Preparation of Isocyanates from Primary Amines and Carbon Dioxide Using Mitsunobu Chemistry[1]

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Primary alkylamines **1** and hindered arylamines **1** give high yields of isocyanates **5** when reacted with carbon dioxide and the Mitsunobu zwitterions **4** generated from dialkyl azodicarboxylates and Bu_3P in dichloromethane at −78 °C. Use of Ph_3P still gave high yields of isocyanates from reactions of primary alkylamines, but only low yields were obtained from reactions of aromatic amines. Reactions which failed to give high yields of isocyanates gave either carbamoylhydrazines **6** and/or dicarbamoylhydrazines **10** and/or triazolinones **7**. The triazolinones were shown to arise from reactions of reactive aryl isocyanates with the Mitsunobu zwitterion. The carbamoylhydrazines were shown not to arise from reaction of isocyanate with reduced dialkyl azodicarboxylates, and a mechanism for their formation is proposed. Single-crystal X-ray analyses confirmed the structures of **6**, **7**, and **10**.

Introduction

The use of polyurethanes continues to grow.[2] All current commercial processes involve the use of isocyanates which have been obtained by reactions of primary amines with phosgene. During the past 20 years a considerable amount of academic- and industrial-based research has been carried out with the aim of developing new commercial routes to isocyanates which do not involve the use of the environmentally unacceptable phosgene. Two main strategies have been pursued. One involves carbonylation of nitroarenes in the presence of an alcohol[3] or carbonylation of amines in the presence of an alcohol and an oxidizing agent.[4] In each case carbamate esters are formed. Once formed, carbamate esters can, in principle, be thermolyzed to give the corresponding isocyanates. Several patents describe pyrolyses at temperatures greater than 300 °C in the presence of additives, e.g. excess boron,[5a] bismuth,[5a] or germanium oxides.[5b] In general, high yields of isocyanates are not obtained, but recently it has been shown that elimination of methanol from carbamate methyl esters can be achieved using a mixture of chlorocatecholborane and triethylamine to give isocyanates in good yields.[6] A second approach involves the reaction of amines with carbon dioxide and dehydration of the resulting carbamate salt. The Monsanto group have reported the use of a range of oxophilic reagents, e.g. $POCl_3$,[7] to achieve in situ dehydration. The preparation of isocyanates by reaction of preformed phosphorus-containing intermediates with carbon dioxide has been reported previously.[8,9] Reactions of amines with carbon dioxide have also been used to prepare alkali metal carbamates[10] and carbamate esters[11] in high yield. A mild and rapid method for isocyanate synthesis involving (dimethylamino)pyridine-catalyzed reactions of di-*tert*-butyl dicarbonate, $(Boc)_2O$, with sterically hindered arylamines has recently been reported together with detailed mechanistic studies.[12]

In this paper we describe a very mild method for the preparation of alkyl isocyanates from primary aliphatic amines and carbon dioxide using a Mitsunobu zwitterion generated from either diisopropyl azodicarboxylate (DIAD) or di-*tert*-butyl azodicarboxylate and triphenylphosphine or tri-*n*-butylphosphine.[13] High yields of isocyanates from hindered aromatic amines can also be obtained but only when the zwitterion generated from Bu_3P is used.

Results and Discussion

Reactions of Aliphatic Amines. Reactions of solutions of primary aliphatic amines **1** in dichloromethane with CO_2 at −5 to −10 °C gave carbamate salts **2** which sometimes precipitated from solution. In a separate flask the Mitsunobu zwitterion **4** was prepared by addition of

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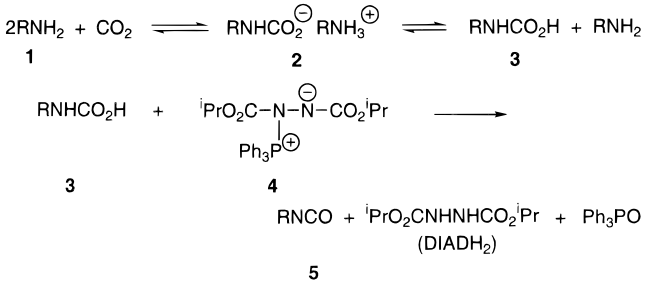


diisopropyl azodicarboxylate (DIAD) to a solution of triphenylphosphine in dichloromethane at −20 °C. Both solutions were cooled to −78 °C, and the zwitterion solution was cannulated into the carbamate-containing solution. More carbon dioxide was passed into the solution after addition and the reaction mixture allowed to warm to ambient temperature and to stand overnight. Dichloromethane was added to achieve a standard volume and an IR spectrum of an aliquot taken. The intensity of the IR band due to the cumulated N=C=O stretch in the isocyanate (in the region 2269 ± 10 cm^{-1}) was compared with those from standard solutions and an estimate of the yield of isocyanate prior to distillation obtained. The product was fractionally distilled first to remove dichloromethane and then to obtain an isolated yield of isocyanate. Yields of distilled products and estimated yields prior to distillation are given in Table 1.

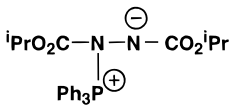
The yields of isocyanates in the reaction mixtures prior to distillation were all excellent for amines with secondary (entries 1 and 5) or tertiary (entries 4 and 7) alkyl substituents and still good for primary aliphatic amines (entries 3 and 6). The excellent recovery of isolated isocyanates testifies to the lack of adversely reactive byproducts, as the difficulties in isolating isocyanates are well established, e.g., leading to the formation of isocyanurates and uretidiones.[14]

The reactions were shown to be very fast. A reaction of isopropylamine was carried out in an NMR tube at −78 °C and the ^{31}P spectrum monitored. The first spectrum recorded ca. 3 min after addition of isopropylamine-derived carbamate to a solution of the zwitterion $^{i}PrO_2C-N(Ph_3P^+)-N^--CO_2{}^{i}Pr$ showed no signal for the zwitterion at 45.2 ppm but only a signal at 28.4 ppm due to Ph_3PO. Accordingly, a reaction of isopropylamine was worked up immediately on warming to ambient temperature and shown to give isocyanate in a yield comparable to that obtained on standing overnight (entry 2).

Reactions of *n*-octylamine, isopropylamine, and 3α-cholestanylamine with CO_2 were carried out using the Mitsunobu zwitterion generated from DIAD and Bu_3P. This zwitterion was generated and used at temperatures below −20 °C in order to avoid its decomposition,[14] but otherwise reaction conditions were identical to those described above involving Ph_3P. Comparable isolated yields were obtained, 60% for *n*-octylamine (cf. entry 6) 84% for isopropylamine (cf. entry 1) and 90% for the cholestanylamine (cf. entry 8).

Reactions using the zwitterion generated from Ph_3P and di-*tert*-butyl azodicarboxylate gave similar conversions to those summarized in Table 1 for reactions of *n*-butylamine (56% IR estimated yield, cf. entry 3) and *tert*-octylamine (90% IR estimated yield, cf. entry 7).

