.6; IR (film) 3337, 1701.

Phenylmethyl *sec*-Butylcarbamate (4). Procedures as described in the synthesis of **1**. A GC yield of 89% was calculated and a 44% isolated yield of benzyl N-*sec*-butylcarbamate (**4**) resulted: mp 49−50.5 °C; ^1H NMR ($CDCl_3$) δ 7.41−7.30 (overlapping m, 5H), 5.14 (s, 2H), 4.6 (br s, NH), 3.69 (m, 1H), 1.50 (quintet, *J* = 7 Hz, 2H), 1.17 (d, *J* = 6.6 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.8, 136.7, 128.4, 128.2, 127.9, 66.4, 48.4, 29.8, 20.7, 10.2; IR ($CHCl_3$) 3441, 1713; MS (EI) *m*/*z* = 207 (M^+). Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.71; H, 8.49; N, 6.87.

Phenylmethyl *tert*-Butylcarbamate (5). Procedures as described in the synthesis of **1**. A GC yield of 90% was calculated and a 41% isolated yield of benzyl *N*-*tert*-butylcarbamate (**5**) resulted: oil; ^1H NMR ($CDCl_3$) δ 7.38−7.32 (overlapping m, 5H), 5.09 (s, 2H), 4.9 (br, NH), 1.36 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.3, 137.4, 129.0, 128.6, 128.5, 66.5, 50.8, 29.5; IR (film) 3346, 1711 (literature 1710); MS (EI) *m*/*z* = 207 (M^+). Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.53; H, 8.14; N, 6.97.

Phenylmethyl Octylcarbamate (6). Procedures as described in the synthesis of **1**. A GC yield of 99.5% was calculated and a 53% isolated yield of benzyl *N*-octylbenzylcarbamate (**6**) resulted after crystallization from hexane: mp 32−33 °C; ^1H NMR ($CDCl_3$) δ 7.41−7.29 (overlapping m, 5H), 5.08 (s, 2H), 4.77 (s, N-H), 3.17 (q, *J* = 6.7 Hz, 2H), 1.48 (m, 2H), 1.26 (overlapping m, 10H), 0.87 (t, *J* = 6.7 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.4, 136.7, 128.5, 128.1, 128.0, 66.6, 41.1, 31.8, 30.0, 29.3, 29.2, 26.7, 22.6, 14.0; IR ($CHCl_3$) 3451, 1713. Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.97; H, 9.57; N, 5.32. Found: C, 72.86; H, 9.51; N, 5.63.

Phenylmethyl Cyclohexylcarbamate (7). Procedures as described in the synthesis of **1**. A GC yield of 97% was calculated and a 50% isolated yield of benzyl *N*-cyclohexylcarbamate (**7**) resulted after crystallization from hot hexane: mp 93–94.5 °C (lit. mp 93–94 °C);[18] ^{1}H NMR ($CDCl_3$) δ 7.40–7.30 (overlapping m, 5H), 5.13 (s, 2H), 4.7 (br, N-H), 3.54 (m, 1H), 1.99–1.1 (cyclohexyl, 10H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 155.5, 136.7, 128.5, 128.1, 128.0, 66.4, 49.9, 33.4, 25.5, 24.7; IR ($CHCl_3$) 3441, 1711; MS (EI) m/z = 233 (M^+). Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.45; H, 8.36; N, 5.98.

Phenylmethyl (Cyclohexylmethyl)carbamate (8). Procedures as described in the synthesis of **1**. A GC yield of 105% was calculated and a 76% isolated yield of benzyl *N*-(cyclohexylmethyl)carbamate (**8**) resulted after crystallization from hot hexane: mp 58.5–61 °C; ^{1}H NMR ($CDCl_3$) δ 7.4–7.3 (overlapping m, 5H), 5.13 (s, 2H), 4.90 (br, NH), 3.07 (t, J = 6.5 Hz, 2H), 1.8–0.9 (overlapping m, 11H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 157.1, 137.3, 129.0, 128.6, 128.5, 67.1, 47.9, 38.8, 31.2, 26.9, 26.3; IR ($CHCl_3$) 3455, 1713; MS m/z = 248 (MH^+). Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.84; H, 8.54; N, 5.63.

Phenylmethyl Phenylcarbamate (9). Procedures as described in the synthesis of **1**. A GC yield of 90% was calculated and a 64% isolated yield of benzyl *N*-phenylcarbamate (**9**) resulted after crystallization from ether/hexane: mp 79–80.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.47–7.33 (overlapping m, 8H), 7.12 (t, J = 7.3 Hz, 2H), 6.81 (br, NH), 5.25 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 153.9, 138.3, 136.6, 129.6, 129.2, 128.9, 124.1, 119.3, 67.6; IR ($CHCl_3$) 3435, 1734; MS (EI) m/z = 227 (M^+). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.84; H, 5.80; N, 6.22.

Butyl Dibutylcarbamate (10). Procedures as in the synthesis of **1**. The *O*-benzyl carbamate product, **10**, was isolated as a clear oil: ^{1}H NMR ($CDCl_3$) δ 4.08 (t, J = 6.6 Hz, 2H), 3.21 (br, 4H), 1.65–1.3 (overlapping m, 12H), 0.95 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 157.1, 65.3, 47.4 (br), 31.7, 31.2 (br), 20.5, 19.7, 14.4, 14.2; IR (film) 1703; MS m/z = 230 (MH^+).

Butyl Diethylcarbamate (11). A 160 cc stainless steal Parr autoclave was charged with 2.19 g (0.03 mol) of diethyl amine, 8.46 g (0.043 mol) of *N*-cyclohexyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidine, 310 mg (0.002 mol) of biphenyl as internal GC standard, and 25 mL of CH_3CN. The autoclave was attached to a pressure head, and at room temperature with stirring was added 160 psig carbon dioxide. Addition of CO_2 resulted in an exothermic reaction with a rise in temperature to ca. 40 °C. Into a Fischer-Porter bottle was added 8.325 g (0.09 mol) of butyl chloride in 10 mL of CH_3CN. This mixture was attached to a pressure head, and 80 psig carbon dioxide was added above the solution. After 1 h the butyl chloride solution was added all at once under 80 psig CO_2 to the preformed carbamate anion solution generated in the autoclave. After addition the pressure was raised to 160 psig with CO_2, and the reaction mixture was warmed to 70 °C for 1.5 h. After this time the reaction mixture was allowed to cool to room temperature, and then the pressure was released. An aliquot was taken and diluted with diethyl ether, $Cl^-{}^+HCyTMG$ precipitated from solution and was filtered off, and by GC analysis a 97% yield of urethane was calculated. The crude material was poured into 100 mL of ethyl acetate and extracted with 2 × 100 mL of 0.5 M aqueous HCl followed by 100 mL of brine. The organic layer was dried over Na_2CO_3, filtered, and concentrated leaving a light yellow oil. This residue was distilled under reduced pressure (ca. 3 torr) collecting the carbamate ester, **11**, at 70–71 °C (3.16 g, 61%): oil; ^{1}H NMR ($CDCl_3$) δ 4.06 (t, J = 6.5 Hz, 2H), 3.26 (q, J = 7.1 Hz, 4H), 1.61 (m, 2H), 1.37 (m, 2H), 1.10 (t, J = 7.2 Hz, 6H), 0.93 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.6, 65.3, 41.9, 31.7, 19.7, 14.2; IR (film) 1700; MS (thermal spray) m/z = 174 (MH^+). Anal. Calcd for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.08. Found: C, 61.84; H, 10.61; N, 7.97.

Butyl Butylcarbamate (12). Procedures as described in the synthesis of **11**, using 1,8-diazabicyclo[5.4.0]undec-7-ene in place of CyTMG. A GC yield of 82% was calculated and a 71% isolated yield of **12** resulted after chromatography on silica gel: oil; ^{1}H NMR ($CDCl_3$) δ 4.75 (br, N-H), 4.05 (t, J = 6.7 Hz, 2H), 3.15 (t, J = 6.9 Hz, 2H), 1.61–1.32 (overlapping m, 8H), 0.92 (t, J = 7.31 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 157.4, 65.1, 41.3, 32.6, 31.6, 20.4, 19.6, 14.2 (overlapping); IR (film) 3337, 1700; MS (thermal spray) m/z = 174 (MH^+).

Butyl Phenylcarbamate (13). Procedures as described in the synthesis of **11**, using 1,8-diazabicyclo[5.4.0]undec-7-ene in place of CyTMG. A GC yield of 67% was calculated, and a 58% isolated yield of **13** resulted after chromatography on silica gel: mp = 63.5–65 °C; ^{1}H NMR ($CDCl_3$) δ 7.44 (d, J = 8 Hz, 2H), 7.34 (t, J = 8 Hz, 2H), 7.09 (t, J = 7.3 Hz, 1H), 6.83 (br, NH), 4.22 (t, J = 6.7 Hz, 2H), 1.70 (m, 2H), 1.45 (m, 2H), 1.00 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 154.4, 138.6, 129.5, 123.8, 119.2, 65.6, 31.5, 19.6, 14.3; IR ($CHCl_3$) 3438, 1730; MS (FAB) m/z = 194 (MH^+). Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.57; H, 7.95; N, 7.29.

2-Propyl Phenylcarbamate (14). Procedures as described in the synthesis of **11**, using 1,8-diazabicyclo[5.4.0]undec-7-ene in place of CyTMG. A GC yield of 54% was calculated, and a 20.5% isolated yield of **14** resulted after chromatography on silica gel (a small amount of diphenylurea was detected by GC): mp = 88–89 °C (lit. mp = 90 °C);[19] ^{1}H NMR (CD_2Cl_2) δ 7.46 (d, J = 8.7 Hz, 2H), 7.35 (t, J = 8 Hz, 2H), 7.10 (t, J = 7.5 Hz, 1H), 6.9 (br, N-H), 5.06 (7 lines, J = 6.3 Hz, 2H), 1.34 (d, J = 6.3 Hz, 6H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 154.2, 139.4, 129.8, 124.0, 119.5, 69.5, 22.8; IR ($CHCl_3$) 3437, 1728; MS (thermal spray) m/z = 180 (MH^+). Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.35; H, 7.45; N, 7.85.