Table 1. Yields of Isocyanates 5 from Reactions of Amines 1 with CO_2 and the Mitsunobu Zwitterion[a]



		yield (%) of isocyanate (**5**)	
entry	amine (**1**) R	estimated by IR	isolated
1	i-Pr	94	86
2	i-Pr	90[b]	–
3	*n*-Bu	76	63
4	*t*-Bu	95	84
5	cyclohexyl	90	80
6	*n*-octyl	69	65
7	*tert*-octyl[c]	93	87
8	3α-cholestanyl	89	86

[a] Reactions in dichloromethane from −78 °C to ambient temperature. Full conditions and isolation procedures are given in the text. [b] Reaction worked up immediately on reaching ambient temperature, ca. 3 h, IR yield only. [c] 2,4,4-Trimethyl-2-pentylamine.

Thus, there is no advantage in using the relatively expensive di-*tert*-butyl azodicarboxylate nor the comparatively unstable zwitterion generated from DIAD and Bu_3P over the Ph_3P−DIAD-derived zwitterion for reactions of aliphatic amines.

THF could also be used as a solvent and a reaction of *tert*-octylamine with CO_2 and the Ph_3P-generated zwitterion gave an excellent yield (quantitative by IR, 93% isolated). Two reactions were carried out in which the zwitterion was generated in THF and added to the amine in supercritical CO_2. Only low yields (25−30%) of isocyanate were obtained, probably due to the very low solubility of the carbamate salt in the CO_2/THF solvent mixture.

Reactions of Aromatic Amines. High yields of isocyanates have been reported from reactions of hindered aromatic amines with di-*tert*-butyl dicarbonate.[12] Lower yields of isocyanates were obtained when less sterically hindered arylamines were reacted due to further reaction of the isocyanates with simultaneously formed *tert*-butyl alcohol. Similarly, high yields of isocyanates were obtained from reactions of hindered arylamines including hindered diamines (entries 13 and 14) with CO_2 and the Mitsunobu zwitterion generated from DIAD and Bu_3P (see Table 2). All of the 2,6-disubstituted anilines gave isolated yields of isocyanates ≥ 65% (entries 9−14). If, however, at least one of the substituents *ortho* to the amine is removed, the yield of isocyanate becomes negligible (entries 15 and 16). Yields of isocyanate were much lower (ca. 20%) when the Mitsunobu zwitterion derived from Ph_3P in place of Bu_3P was used in reactions of mesidine (entry 21) and 2,6-diisopropylaniline (entry 22) (Table 3). Reactions of mesidine using Ph_3P and Bu_3P were also carried out in an NMR tube at −78 °C and the ^{31}P spectra monitored. The signal due to the zwitterion $^{i}PrO_2C-N(Bu_3P^+)-N^--CO_2{}^{i}Pr$ (67.5 ppm) disappeared immediately the spectrum was recorded after mixing and was replaced by a signal at 53.1 ppm due to Bu_3PO together with a very small signal at 76.9 ppm which disappeared on warming leaving only the signal due to Bu_3PO (now 46.4 ppm at ambient temperature, lit.[15] 46.9 ppm).

In contrast, the reaction involving the Ph_3P-derived zwitterion was much slower, and the initial spectrum (ca.

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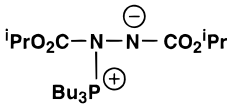
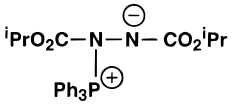
Table 2. Yields of Isocyanates from Reactions of Hindered Aromatic Amines with CO_2 and the Mitsunobu Zwitterion



		yield (%) of isocyanate (**5**)	
entry	amine (**1**) R	estimated by IR	isolated
9	2,4,6-tri-MeC_6H_2	100	92
10	2,6-di-EtC_6H_3	80	75
11	2-Et-6-MeC_6H_3	77	72
12	2,6-di-^{i}PrC_6H_3	100	89
13	2,4,6-trimethylbenzene-1,3-diamine	68	65
14	4,4′-methylenebis(2,6-dimethylaniline)	84	81
15	2-^{i}PrC_6H_4	<2	*a*
16	C_6H_5	<2	*b*

[a] A mixture of three products including carbamoylhydrazine (**6**; Ar = 2-^{i}PrC_6H_4), dicarbamoylhydrazine (**10**; Ar = 2-^{i}PrC_6H_4), and symmetrical urea was formed. [b] A mixture of the carbamoylhydrazine (**6**; Ar = Ph) and dicarbamoylhydrazine (**10**; Ar = Ph) was formed.

Table 3. Reactions of Aromatic Amines with CO_2 and the Mitsunobu Zwitterion

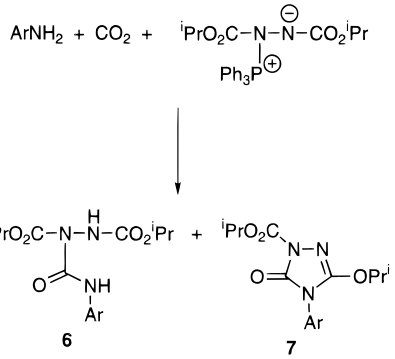


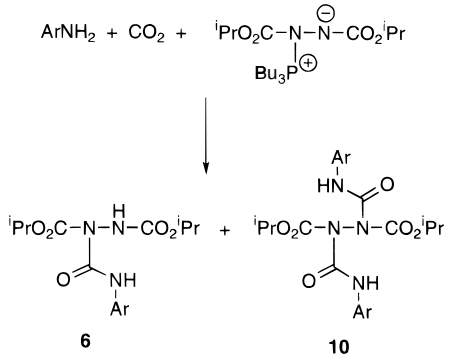
		product ratios (%)		
entry	amine (**1**) R	isocyanate[a] (**5**)	carbamoyl hydrazine[b] (**6**)	triazolinone[b] (**7**)
17	C_6H_5	2	41	57
18	C_6H_5[c]	2	62[d]	–
19	4-$MeOC_6H_4$	–	44	56
20	3-$O_2NC_6H_4$	–	–	100
21	2,4,6-tri-MeC_6H_2	20	80	–
22	2,6-di-^{i}PrC_6H_3	20	80	–
23	$C_6H_5CH_2$	5	89	6

[a] Estimated by IR. [b] Ratio estimated from ^{1}H NMR spectra. [c] Reaction using Bu_3P-derived zwitterion; other product dicarbamoylhydrazine isolated in 23% yield. [d] Isolated yield.

3 min after mixing) showed unreacted zwitterion **4** (40%), Ph_3PO (26%), and further resonances at 51 (24%) and 50.3 and 49.1 ppm (ca. 10%). As the reaction was allowed to warm in the spectrometer, the relative intensity of the signal due to Ph_3PO increased until it was the only observable resonance for a spectrum recorded at −15 °C. The difference in reactivity between the two zwitterions is unexpected as protonation by the carbamic acid should be rapid.