Dibenzyl N-Cbz-aspartate (15). A Fischer-Porter bottle was charged with 2.66 g (0.02 mol) of L-aspartic acid, 12.77 g (0.084 mol) of 1,8-diazabicyclo[5.4.0]undec-7-ene, and 25 mL of CH_3CN. The Fischer-Porter bottle was attached to a pressure head, and at room temperature with stirring was added 80 psig carbon dioxide. Addition of CO_2 resulted in an exothermic reaction with a rise in temperature to ca. 40 °C. Into a second Fischer-Porter bottle was added 15 g (0.12 mol) of benzyl chloride in 10 mL of CH_3CN. This mixture was attached to a pressure head, and 80 psig CO_2 was added above the solution. After 1 h the benzyl chloride solution was added all at once under 80 psig CO_2 to the preformed carbamate anion solution generated in the first Fischer-Porter bottle. After addition the reaction mixture was warmed to 55 °C for 3 h. After this time the reaction mixture was allowed to cool to room temperature and then the pressure was released. The crude material was poured into 100 mL of diethyl ether and extracted with 2 × 100 mL of 0.5 M aqueous HCl followed by 100 mL of brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The excess benzyl chloride was removed by adding hexane to the crude residue leaving a light yellow oil. Crystallization from diethyl ether/hexane gave 5.34 g (60%) of dibenzyl N-Cbz-aspartate. Product was identified by ^{1}H and ^{13}C NMR spectroscopy and was identical to authentic material: $[\alpha]^{23}_D$ = −1.8 (authentic material = −1.9). Anal. Calcd for $C_{26}H_{25}NO_6$: C, 69.77; H, 5.63; N, 3.13. Found: C, 69.35; H, 5.68; N, 2.96.

1,4-Phenylenebis(phenylmethyl carbamate) (16). A Fischer-Porter bottle was charged with 1.08 g (0.01 mol) of *p*-phenylenediamine, 6.33 g (0.025 mol) of *N*-cyclohexyl-*N'*,*N'*,*N''*,*N''*-tetraethylguanidine, and 20 mL of CH_3CN. The Fischer-Porter bottle was attached to a pressure head and at room temperature with stirring was added 40 psig carbon dioxide. Addition of CO_2 resulted in an exothermic reaction with a rise in temperature to ca. 40 °C. Into a second Fischer-Porter bottle was added 5.06 g (0.04 mol) of benzyl chloride in 10 mL of CH_3CN. This mixture was attached to a pressure head and 40 psig carbon dioxide was added above the solution. After 1 h the benzyl chloride solution was added all at once under 40 psig CO_2 to the preformed carbamate anion solution generated in the first Fischer-Porter bottle. After addition the

(18) See endnote no. 42 in: Aresta, M; Quaranta, E. *Tetrahedron* **1992**, *48*, 1515–1530.

(19) 2-Propyl phenylcarbamate is a herbicide (Propham). *The Merck Index*, 10th ed.; Windholz, M., Ed., 1983; p 1126.

reaction mixture was warmed to 55 °C for 4 h (during which time a white solid precipitated from solution). After this time the reaction mixture was allowed to cool to room temperature, and then the pressure was released. The white solid was collected by filtration and then washed with 100 mL of CH_3CN and 100 mL of diethyl ether. After being air-dried, a 70% (2.64 g) isolated yield of **16** was obtained: mp = 235–237°C; ^{1}H NMR (DMSO-d_6) δ 9.61 (s, 2H, NH), 7.4–7.3 (overlapping m, 14H), 5.11 (s, 4H). Anal. Calcd for $C_{22}H_{20}N_2O_4$: C, 70.19; H, 5.36; N, 7.45. Found: C, 69.59; H, 5.34; N, 7.27.[20]

(Methylenedi-*p*-phenylene)bis(phenylmethyl carbamate) (17). Procedures as in the synthesis of **16**. A white solid was collected by filtration and then washed with 100 mL of CH_3CN and 100 mL of diethyl ether. After being air-dried, a 50% (3.51 g) isolated yield of **17** was obtained: mp = 201–203 °C; ^{1}H NMR (DMSO-d_6) δ 9.66 (s, 2H, NH), 7.4–7.3 (overlapping m, 14H), 7.09 (d, J = 8.6 Hz, 4H), 5.12 (s, 4H), 3.78 (s, 2H); IR ($CHCl_3$) 3428, 1727. Anal. Calcd for $C_{29}H_{26}N_2O_4$: C, 74.65; H, 5.62; N, 6.01. Found: C, 74.36; H, 5.63; N, 5.71.

1,4-Phenylenebis(ethyl carbamate) (18). A 160 cc Parr autoclave was charged with 4.32 g (0.04 mol) of *p*-phenylenediamine, 25.3 g (0.1 mol) of *N*-cyclohexyl-*N'*,*N'*,*N''*,*N''*-tetraethylguanidine, and 50 mL of CH_3CN. The autoclave was attached to a pressure head, and at room temperature with stirring was added 40 psig carbon dioxide. Addition of CO_2 resulted in an exothermic reaction with a rise in temperature to ca. 40 °C. Into a second Fischer-Porter bottle was added ca. 15 mL (13 g, 0.2 mol) of ethyl chloride. This was attached to a pressure head, and 40 psig carbon dioxide was added above the solution. After 1 h the ethyl chloride solution was added all at once under 40 psig CO_2 to the preformed carbamate anion solution generated in the autoclave. After addition the reaction mixture was warmed to 85 °C for 20 h. After this time the reaction mixture was allowed to cool to room temperature and then the pressure was released. The crude reaction mixture was poured into 250 mL of 0.5 M aqueous HCl. A tan precipitate formed and was collected by filtration. This was washed several times with water. After being air-dried, a 73% (7.33 g) isolated yield of **18** was obtained: mp = 199–202 °C; ^{1}H NMR (DMSO-d_6) δ 9.45 (s, 2H, NH), 7.36 (s, 4H), 4.11 (q, J = 7.1 Hz, 4H), 1.24 (t, J = 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (DMSO-d$_6$) δ 153.5, 133.9, 118.7, 59.9, 14.4; IR ($CHCl_3$) 3434, 1728.