Unhindered arylamines gave very low yields of isocyanates for reactions using the Ph_3P-derived zwitterion. The major products were either carbamoylhydrazines **6** or triazolinones **7** (entries 17, 19, 20, 23). The structures of the carbamoylhydrazine (**6**; Ar = Ph) and the triazolinone (**7**; Ar = Ph) were confirmed by single-crystal X-ray structure analyses. The triazolinones **7** have been shown to be formed by reaction of aryl isocyanates with Mitsunobu zwitterions.[16] This was confirmed by reaction of 4-methoxyphenyl isocyanate (**5**; R = 4-$MeOC_6H_4$) with the zwitterion **4** which gave the 4-methoxyphenyltriazolinone (**7**; Ar = 4-$MeOC_6H_4$). The carbamoylhydrazines **6** could arise by attack of the anion **8** at the carbonyl group of the cation **9** (reaction i in Scheme 1). Deprotonation of **9** by the anion **8** leads to isocyanate formation (reaction ii in Scheme 1). The ease of breaking the N−H bond (reaction ii) should increase as its acidity is enhanced by the substitution of electron-withdrawing groups on the aryl ring. In agreement with this, reaction of 3-nitroaniline gave only the triazolinone **7** (formed via reaction of in situ isocyanate with unreacted zwitterion **4**) whereas similar reactions of the less acidic aniline and 4-methoxyaniline gave nearly 50% of carbamoylhydrazines **6**. However, this simple explanation based on amine acidity does not accord with the high yields of isocyanates formed from the very nonacidic alkylamines. The sensitivity of the fate of the reaction to the nature of the substituents on phosphorus is also hard to explain. A reaction of aniline using the Bu_3P-derived zwitterion gave a mixture of the carbamoylhydrazine (**6**; Ar = Ph) and the dicarbamoyl compound (**10**; Ar = Ph) (entry 18). The structure of **10** was confirmed by single-crystal X-ray analysis. Again, this product was shown not to arise from reaction of phenyl isocyanate with the phenylcarbamoylhydrazine (**6**; Ar = Ph). It is possible that the dicarbamoyl compound **10** is formed by a mechanism similar to that recently proposed to account for the formation of





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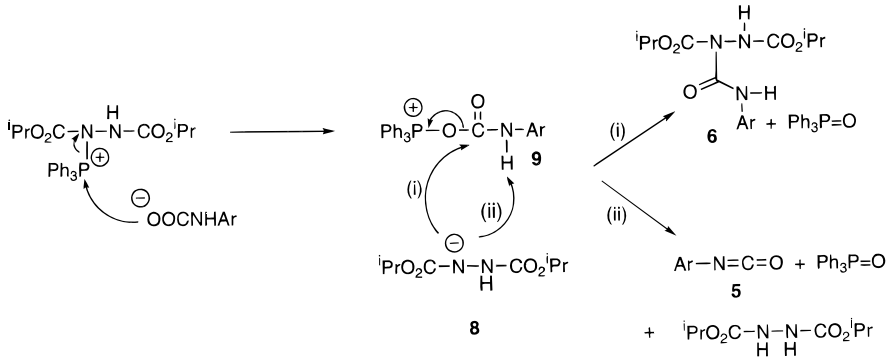
Scheme 1



diacylhydrazines from reactions of carboxylate ions with the Mitsunobu zwitterion **4**.[17]

Reaction of an Amino Acid Derivative. Reaction of L-phenylalanine ethyl ester (**1**; R = $EtO_2C(PhCH_2)$-CH) with CO_2 and the Bu_3P-derived zwitterion gave isocyanate (69% isolated yield). In contrast, a reaction using the Ph_3P-derived zwitterion gave only carbamoylhydrazine (**6**; Ar = $EtO_2C(PhCH_2)CH$) which was isolated in 64% yield. The L-phenylalanine ethyl ester thus shows a similar reactivity pattern to the hindered aromatic amines. The isocyanate was formed without significant racemization emphasizing the benefits of the very mild reaction conditions.

Pyrolysis of Carbamoylhydrazines. The mass spectra of the carbamoylhydrazines **6**, determined under volatilizing/ionizing conditions (T = 200 °C, 70 eV), all showed a very weak parent ion signal M^+ and a strong signal with an m/z corresponding to that of the derived isocyanate. Similarly, gas chromatography of these compounds with an inlet port temperature of 250 °C also led to the formation of isocyanate. Accordingly two carbamoylhydrazines were heated under reduced pressure (20 mmHg) at 200 °C, and the volatile isocyanate was collected together with a small amount of *N*,*N*′-bis-(isopropylcarboxy)hydrazine, $DIADH_2$. Thus, thermolysis of the carbamoylhydrazines **6**, Ar = 2,4,6-tri-MeC_6H_2, and **6**, Ar = $PhCH_2$, gave 81 and 56% yields of the corresponding isocyanates. Thermogravimetric analysis of these and the other carbamoylhydrazines suggested that thermolysis to give isocyanate occurred for all samples in the temperature range 200−230 °C. The dicarbamoylhydrazine **10** was also thermolyzed and gave phenyl isocyanate and $DIADH_2$ in a molar ratio of 2:1. Thus, isocyanates can be obtained from reactions of amines which give carbamoylhydrazines as the initial product, e.g., benzyl isocyanate can be obtained in good yield from the related carbamoylhydrazine (entry 23, Table 3).

Experimental Section

All operations unless otherwise specified were carried out under an atmosphere of dry nitrogen using dry solvents that were distilled prior to use.

Materials. Amines were purchased from either Aldrich or Fluka, stirred over CaH_2, and distilled before use. 3α-Cholestanylamine, mp 89−90 °C (lit.[18] mp 87−88 °C) was prepared from 3β-cholestanol by the method of Bose et al.[18] Carbon dioxide was BOC anaerobic grade (moisture level 13 ± 4 ppm). Phosphines and azodicarboxylates were purchased from Aldrich and used as received. Authentic samples of isocyanates were either purchased from Aldrich or prepared from the appropriate amine and trichloromethyl chloroformate.[19] Petroleum ether refers to the fraction of petroleum bp 60−80 °C.