1,4-Cyclohexanediylbis(ethyl carbamate) (19). Procedures as in the synthesis of **18** with the exception that the reaction was carried out at 80 °C for 14 h using *N*-methylpyrrolidinone as solvent. The crude reaction material was poured into 200 mL of ethyl acetate and extracted with 2 × 200 mL of 0.5 M aqueous HCl followed by 200 mL of brine. The organic layer was dried over Na_2CO_3, filtered, and concentrated leaving a light yellow residue. This was washed with a 50:50 solution of diethyl ether/hexane giving 5.15 g (0.02 mol, 60.5%) of **19** as an analytically pure white solid: mp = >120 °C (slow melt); IR ($CHCl_3$) 3438, 1713; MS (FAB) m/z = 265 (M^+ + Li). Anal. Calcd for $C_{12}H_{22}N_2O_4$: C, 55.78; H, 8.59; N, 10.85. Found: C, 55.82; H, 8.42; N, 10.85.

1,2-Cyclohexanediylbis(ethyl carbamate) (20). Procedures as in the synthesis of **18**: 5.08 g (60%) of **20** as an analytically pure white solid; mp = >73 °C (slow melt); IR ($CHCl_3$) 3432, 1713. MS (FAB) m/z = 265 (M^+ + Li). Anal. Calcd for $C_{12}H_{22}N_2O_4$: C, 55.78; H, 8.59; N, 10.85. Found: C, 55.94; H, 8.51; N, 10.90.

(Methylenedicyclohexane-1,4-diyl)bis(phenylmethyl carbamate) (21). Procedures as in the synthesis of **18** with the exception that the reaction was carried out at 55 °C for 16 h in *N*-methylpyrrolidinone as solvent and benzyl chloride as the electrophile. The crude material was poured into 200 mL of H_2O, and a white precipitate formed. This white material was collected by filtration and was washed with water followed by air drying at room temperature overnight giving 3.63 g (78%) of the dicarbamate **21**: IR ($CHCl_3$) 3441, 1713. Anal. Calcd for $C_{29}H_{38}N_2O_4$: C, 72.77; H, 8.0; N, 5.85. Found: C, 72.79; H, 8.16; N, 5.94.

(20) Elemental analysis showed a slightly low value for carbon (0.6% low).

(Methylenedicyclohexane-1,4-diyl)bis(butyl carbamate) (22). Procedures as in the synthesis of **18** with the exception that the reaction was carried out at 85 °C for 6 h in acetonitrile as solvent and butyl chloride as the electrophile. The crude material was poured into 100 mL of ethyl acetate and extracted with 2 × 100 mL of 0.5 M aqueous HCl followed by 100 mL of brine. The organic layer was dried over Na_2CO_3, filtered, and concentrated leaving a light yellow residue. This was passed through a short column of silica gel using CH_2Cl_2 as an eluent giving 5.48 g (89%) of the bis(butyl carbamate) **22**: IR ($CHCl_3$) 3449, 1705; MS m/z = 411 (MH^+). Anal. Calcd for $C_{23}H_{42}N_2O_4$: C, 67.28; H, 10.31; N, 6.82. Found: C, 67.27; H, 10.09; N, 6.84.

(Methylenedicyclohexane-1,4-diyl)bis(2-methoxyethyl carbamate) (23). Procedures as described in the synthesis of **18**, using 2-chloroethyl methyl ether in place of ethyl chloride. A 70% isolated yield of the dicarbamate **23** resulted after chromatography on silica gel: IR ($CHCl_3$) 3441, 1715; MS m/z = 415 (MH^+). Anal. Calcd for $C_{21}H_{38}N_2O_6$: C, 60.85; H, 9.24; N, 6.76. Found: C, 60.68; H, 9.59; N, 6.80.

1,6-Hexanediylbis(phenylmethyl carbamate) (24). Procedures as in the synthesis of **18** with the exception that the reaction was carried out at 55 °C for 18 h in *N*-methylpyrrolidinone as solvent and benzyl chloride as the electrophile. The crude material was poured into 200 mL of H_2O and a white precipitate formed. This white material was collected by filtration and was washed with water followed by air-drying at room temperature overnight giving 9.75 g (63.5%) of the dicarbamate **24**: mp 130–132 °C; ^{1}H NMR ($CDCl_3$) δ 7.4–7.3 (overlapping m, 10H), 5.13 (s, 4H), 4.85 (br, NH, 2H), 3.21 (q, J = 6.3 Hz, 4H), 1.52 (br m, 4H), 1.36 (br, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 157.0, 137.2, 129.0, 128.6 (overlapping), 67.1, 41.4, 30.4, 26.7; IR ($CHCl_3$) 3453, 1713; MS (FAB) m/z = 385 (MH^+). Anal. Calcd for $C_{22}H_{28}N_2O_4$: C, 68.73; H, 7.34; N, 7.29. Found: C, 68.70; H, 7.40; N, 7.19.

1,6-Hexanediylbis(ethyl carbamate) (25). Procedures as in the synthesis of **18**: 4.88 g (57%) of **25** as an analytically pure white solid; mp = 84–86 °C; ^{1}H NMR (DMSO-d_6) δ 7.01 (br t, 2 H), 3.97 (q, J = 7 Hz, 4 H), 2.95 (q, J = 6.5 Hz, 4H), 1.4–1.2 (m, 8H), 1.15 (t, J = 7 Hz, 6H); ^{13}C{^{1}H} NMR (DMSO-d_6) δ 156.1, 59.3, 40.0, 29.3, 25.9, 14.6; IR ($CHCl_3$) 3447, 1713; MS (FAB) m/z = 267 (M^+ + Li). Anal. Calcd for $C_{12}H_{24}N_2O_4$: C, 55.35; H, 9.30; N, 10.76. Found: C, 55.40; H, 9.10; N, 10.63.