Analytical. Flash chromatography was performed using E. Merk 230−400 mesh silica gel. ^1H NMR spectra were measured at 200, 300, or 400 MHz, ^{13}C at 50.3 or 100.6 MHz, and ^{31}P at 162 MHz. Mass spectra including accurate mass measurements (EI) were obtained at 70 eV. Analytical gas−liquid chromatography was carried out using a 1.8 m × 0.5 mm stainless steel column of 10% S.E. 30 on acid-washed DMCS chromosorb W 80/100. X-ray crystallographic measurements were performed by Dr. E. Tiekink, University of Adelaide, and Dr. G. Fallon, Monash University.[20]

General Procedure for the Synthesis of Isocyanates. Anaerobic grade carbon dioxide was gently bubbled through a solution containing freshly distilled amine in CH_2Cl_2 while it was cooled to −10 to −5 °C. More carbon dioxide was then vigorously bubbled through the solution for 30−60 min. In a separate flask, a stirred cold solution (−20 °C) containing PPh_3 in CH_2Cl_2 was treated with diisopropyl azodicarboxylate (DIAD) or di-*tert*-butyl azodicarboxylate. The ratio of amine, phosphine, and azodicarboxylate was 1:1.2:1.2, respectively. Both reaction vessels were cooled to −78 °C prior to cannulation of the zwitterion solution into the carbamate salt solution. The reaction mixture was allowed to warm slowly to room temperature over a period of 30−60 min while maintaining a steady stream of CO_2. The mixture was then stirred overnight under 1 atm of CO_2. IR analysis of the subsequent solution made up to a specific volume with CH_2Cl_2 was used to determine the yield of in situ produced isocyanate. The isocyanates were isolated either by fractional distillation or column chromatography.

Reactions using PBu_3 in place of PPh_3 used equimolar ratios of amine, PBu_3, and DIAD and were worked up immediately when the reaction mixture reached ambient temperature.

Synthesis of Alkyl Isocyanates. All reactions involved the use of Ph_3P unless otherwise stated.

Isopropyl Isocyanate (5; R = i-Pr). Anaerobic grade CO_2 was bubbled through a cold solution (−10 °C) of isopropylamine (1.5 mL, 17.6 mmol) in CH_2Cl_2 (45 mL) for 30 min. In a separate flask, DIAD (4.2 mL, 21.3 mmol) was added over a 2 min period via syringe to a cold solution (−20 °C) containing PPh_3 (5.54 g, 22.5 mmol) in CH_2Cl_2 (65 mL). The resultant pale yellow solution was cooled to −78 °C and then transferred via cannula to the precooled (−78 °C) carbamate salt solution. Carbon dioxide addition was continued for an additional 30 min, and the pale yellow homogeneous solution was allowed to warm to room temperature. The solution was stirred

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(18) Bose, A. K.; Kistner, J. F.; Farber, L. *J. Org. Chem.* **1962**, *27*, 2925.
(19) Kurita, K.; Matsumura, T.; Iwakura, Y. *J. Org. Chem.* **1976**, *41*, 2070.
(20) The atomic coordinates for these structures have been deposited with the Cambridge Crystallographic Data Centre and can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CBZ IEZ, U.K.

overnight under CO_2 (1 atm). The mixture became almost colorless over the 24 h reaction period. The solution was diluted to 100 mL with freshly distilled CH_2Cl_2. An IR analysis on the diluted solution showed it to contain isopropyl isocyanate (1.41 g, 94% in situ yield). Most of the CH_2Cl_2 was removed by fractional distillation prior to separation of the isocyanate from Ph_3PO and $DIADH_2$ by trap-to-trap distillation (0.01 mmHg). A final fractional distillation yielded a clear, colorless oil (1.29 g, 86%): bp 73−75 °C (lit.[21] bp 76 °C); IR (CH_2Cl_2) 2267 cm^{-1} (NCO); ^1H NMR (200 MHz, $CDCl_3$) δ 1.29 (d, 6H, J = 6.5 Hz), 3.74 (sept, 1H, J = 6.4 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 24.9, 47.3, 122.6; MS (EI) m/z 85 (M^+, 44). A reaction of isopropylamine (0.21 g, 3.5 mmol) using the Bu_3P-derived zwitterion gave the isocyanate (0.18 g, 84%) after distillation.

***n*-Butyl Isocyanate (5; R = n-Bu).** Reaction of *n*-butylamine (0.33 g, 4.6 mmol) gave *n*-butyl isocyanate after distillation as a clear colorless oil (0.28 g, 63%): bp 114−115 °C (lit.[22] bp 115 °C); IR (CH_2Cl_2) 2278 cm^{-1} (NCO); ^1H NMR (200 MHz, $CDCl_3$) δ 0.94 (t, 3H, J = 7.1 Hz), 1.32−1.67 (bm, 4H), 3.30 (t, 2H, J = 6.4 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 13.2, 19.6, 33.2, 42.6, 121.9; MS (EI) m/z 99 (M^+, 10).

***tert*-Butyl Isocyanate (5; R = t-Bu).** Reaction of *tert*-butylamine (0.70 g, 9.5 mmol) gave *tert*-butyl isocyanate as a colorless oil (0.79 g, 84%) bp 84 °C (lit.[21] bp 84−85 °C); IR (CH_2Cl_2) 2258 cm^{-1} (NCO); ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (s, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 31.9, 55.5, 122.6; MS (EI) m/z 99 (M^+, 100).

Cyclohexyl Isocyanate (5; R = C_6H_{11}). Reaction of cyclohexylamine (0.87 g, 8.7 mmol) gave cyclohexyl isocyanate as a colorless oil (0.88 g, 80%): bp 67 °C/15 mmHg (lit.[23] bp 150−155 °C); IR (CH_2Cl_2) 2263 cm^{-1} (NCO); ^1H NMR (400 MHz, $CDCl_3$) δ 1.23−1.91 (m, 10H), 3.40−3.46 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.9, 25.3, 34.9, 53.4, 122.6; MS (EI) m/z 125 (M^+, 6).

***n*-Octyl Isocyanate (5; R = C_8H_{17}).** Reaction of *n*-octylamine (0.47 g, 3.6 mmol) gave *n*-octyl isocyanate after distillation as a clear, colorless oil (0.37 g, 65%): bp 85 °C/15 mmHg (lit.[23] bp 42−44 °C/0.03 mmHg); IR(CH_2Cl_2) 2274 cm^{-1} (NCO); ^1H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, 3H, J = 6.8 Hz), 1.28−1.67 (bm, 12H), 3.28 (t, 2H, J = 6.7 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 13.9, 22.5, 26.5, 28.9, 29.1, 31.2, 31.7, 42.9, 122.0; MS (EI) m/z 140 ($M^+ - CH_3$, 1).

2,4,4-Trimethyl-2-pentyl Isocyanate (*tert*-octyl isocyanate 5; R = *tert*-octyl). Reaction of *tert*-octylamine (0.24 g, 1.9 mmol) gave *tert*-octyl isocyanate as a colorless oil (0.25 g, 87%) bp 64 °C/15 mmHg (lit.[24] bp 170−172 °C); IR (CH_2Cl_2) 2263 cm^{-1} (NCO); ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 9H), 1.41 (s, 6H), 1.52 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 31.2, 31.6, 32.8, 55.3, 58.2, 121.8; MS (EI) m/z 140 ($M^+ - CH_3$, 3.5). A reaction on the same scale only using THF as solvent gave the isocyanate (0.27 g, 93%).

3α-Cholestanyl Isocyanate (5; R = 3α-cholestanyl). Reaction of 3α-cholestanylamine (0.2 g, 0.52 mmol) gave the isocyanate as a white precipitate after flash chromatography (SiO_2, pentane) (0.19 g, 86%) mp 72−74.5 °C (lit.[25] mp 70−72 °C); IR (CH_2Cl_2) 2268 cm^{-1} (NCO); ^1H NMR (200 MHz, $CDCl_3$) δ 0.65−2.00 (m, 46H), 3.87 (bs, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 11.8, 12.3, 18.8, 20.9, 22.7, 23.0, 24.0, 24.3, 28.2, 28.43, 28.45, 28.8, 30.0, 32.9, 35.2, 35.6, 36.0, 36.2, 36.3, 39.7, 40.1, 40.3, 42.8, 51.9, 54.3, 56.4, 56.6, 122.1; HRMS (EI) m/z calcd for $C_{28}H_{47}NO$ 413.3657, found 413.3641. A reaction of 3α-cholestanylamine (0.32 g) using the Bu_3P-derived zwitterion gave the isocyanate (0.31 g, 90%) after flash chromatography.

Hindered Aryl Isocyanates. All reactions involved the use of Bu_3P.

2,4,6-Trimethylphenyl Isocyanate (5; R = 2,4,6-tri-Me-C_6H_2). Reaction of 2,4,6-trimethylaniline (0.29 g, 2.1 mmol) gave the isocyanate as colorless needles (0.32 g, 92%) after flash chromatography (SiO_2, pentane) mp 40−41 °C (lit.[12] mp 42 °C); IR (CH_2Cl_2) 2284 cm^{-1} (NCO); ^1H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.23 (s, 6H), 6.78 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 18.6, 20.6, 124.3, 128.6, 128.7, 132.6, 135.0; HRMS (EI) m/z calcd for $C_{10}H_{11}NO$ 161.0841, found 161.0839.

2,6-Diethylphenyl Isocyanate (5; R = 2,6-di-EtC_6H_3). Reaction of 2,6-diethylaniline (0.27 g, 1.8 mmol) gave the isocyanate as a colorless oil (0.24 g, 75%) after flash chromatography (SiO_2, pentane) and was identified by comparison with an authentic sample prepared from 2,6-diethylaniline and trichloromethyl chloroformate[19] bp 65 °C/0.5 mmHg; IR (CH_2Cl_2) 2288 cm^{-1} (NCO); ^1H NMR (200 MHz, $CDCl_3$) δ 1.23 (t, 6H, J = 7.6 Hz), 2.67 (q, 4H, J = 7.5 Hz), 7.06 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.2, 25.7, 124.1, 125.9, 126.5, 130.0, 138.9; HRMS (EI) m/z calcd for $C_{11}H_{13}NO$ 175.0997, found 175.0994.

2,6-Dimethylphenyl Isocyanate (5; R = 2,6-di-MeC_6H_3). Reaction of 2,6-dimethylaniline (0.34 g, 2.8 mmol) gave the isocyanate as a colorless oil (0.37 g, 89%) after flash chromatography (SiO_2, pentane) and was identified by comparison with an authentic sample prepared from 2,6-dimethylaniline and trichloromethyl chloroformate[19] bp 65 °C/0.6 mmHg; IR (CH_2Cl_2) 2277 cm^{-1} (NCO); ^1H NMR (200 MHz, $CDCl_3$) δ 2.30 (s, 6H), 7.00 (m, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 18.7, 124.6, 125.5, 128.1, 131.4, 133.0; HRMS (EI) m/z calcd for C_9H_9NO 147.0684, found 147.0678.

2-Ethyl-6-Methylphenyl Isocyanate (5; R = 2-Et-6-Me-C_6H_3). Reaction of 2-ethyl-6-methylaniline (0.29 g, 2.1 mmol) gave the isocyanate as a colorless oil (0.25 g, 72%) after flash chromatography (SiO_2, pentane) and was identified by comparison with an authentic sample prepared from 2-ethyl-6-methylaniline and trichloromethyl chloroformate[19] bp 115 °C/0.05 mmHg; IR (CH_2Cl_2) 2277 cm^{-1} (NCO); ^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, 3H, J = 7.6 Hz), 2.29 (s, 3H), 2.64 (q, 2H, J = 7.6 Hz), 7.00 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.1, 18.7, 25.6, 124.3, 125.6, 126.4, 128.0, 130.6, 133.2, 138.6; HRMS (EI) m/z calcd for $C_{10}H_{11}NO$ 161.0841, found 161.0839.

2,6-Diisopropylphenyl Isocyanate (5; R = 2,6-di-^{i}Pr-C_6H_3). Reaction of 2,6-diisopropylaniline (0.47 g, 2.6 mmol) gave the isocyanate as a clear, colorless oil (0.48 g, 89%) after flash chromatography (SiO_2, pentane) and was identified by comparison with an authentic sample prepared from reaction of 2,6-diisopropylaniline and trichloromethyl chloroformate[19] bp 69 °C/0.2 mmHg; IR (CH_2Cl_2) 2293 cm^{-1} (NCO); ^1H NMR (200 MHz, $CDCl_3$) δ 1.25 (d, 12H, J = 6.8 Hz), 3.22 (sept, 2H, J = 6.8 Hz), 7.00−7.22 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 22.9, 29.7, 123.5, 123.8, 126.2, 128.9, 143.1; HRMS (EI) m/z calcd for $C_{13}H_{17}NO$ 203.1310, found 203.1309.

2,4,6,-Trimethylphenyl 1,3-Diisocyanate. Reaction of 2,4,6-trimethylbenzene-1,3-diamine (0.22 g, 1.5 mmol) gave the diisocyanate as colorless needles (0.17 g, 65%) after flash chromatography (SiO_2, pentane) and was identified by comparison with an authentic sample prepared from reaction of 2,4,6-trimethylbenzene-1,3-diamine and trichloromethyl chloroformate:[19] mp 57−59.5 °C; IR (CH_2Cl_2) 2284 cm^{-1} (NCO); ^1H NMR (200 MHz, $CDCl_3$) δ 2.24 (s, 9H), 6.84 (s, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 14.6, 18.5, 124.5, 127.7, 129.4, 129.8, 130.5; HRMS (EI) m/z calcd for $C_{11}H_{10}N_2O_2$ 202.0742, found 202.0745.

4,4′-Methylenebis(2,6-dimethylphenyl isocyanate). Reaction of 4,4′-methylenebis(2,6-dimethylaniline) (0.30 g, 1.2 mmol) gave the diisocyanate as colorless needles (0.29 g, 81%) after flash chromatography (SiO_2, pentane) and was identified by comparison with an authentic sample of the titled isocyanate prepared from reaction of 4,4′-methylenebis(2,6-dimethylaniline) and trichloromethyl chloroformate:[19] mp 124−126 °C; IR (CH_2Cl_2) 2283 cm^{-1} (NCO); ^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 12H), 3.75 (s, 2H), 6.82 (s, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 18.7, 40.8, 124.4, 128.5, 129.4, 133.1, 138.2; HRMS (EI) m/z calcd for $C_{19}H_{18}N_2O_2$ 306.1368, found 306.1369.