2-Methyl-1,5-pentanediylbis(phenylmethyl carbamate) (26). Procedures as in the synthesis of **18** with the exception that the reaction was carried out at 55 °C for 15 h in acetonitrile as solvent and benzyl chloride as the electrophile. The crude pale yellow solution was concentrated and then poured into 300 mL of H_2O and 200 mL of EtOAc. The aqueous layer was extracted two times with ca. 100 mL of EtOAc and the combined EtOAc layers with 100 mL of H_2O and then 100 mL of brine. The organic layers were dried over Na_2CO_3, filtered, and concentrated. The residue was dissolved into diethyl ether and hexane added. Upon cooling in the freezer 25.7 g (67%) of the bis-benzyl carbamate **26** was isolated as a white solid: mp = 79–81 °C; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 156.6, 156.5, 136.6, 128.5, 128.0, 66.6, 46.7, 41.1, 33.3, 30.8, 27.2, 17.4; IR ($CHCl_3$) 3449, 1711. Anal. Calcd for $C_{22}H_{28}N_2O_4$: C, 68.71; H, 7.34; N, 7.29. Found: C, 68.54; H, 7.40; N, 7.03.

1,2-Ethanediylbis(phenylmethyl carbamate) (27). Procedures as in the synthesis of **16** with the exception that the reaction was carried out at 55 °C for 16 h. The crude pale yellow solution was concentrated and then poured into 100 mL of H_2O and 100 mL of EtOAc. The aqueous layer was extracted two times with ca. 50 mL of EtOAc and the combined EtOAc layers with 2 × 50 mL of 0.5 M aqueous HCl and then 100 mL of brine. The organic layers were dried over Na_2CO_3, filtered, and concentrated. The residue was dissolved into diethyl ether and hexane added. Upon cooling in the freezer 1.8 g (55%) of the bis-benzyl carbamate **27** was isolated as a white solid: mp = 171–174 °C; ^{1}H NMR (DMSO-d_6) δ 7.35–7.25 (overlapping 12H), 5.00 (s, 4H), 3.05 (br s, 4H); IR ($CHCl_3$) 3447, 1711. Anal. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.80; H, 6.22; N, 8.35.

[4-[[[(Phenylmethoxy)carbonyl]amino]methyl]-1,8-oc-

tanediyl]bis(phenylmethyl carbamate) (28). A 160 cc stainless steel Parr autoclave was charged with 5.19 g (0.03 mol) of 4-(aminomethyl)-1,8-octanediamine (TAN), 17.9 g (0.096 mol) of *N*-cyclohexyl-*N',N',N'',N''*-tetramethylguanidine, and 30 mL of 1-methyl-2-pyrrolidinone (NMP). The autoclave was attached to a pressure head, and at room temperature with stirring was added 160 psig carbon dioxide. Addition of CO_2 resulted in an exothermic reaction with a rise in temperature to ca. 40 °C. Into a Fischer-Porter bottle was added 22.8 g (0.18 mol) of benzyl chloride. This was attached to a pressure head, and 80 psig carbon dioxide was added above the solution. After 1 h the benzyl chloride solution was added all at once under 80 psig CO_2 to the preformed carbamate anion solution generated in the first Fischer-Porter bottle. After addition the pressure was raised again to 160 psig with carbon dioxide, and the reaction mixture was warmed to 55 °C for 18 h. After this time the reaction mixture was allowed to cool to room temperature and then the pressure was released. The crude material was poured into 100 mL of ethyl acetate and extracted with 2 × 100 mL of 0.5 M aqueous HCl followed by 100 mL of brine. The organic layer was dried over Na_2CO_3, filtered, and concentrated. After crystallization from ethyl acetate/hexane an isolated yield of 58% (9.01 g) of the tricarbamate **28** resulted: mp 78–80 °C; ^{1}H NMR ($CDCl_3$) δ 7.4–7.34 (m, 5H), 5.1 (s, 6H), 5.1–5.0 (br, NH, 3H), 3.2–3.05 (m, 6H), 1.6–1.2 (overlapping m, 11H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 157.4, 157.1, 137.2, 129.0, 1286, 67.2, 67.1, 44.0, 41.6, 38.6, 31.4, 30.7, 28.9, 27.3, 23.9; IR ($CHCl_3$) 3453, 1713. Anal. Calcd for $C_{33}H_{41}N_3O_6$: C, 68.85; H, 7.18; N, 7.30. Found: C, 69.39; H, 7.32; N, 7.32.