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Formation of Carbamoylhydrazines 6, Triazolinones 7, and Dicarbamoylhydrazines 10. Reactions of unhindered aromatic amines with CO_2 and $^iPrO_2C-N(Ph_3P^+)-N^--CO_2{}^iPr$. **Aniline.** Reaction of aniline (0.31 g, 3.3 mmol) in CH_2Cl_2 (20 mL) with CO_2 and the zwitterion derived from PPh_3 (1.0 g, 3.9 mmol) and DIAD (0.80 g, 3.9 mmol) in CH_2Cl_2 (20 mL) under the conditions described previously gave a viscous yellow oil (2.1 g) which was shown to contain a mixture of the carbamoylhydrazine (**6**; Ar = Ph) and the triazolinone (**7**; Ar = Ph) in the ratio ca. 2:3 with ca. 2% isocyanate by ^{1}H NMR and IR. Flash chromatography (SiO_2, 30% ethyl acetate/petroleum ether) gave samples of *N*-(phenylcarbamoyl)-*N*,*N*′-bis(isopropylcarboxy)hydrazine (**6**; Ar = Ph) as a yellow viscous oil which solidified on standing (0.22 g, 20%) [mp 89.5−92.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (d, 6H, J = 5.8 Hz), 1.34 (d, 6H, J = 6.2 Hz), 5.02 (overlapping septs, 2H, J = 6.2 Hz), 6.99 (bs, 1H), 7.10 (t, 1H, J = 7.3 Hz), 7.31 (t, 2H, J = 7.4 Hz), 7.50 (d, 2H, J = 7.4 Hz), 10.53 (s, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 21.8, 22.0, 70.5, 72.9, 119.0, 124.4, 129.1, 137.5, 155.4, 155.2; HRMS (EI) *m*/*z* calcd for $C_{15}H_{21}N_3O_5$ 323.1481, found 323.1479] and isopropyl 3-isopropoxy-5-oxophenyl-Δ^2,1,2,4-triazoline-1-carboxylate (**7**; Ar = Ph) [mp 87.5−90 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.39 (d, 6H, J = 6.4 Hz), 1.43 (d, 6H, J = 6.4 Hz), 5.23 (sept, 1H, J = 6.3 Hz), 5.28 (sept, 1H, J = 6.2 Hz), 7.34−7.51 (m, 5H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 21.69, 21.71, 72.3, 75.0, 125.8, 128.4, 129.1, 130.8, 148.7, 149.0, 150.4; MS(EI) *m*/*z* 305 (M^+, 2). Anal. Calcd for $C_{15}H_{19}N_3O_4$: C, 59.01; H,6.27; N, 13.79. Found: C, 59.19; H, 6.18; N, 13.76.]

Authentic samples of this and other triazolinones were prepared by the literature method[16] and were found to have identical physical and spectroscopic properties to the materials obtained from the amine−CO_2 reactions.

4-Methoxyaniline. Reaction of 4-methoxyaniline (0.31 g, 2.50 mmol) as above gave a product (1.62 g) which on flash chromatography (SiO_2, 30% ethyl acetate/petroleum ether) gave *N*-(4-methoxyphenylcarbamoyl)-*N*,*N*′-bis(isopropylcarboxy)-hydrazine (**6**; Ar = 4-$MeOC_6H_4$) as a colorless oil (0.21 g, 23%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.28 (bd, 6H, J = 6.5 Hz), 1.34 (d, 6H, J = 6.2 Hz), 3.78 (s, 3H), 5.03 (sept, 2H, J = 6.2 Hz), 6.82−6.89 (m, 2H), 6.98 (bs, 1H), 7.36−7.44 (m, 2H), 10.35 (bs, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 21.7, 21.9, 55.4, 70.3, 72.6, 114.1, 121.9, 130.3, 150.5, 155.3, 155.4, 156.4; HRMS (EI) *m*/*z* calcd for $C_{16}H_{23}N_3O_6$ 353.1587, found 353.1575. Further elution gave isopropyl 3-isopropoxy-5-oxo-4-(methoxyphenyl)-Δ^2,1,2,4-triazoline-1-carboxylate (**7**; Ar = 4-$MeOC_6H_4$) as a white precipitate: mp 88−91 °C; IR (Nujol) 1802, 1626 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.38 (d, 6H, J = 6.2 Hz), 1.41 (d, 6H, J = 6.3 Hz), 3.82 (s, 3H), 5.22 (sept, 1H, J = 6.2 Hz), 5.27 (sept, 1H, J = 6.2 Hz), 6.96 (m, 2H), 7.27 (m, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 21.7, 55.5, 72.3, 74.8, 114.4, 123.5, 127.3, 148.8, 149.3, 150.8, 159.5; MS(EI) *m*/*z* 335 (M^+, 7). Anal. Calcd for $C_{16}H_{21}N_3O_5$: C, 57.30; H, 6.30; N, 12.53. Found: C, 57.17; H, 6.35; N, 12.45.

3-Nitroaniline. This reaction gave only the triazolinone (**7**; Ar = 3-$O_2NC_6H_4$). Spectroscopic data were identical with those for an analytically pure authentic sample[16] prepared by reaction of 3-nitrophenyl isocyanate with the zwitterion derived from DIAD and PPh_3. Isopropyl 3-isopropoxy-5-oxo-4-(nitrophenyl)-Δ^2,1,2,4-triazoline-1-carboxylate (**7**; Ar = 3-$O_2NC_6H_4$): mp 120−122.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.43 (d, 6H, J = 6.2 Hz), 1.46 (d, 6H, J = 6.3 Hz), 5.25 (sept, 1H, J = 6.3 Hz), 5.33 (sept, 1H, J = 6.2 Hz), 7.69 (t, 1H, J = 8.0 Hz), 7.85 (ddd, 1H, J = 8.1, 2.1 and 1.2 Hz), 8.27 (ddd, 1H, J = 8.3, 2.2 and 1.2 Hz), 8.37 (t, 1H, J = 2.0 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 21.7, 72.7, 75.9, 120.5, 123.0, 130.1, 131.0, 132.0, 148.36, 148.40, 149.5; MS (EI) *m*/*z* 308 ($M^+ - (CH_3)_2O$, 1). Anal. Calcd for $C_{15}H_{18}N_4O_6$: C, 51.43; H, 5.18; N, 15.99. Found: C, 51.42; H, 5.27; N, 16.02.

2,4,6-Trimethylaniline. The product from a reaction of 2,4,6-trimethylaniline (0.29 g, 2.14 mmol) on chromatography (SiO_2, 20% ethyl acetate/petroleum ether) gave 2,4,6-trimethylphenyl isocyanate (**5**; R = 2,4,6-tri-MeC_6H_2) (0.05 g, 15%), mp 40−42 °C, with spectral data identical to that of an authentic sample described previously and *N*-(2,4,6-trimethylphenylcarbamoyl)-*N*,*N*′-bis(isopropylcarboxy)hydrazine (**6**; Ar = 2,4,6-tri-MeC_6H_2) (0.54 g, 69%): mp 137−138 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25 (d, 6H, J = 6.2 Hz), 1.35 (d, 6H, J = 6.2 Hz), 2.22 (s, 6H), 2.26 (s, 3H), 4.99 (b sept, 1H, J = 6.1 Hz), 5.08 (b sept, 1H, J = 6.3 Hz), 6.57−6.76 (bm, 1H), 6.89 (s, 2H), 9.63 (bs, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 18.2, 20.9, 21.7, 21.8, 70.3, 72.4, 128.8, 130.9, 135.2, 136.8, 151.3, 155.3, 155.5. Anal. Calcd for $C_{18}H_{27}N_3O_5$: C, 59.16; H, 7.45; N, 11.50. Found: C, 59.11; H, 7.56; N, 11.46.

2,6-Diisopropylaniline. The products from a reaction of 2,6-diisopropylaniline (0.28 g, 1.6 mmol) were shown to be isocyanate (**5**; R = 2,6-di-$^iPrC_6H_3$) with spectral data identical to that of an authentic sample as above and *N*-(2,6-diisopropylphenylcarbamoyl)-*N*,*N*′-bis(isopropylcarboxy)hydrazine (**6**; Ar = 2,6-di-$^iPrC_6H_3$). Flash chromatography (SiO_2, 20% ethyl acetate/petroleum ether) gave a pure sample of (**6**; Ar = 2,6-di-$^iPrC_6H_3$) as a waxy solid (0.46 g, 71%): mp 101−104 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.18−1.37 (m, 24H), 3.12 (bm, 2H), 5.09 (overlapping septs, 2H, J = 6.3 Hz), 6.85 (bm, 1H), 7.13−7.31 (m, 3H), 9.68 (s, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 21.87, 21.93, 23.7, 28.8, 70.3, 72.5, 123.6, 128.4, 130.8, 146.3, 152.4, 155.5, 155.7; HRMS (EI) *m*/*z* calcd for $C_{21}H_{33}N_3O_5$ 407.2420, found 407.2426.

Benzylamine. The products from a reaction of benzylamine (0.29 g, 2.7 mmol) were benzyl isocyanate (**5**; R = $C_6H_5CH_2$), carbamoylhydrazine (**6**; Ar = $C_6H_5CH_2$), and triazolinone (**7**; Ar = $C_6H_5CH_2$). Flash chromatography (SiO_2, 60% ethyl acetate/petroleum ether) gave *N*-(benzylcarbamoyl)-*N*,*N*′-bis-(isopropylcarboxy)hydrazine (**6**; Ar = $C_6H_5CH_2$) (0.84 g, ca. 90%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25−1.30 (m, 12H), 4.49 (m, 2H), 4.98 (sept, 2H, J = 6.2 Hz), 7.21 (bm, 1H), 7.29 (m, 5H), 8.70 (bm, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 21.7, 22.0, 44.9, 70.1, 72.2, 127.5, 127.6, 128.4, 138.0, 153.4, 155.2, 155.5; MS (ES) *m*/*z* 697 ($2M^+$ + Na). Anal. Calcd for $C_{16}H_{23}N_3O_5$: C, 56.96; H, 6.87; N, 12.46. Found: C, 57.05; H, 7.02; N, 12.40. Benzyl isocyanate was identified by IR with an N=C=O stretch at 2273 cm^{-1} and isopropyl 3-isopropoxy-5-oxo-4-benzyl-Δ^2,1,2,4-triazoline-1-carboxylate (**7**; Ar = $C_6H_5CH_2$) by comparison of spectroscopic data with that of an analytically pure authentic sample[16] prepared by reaction of benzyl isocyanate with the zwitterion derived from DIAD and PPh_3. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.36 (d, 6H, J = 6.2 Hz), 1.40 (d, 6H, J = 6.3 Hz), 4.68 (s, 2H), 5.17 (overlapping septs, 2H, J = 6.3 Hz), 7.27−7.38 (m, 5H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 21.9, 44.0, 72.3, 74.8, 128.4, 128.6, 128.8, 135.2, 148.9, 150.1, 151.5; MS (EI) *m*/*z* 319 (M^+, <1). Anal. Calcd for $C_{16}H_{21}N_3O_4$: C, 60.20; H, 6.60; N, 13.20. Found: C, 59.97; H, 6.67; N, 12.98.

L-Phenylalanine Ethyl Ester. Reaction of L-phenylalanine ethyl ester (0.39 g, 2.0 mmol) afforded a trace of the isocyanate (**5**; R = $EtO_2C(PhCH_2)CH$). Flash chromatography of the product (SiO_2, 20% ethyl acetate/petroleum ether) yielded *N*-((1-(ethoxycarbonyl)-2-phenylethyl)carbamoyl)-*N*,*N*′-bis(isopropylcarboxy)hydrazine (**6**; R = $EtO_2C(PhCH_2)CH$) as a colorless oil which slowly solidified on standing (0.55 g, 64%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, 3H, J = 7.1 Hz), 1.23−1.32 (m, 12H), 3.15 (m, 2H), 4.15 (q, 2H, J = 7.1 Hz), 4.72 (m, 1H), 4.99 (overlapping septs, 2H, J = 6.2 Hz), 6.75 (bm, 1H), 7.16−7.30 (m, 5H); 8.75 (d, 1H, J = 6.0 Hz); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 14.2, 21.8, 22.0, 38.0, 55.4, 61.5, 70.3, 72.4, 127.1, 128.6, 129.5, 135.8, 152.6, 154.7, 155.3, 171.2; MS (EI) *m*/*z* 424 (M^+, <1); HRMS (EI) *m*/*z* calcd for $C_{20}H_{29}N_3O_7$ + Na 446.1904, found 446.1907.

Reactions of Unhindered Aromatic Amines with CO_2 and $^iPrO_2C-N(Bu_3P^+)-N^--CO_2{}^iPr$. 2-Isopropylaniline. Reaction of 2-isopropylaniline (0.29 g, 2.1 mmol) yielded a trace amount of isocyanate (**5**; R = 2-$^iPrC_6H_4$). Three other products carbamoylhydrazine (**6**; Ar = 2-$^iPrC_6H_4$), dicarbamoylhydrazine (**10**; Ar = 2-$^iPrC_6H_4$), and the corresponding symmetrical urea were isolated by careful chromatography (SiO_2, 20% ethyl acetate/petroleum ether). *N*,*N*′-Bis(2-isopropylphenylcarbamoyl)-*N*,*N*′-bis(isopropylcarboxy)hydrazine (**10**; Ar = 2-$^iPrC_6H_4$) was eluted first and obtained as an oil which solidified on standing (0.12 g, 11%): mp 142−145.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.27−1.35 (m, 24H), 3.15 (sept, 2H, J = 6.8 Hz), 5.13 (sept, 2H, J = 6.2 Hz), 7.12−7.32 (m, 6H), 7.79−7.84 (m, 2H), 10.35 (s, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 21.8, 21.9, 22.9,