Large scale reaction: A 5 gal reactor was charged with 675 g (3.9 mol) of 4-(aminomethyl)-1,8-diaminooctane (TAN), 3.06 kg (12.09 mol) of *N*-cyclohexyl-*N',N',N'',N''*-tetraethylguanidine and 5.6 L of CH_3CN. The reactor was pressurized to 200 psig with carbon dioxide (exothermic reaction with a rise in temperature to ca. 59 °C). After 1 h 3 kg (23.7 mol) benzyl chloride was added to the reaction mixture, the pressure was reduced to 60 psig and the reaction was then heated to 56 °C for 16 h. After this period of time the reaction was allowed to cool to room temperature and the pressure was released. The crude yellow solution was divided into 11 parts each of which was worked up identically. Each portion was extracted with ethyl acetate (750 mL) and water (750 mL). The ethyl acetate layer was extracted with 500 mL of water and then 500 mL of brine. The aqueous layers were extracted with 500 mL of ethyl acetate. The combined ethyl acetate layers were dried over solid Na_2CO_3, filtered, and concentrated. The product **28** was purified by precipitation from ethyl acetate/hexane in the freezer giving 1.344 kg (60%) of the tris-benzyl carbamate. Addition of solid sodium hydroxide to the aqueous layer from above caused separation of aqueous salts and free base. The base was collected and distilled giving 2.8 kg (91.5%) of recovered purified CyTEG.

[4-[[(Butoxycarbonyl)amino]methyl]-1,8-octanediyl]-bis(butyl carbamate) (29). Procedures as in the synthesis of **18** with the exception that the reaction was carried out at 85 °C for 18 h in *N*-methylpyrrolidinone as solvent and butyl chloride as the electrophile. The crude material was poured into 200 mL of ethyl acetate and extracted with 2 × 200 mL of 0.5 M aqueous HCl followed by 200 mL of brine. The organic layer was dried over Na_2CO_3, filtered, and concentrated leaving a light yellow residue. This was crystallized from ethyl acetate/hexane giving 36.5 g (85.5%) of the tributyl carbamate **29**: mp 60–61 °C; ^{1}H NMR ($CDCl_3$) δ 4.85 (br, NH, 3H), 4.05 (t, J = 6.6 Hz, 6H), 3.2–3.05 (m, 6H), 1.65–1.2 (overlapping m, 23H), 0.93 (t, J = 7.3 Hz, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 157.7, 157.5, 65.2, 65.1, 44.0, 41.5, 40.9, 38.6, 31.6, 31.5, 30.8, 28.9, 27.4, 24.0, 19.6, 14.2; IR ($CHCl_3$) 3455, 1709. Anal. Calcd for $C_{24}H_{47}N_3O_6$: C, 60.86; H, 10.0; N, 8.87. Found: C, 60.79; H, 10.38; N, 8.87.

[4-[[(Ethoxycarbonyl)amino]methyl]-1,8-octanediyl]-bis(ethyl carbamate) (30). A 1 gal reactor was charged with 173 g (1 mol) of 4-(aminomethyl)-1,8-diaminooctane (TAN), 835 g (3 mol) of *N*-cyclohexyl-*N',N',N'',N''*-tetraethylguanidine and 1.2 L of CH_3CN. The reactor was pressurized to 80 psig with carbon dioxide (exothermic reaction with a rise in temperature to ca. 48 °C). After 2 h ca. 310 mL (276 g, 4.28 mol) of ethyl chloride was added to the reaction mixture and the reaction was then heated to 78 °C for 16 h. After this period of time the reaction was allowed to cool to room temperature and the pressure was released. The crude yellow solution was extracted with toluene (1 L) and aqueous 0.5 M HCl (1 L). The toluene layer was extracted with an additional liter of H_2O. The toluene layers were combined and extracted with brine (1 L) and then concentrated (product did not crystallize out of toluene). The product was isolated by precipitation from ethyl acetate/hexane in the freezer (232 g, 60%): mp = 44–46.5 °C; ^{1}H NMR (DMSO-d_6) δ 6.95 (s, 3H, NH), 3.96 (q, J = 6.9 Hz 6H), 3.0–2.8 (overlapping m, 6H), 1.38–1.36 (overlapping m, 5H), 1.20–1.12 (overlapping m, 15 H); $^{13}C\{^1H\}$ (DMSO-d_6) δ 156.4, 156.1, 59.2, 43.0, 40.5, 40.0, 37.4, 30.6, 29.7, 28.1, 26.3, 23.1, 14.5.3; IR ($CHCl_3$) 3451, 1711. Addition of solid sodium hydroxide to the aqueous layer from above caused separation of aqueous salts and free base. The base was collected and distilled giving 778 g (93.2%) of recovered purified CyTEG.

***N,N'*-Dibutyl 1,4-Butanediylbis(butyl carbamate) (31).** Procedures as in the synthesis of **18** with the exception that the reaction was carried out at 75 °C for 16 h in acetonitrile as solvent and 1,4-dichlorobutane as the electrophile. The crude material was poured into 200 mL of ethyl acetate and extracted with 2 × 200 mL of 0.5 M aqueous HCl followed by 200 mL of brine. The organic layer was dried over Na_2CO_3, filtered, and concentrated leaving a light yellow residue. This was chromatographed on silica gel using ethyl acetate/hexane giving 21 g (70%) of the dicarbamate **31**: oil; ^{1}H NMR ($CDCl_3$) δ 4.1 (m, 4H), 3.2 (br m, 8H), 1.7 (m, 4H), 1.51 (m, 8H), 1.30 (sextet, J = 7.4 Hz, 8H), 0.92 (t, J = 7.3 Hz, 12H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.8, 65.1, (47.6, 47.1)[17], (31.3, 30.8), 26.4, 20.5, 14.3; IR (film) 1701; MS (FAB) m/z = 401 (MH^+). Anal. Calcd for $C_{22}H_{44}N_2O_4$: C, 65.96; H, 11.07; N, 6.99. Found: C, 66.22; H, 11.12; N, 7.40.