23.1, 28.2, 72.9, 123.7, 125.6, 125.7, 126.5, 134.3, 140.0, 149.6, 154.6; HRMS (EI) *m/z* calcd for $C_{28}H_{38}N_4O_6$ 526.2791, found 526.2773. *N*-(2-Isopropylphenylcarbamoyl)-*N*,*N*′-bis(isopropylcarboxy)hydrazine (**6**; Ar = 2-^{i}PrC$_6$H$_4$) was obtained as an oil which solidified on standing (0.16 g, 20%): mp 100−102 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25 (d, 12H, J = 6.8 Hz), 1.31 (d, 6H, J = 6.3 Hz), 3.15 (sept, 1H, J = 6.8 Hz), 5.00 and 5.10 (overlapping septs, 2H, J = 6.3 Hz), 6.88 (s, 1H), 7.11−7.31 (m, 3H), 7.82 (d, 1H, J = 6.7 Hz), 10.43 (s, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 21.9, 22.0, 23.0, 28.1, 70.0, 70.4, 123.4, 125.5, 126.4, 134.3, 139.9, 151.2, 155.4, 155.7; HRMS (EI) *m/z* calcd for $C_{18}H_{27}N_3O_5$ 365.1951, found 365.1945. Further elution gave *N*,*N*′-bis(2-isopropylphenyl)urea (0.03 g, 4%): mp 220−222 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (d, 12H, J = 6.8 Hz), 3.18 (sept, 2H, J = 6.8 Hz), 7.05 (dt, 2H, J = 1.4, 7.5 Hz), 7.12 (dt, 2H, J = 1.7, 7.4 Hz), 7.26 (dd, 2H, J = 1.7, 7.7 Hz), 7.60 (dd, 2H, J = 1.4, 7.9 Hz), 8.17 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 23.1, 26.8, 123.9, 124.0, 125.2, 125.7, 135.7, 139.7, 154.0; HRMS (EI) *m/z* calcd for $C_{19}H_{24}N_2O$ 296.1889, found 296.1893.

Aniline. A trace of isocyanate (**5**; R = C_6H_5) from the reaction of aniline (0.31 g, 3.3 mmol) was indicated by IR spectroscopy of the product. Chromatography of the product (SiO_2, 20% ethyl acetate/petroleum ether) first gave carbamoylhydrazine (**6**; Ar = C_6H_5) (0.66 g, 62%) whose spectroscopic data were identical to those obtained for the sample described previously. Further elution gave *N*,*N*′-bis(phenylcarbamoyl)-*N*,*N*′-bis(isopropylcarboxy)hydrazine (**10**; Ar = C_6H_5) as a white solid (0.34 g, 23%): mp 162.5−165 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.30 (d, 12H, J = 6.2 Hz), 5.10 (sept, 2H, J = 6.3 Hz), 7.10 (bt, 2H, J = 7.5 Hz), 7.32 (bt, 4H, J = 7.5 Hz), 7.52 (bd, 4H, J = 7.6 Hz), 10.5 (bs, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 21.7, 21.8, 73.2, 120.1, 124.4, 129.1, 137.4, 148.7, 154.4; MS (EI) *m/z* 442 (M^+, 8). Anal. Calcd for $C_{22}H_{26}N_4O_6$: C, 59.72; H, 5.92; N, 12.66. Found: C, 59.60; H, 5.64; N, 12.58.

L-Phenylalanine Ethyl Ester. Reaction of L-phenylalanine ethyl ester (0.39 g, 2.0 mmol) gave the isocyanate (**5**; R = $EtO_2C(PhCH_2)CH$) as a colorless oil (0.31 g, 69%) after flash chromatography (SiO_2, 20% ethyl acetate/petroleum ether): bp 139 °C/0.8 mmHg (lit.[23] bp 96−106 °C/0.1−0.3 mmHg); IR (CH_2Cl_2) 2263 cm^{-1} (NCO); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.28 (t, 3H, J = 7.1 Hz), 3.02 (dd, 1H, J = 4.8, 13.7 Hz), 3.15 (dd, 1H, J = 7.6, 13.7 Hz), 4.23 (dd, 1H, J = 4.8, 7.6 Hz), 4.24 (q, 2H, J = 7.1 Hz), 7.17−7.33 (m, 5H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 14.2, 40.1, 58.7, 62.7, 127.2, 127.5, 128.7, 129.5, 135.7, 170.7; MS (EI) *m/z* 204 ($M^+ - CH_3$, 6); $[\alpha]^{26}_D$ −78.8° (*c* 1.0, toluene) (lit.[26] $[\alpha]^{18}_D$ −82.5° (*c* 1.0, toluene)).

^{31}P NMR Experiments. Triphenylphosphine (1.1 g, 4.2 mmol) and DIAD (0.85 g, 4.2 mmol) were reacted at −20 °C in CH_2Cl_2 (20 mL). A ^{31}P NMR spectrum was recorded at −20 °C and showed a signal at 45.2 ppm for the zwitterion. A preformed solution of the carbamate salt formed from isopropylamine (0.21 g, 3.5 mmol) and CO_2 in CH_2Cl_2 (20 mL) at −78 °C was then added. A portion was immediately cannulated into an NMR tube precooled to −78 °C and a ^{31}P NMR spectrum recorded. Only a single resonance at 28.4 ppm was observed, and the spectrum did not change on warming to ambient temperature.

A similar experiment using 2,4,6-trimethylaniline (0.29 g, 2.1 mmol) showed, after mixing at −78 °C, ^{31}P NMR resonances due to the zwitterion **4** (45.7 ppm, 40%), Ph_3PO (28.4 ppm, 26%), and further resonances at 51.3 (24%) and 50.3 and 49.1 ppm (10%). These resonances other than that due to Ph_3PO decreased slowly as the temperature was increased to −35 °C and then quickly so that at −15 °C only a single signal due to Ph_3PO was observed.

Another experiment was carried out using 2,4,6-trimethylaniline (0.29 g, 2.1 mmol) in CH_2Cl_2 (20 mL) but with the zwitterion prepared from Bu_3P (0.44 g, 2.2 mmol) and DIAD (0.44 g, 2.2 mmol) in CH_2Cl_2 (20 mL). A ^{31}P NMR spectrum of the solution after mixing at −78 °C showed a major resonance due to Bu_3PO at 53.1 ppm and a minor resonance at 76.9 ppm possibly due to a trace of zwitterion. The minor signal disappeared on warming, and the signal due to Bu_3PO remained (now 46.4 ppm at ambient temperature, lit.[15] 46.9 ppm).

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Supporting Information Available: ORTEP drawings of carbamoylhydrazine (**6**; Ar = Ph), triazolinone (**7**; Ar = Ph), and dicarbamoylhydrazine (**10**; Ar = Ph). This material is available free of charge via the Internet at http://pubs.acs.org.

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