1,4-Butanediylbis(butyl carbamate) (32). Procedures as in the synthesis of **18**. A GC yield of 91.5% was calculated using biphenyl as an internal standard. Product isolated by pouring crude reaction material into water and collecting the white solid by filtration. After washing with water and air-drying a 77% isolated yield of the dicarbamate **32** resulted: mp = 114–115 °C; ^{1}H NMR ($CDCl_3$) δ 4.7 (br, NH, 2H), 4.09 (br, H), 3.17 (br q, J = 6 Hz, 4H), 1.69 (br, 4H), 1.52–1.31 (overlapping m, 8H), 0.93 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 157.2, 64.8, 41.2, 32.6, 26.2, 20.4, 14.2; IR ($CHCl_3$) 3453, 1711; MS (thermal spray) m/z = 289 (MH^+). Anal. Calcd for $C_{14}H_{28}N_2O_4$: C, 58.31; H, 9.79; N, 9.71. Found: C, 58.71; H, 10.05; N, 9.80.

***N,N'*-Diethyl 1,2-Ethanediylbis(ethyl carbamate) (33).** Procedures as in the synthesis of **18**. A GC yield of 85% was calculated using biphenyl as an internal standard and an isolated yield of 45% of the dicarbamate **33** resulted: oil; ^{1}H NMR ($CDCl_3$) δ 4.27 (s, 4H), 3.27 (br q, J = 6.3 Hz, 8H), 1.10 (t, J = 7.2 Hz, 12H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 156.1, 63.8, 42.1 (br), 14.2 (br); IR (film) 1701; MS (thermal spray) m/z = 261 (MH^+).

Oligourethane from Piperazine, CO_2, and 1,4-Dichlorobutane (chloro terminated). A 160 cc Parr autoclave was charged with 3.44 g (0.04 mol) of piperazine, 16.75 g (0.10 mol) of *N*-cyclohexyl-*N',N',N'',N''*-tetramethylguanidine, and 35 mL of CH_3CN. The autoclave was attached to a pressure head, and at room temperature with stirring was added 160 psig carbon dioxide. Addition of CO_2 resulted in an exothermic reaction with a rise in temperature to ca. 40 °C. Into a Fischer-Porter bottle was added 5.6 g (0.044 mol) of 1,4-dichlorobutane in 10 mL of CH_3CN. This mixture was attached to a pressure head and 80 psig carbon dioxide was added above the solution. After 1 h the dichlorobutane solution was added all at once under 80 psig CO_2 to the preformed carbamate anion solution generated in the autoclave. After addition the pressure was raised to 160 psig with carbon dioxide and the reaction mixture was warmed to 70 °C for 18 h. After this time the reaction mixture was allowed to cool to room temperature and then the pressure was released. The reaction mixture was poured into 150 mL of water giving a tan solid. This solid was collected by filtration, washed with water, CH_3CN, and diethyl ether (7.27 g): IR ($CHCl_3$) 1688. M_n = 3390 by NMR end group analysis.

Oligourethane from Piperazine, CO_2, and 1,4-Dichlorobutane (amine terminated). A 160 cc Parr autoclave was charged with 3.44 g (0.04 mol) of piperazine, 16.75 g (0.10 mol) of *N*-cyclohexyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidine, and 35 mL of CH_3CN. The autoclave was attached to a pressure head and at room temperature with stirring was added 160 psig carbon dioxide. Addition of CO_2 resulted in an exothermic reaction with a rise in temperature to ca. 40 °C. Into a Fischer-Porter bottle was added 4.57 g (0.036 mol) of 1,4-dichlorobutane in 10 mL of CH_3CN. This mixture was attached to a pressure head, and 80 psig carbon dioxide was added above the solution. After 1 h the dichlorobutane solution was added all at once under 80 psig CO_2 to the preformed carbamate anion solution generated in the autoclave. After addition the pressure was raised to 160 psig with carbon dioxide and the reaction mixture was warmed to 70 °C for 18 h. After this time the reaction mixture was allowed to cool to room temperature and then the pressure was released. The reaction mixture was poured into 150 mL of 0.5 M aqueous NaOH giving a tan solid. This solid was collected by filtration, washed with water, CH_3CN, and diethyl ether (5.5 g, 64%): ^1H NMR ($CDCl_3$) δ oligomer backbone 4.17 (m), 3.49 (s), 1.76 (m); Oligomer terminus 3.49 (shoulder), 2.86 (m); IR ($CDCl_3$) 3321 (N−H), 1690; M_n = 3250 by NMR end group analysis.

Segmented Polyurethane. A 160 cc Parr stainless steel autoclave was charged with 10.5 g (0.05 mol) of 4,4'-methylenebis(cyclohexylamine), 26.6 g (0.105 mol) of *N*-cyclohexyl-*N'*,*N'*,*N''*,*N''*-tetraethylguanidine, and 40 mL of 1-methyl-2-pyrrolidinone (NMP). With stirring (350−400 rpm), 160 psig carbon dioxide pressure was added above the reaction mixture (exothermic reaction with internal temperature reaching 50 °C). After 1 h 7.62 g (0.06 mol) 1,4-dichlorobutane in 10 mL of NMP was added all at once to the reaction mixture. The reaction was heated to 85 °C for 5 h. After this time the reaction was allowed to cool to 40 °C and an additional 5 g (0.039 mol) of 1,4-dichlorobutane was added to the reaction mixture. The reaction was heated again to 85 °C for 14 h after which time the reaction was allowed to cool to room temperature and the pressure was released. The crude reaction mixture (thick light yellow homogeneous solution) was slowly dripped into 200 mL of water giving a white precipitate. The precipitate was collected by filtration and washed with water, acetonitrile, and finally diethyl ether. The product was dried in a vacuum oven at 60 °C: IR ($CHCl_3$) 3443, 1707; M_n = 1570 (NMR end group analysis).

A 300 cc stainless steel Parr autoclave was charged with 10 g (0.005 mol) of Jeffamine-D-2000, 3.04 g (0.012 mol) of *N*-cyclohexyl-*N'*,*N'*,*N''*,*N''*-tetraethylguanidine, 8 g (ca. 0.005 mol) of the prepolymer generated in the above procedure, and 60 mL of NMP. The autoclave was attached to its pressure head, and 160 psig of CO_2 was added above the reaction mixture. After 1 h the mixture was heated to 105 °C for 3 d. After this period of time the reaction was allowed to cool to room temperature and the pressure was released. The thick yellow solution was slowly dripped into water giving a stringy white solid. This solid was collected, washed with water, and air-dried: IR ($CHCl_3$) 3441, 1709; GPC analysis: M_n = 8000; M_w = 17800, M_w/M_n = 2.2.

Comparison of Added Base on Phenylmethyl Butylcarbamate Generation. General procedure: A Fischer Porter bottle was charged with 1.46 g (0.02 mol) of *n*-butylamine, base (0.027 mol), 154 mg (0.001 mol) of biphenyl as internal GC standard, and 20 mL of CH_3CN. The Fischer-Porter bottle was attached to a pressure head, and at room temperature with stirring was added 80 psig carbon dioxide. Addition of CO_2 resulted in an exothermic reaction with a rise in temperature to ca. 40 °C. Into a second Fischer-Porter bottle was added 10.12 g (0.08 mol) of benzyl chloride in 10 mL of CH_3CN. This mixture was attached to a pressure head, and 80 psig carbon dioxide was added above the solution. After 1 h the benzyl chloride solution was added all at once under 80 psig CO_2 to the preformed carbamate anion solution generated in the first Fischer-Porter bottle. After addition the reaction mixture was warmed to 55 °C. Aliquots were taken periodically and were diluted with diethyl ether, Cl^- $^+$HCyTMG was filtered off, and GC yields were calculated. The results of this study are given in Table 2.

General Procedures for Relative Rate Studies. A Fischer-Porter bottle was charged with 0.73 g (0.01 mol) of diethylamine, 0.01 mol of a second amine, 5.32 g (0.027 mol) of CyTMG, 154 mg (0.001 mol) of biphenyl as internal GC standard, and 25 mL of CH_3CN. The Fischer-Porter bottle was attached to a pressure head and at room temperature with stirring was added 80 psig carbon dioxide. Addition of CO_2 resulted in an exothermic reaction with a rise in temperature to ca. 40 °C. Into a second Fischer-Porter bottle was added 0.25 g (0.002 mol) of benzyl chloride in 10 mL of CH_3CN. This mixture was attached to a pressure head, and 80 psig carbon dioxide was added above the solution. After 1 h the benzyl chloride solution was added all at once under 80 psig CO_2 to the preformed carbamate anion solution generated in the first Fischer-Porter bottle. After addition the reaction mixture was warmed to 40 °C. Aliquots were taken periodically and were diluted with diethyl ether, Cl^- $^+$HCyTMG filtered off and GC yields calculated.

Kinetic Procedures. The following example is general for the procedures used in all kinetic experiments in this report.

Stock solutions of reagents used were made as follows: Into a 50 mL volumetric flask was added 5.47 g (0.075 mol) of diethylamine and this was diluted to 50 mL with acetonitrile giving a 1.5 M solution. Into a second 50 mL volumetric flask was added 16.25 g (0.0825 mol) of CyTMG and this was diluted to 50 mL with acetonitrile giving a 1.65 M solution. Into a third 50 mL volumetric flask was added 0.63 g (0.005 mol) of benzyl chloride and 0.385 g (0.0025 mol) of biphenyl, and this mixture was diluted to 50 mL with acetonitrile giving a 0.1 M solution of benzyl chloride and a 0.05 M solution of biphenyl.

Into a Fischer-Porter bottle was added 10 mL of the diethylamine stock solution and 10 mL of the CyTMG stock solution. This mixture was attached to a pressure head, and 80 psig carbon dioxide was added above the solution. After 45 min this solution was heated to 50 °C.

Into a second Fischer-Porter bottle was added 10 mL of the benzyl chloride/biphenyl stock solution and 10 mL of acetonitrile. This solution was attached to a pressure head and 80 psig carbon dioxide was added above the solution. This solution was also heated to 50 °C.

After both solutions had equilibrated at 50 °C the benzyl chloride/biphenyl solution was added all at once to the carbamate solution. Aliquots were taken periodically and all aliquots were diluted with diethyl ether and quenched with 0.5 M aqueous HCl. Each aliquot was analyzed by gas chromatography, and the ratio of benzyl chloride to biphenyl was calculated.

NMR Spectroscopy Studies. Addition of $^{13}CO_2$ to a mixture of amine and CyTMG in CD_3CN at 0 °C gave homogeneous carbamate salt solutions which were analyzed by ^1H, $^{13}C\{^1H\}$, and $^{15}N\{^1H\}$ NMR spectroscopy.

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Supplementary Material Available: Spectra (^1H NMR and ^{13}C NMR) for compounds **19**−**23** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; ordering information is given on any current masthead page.

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