Carbonylation of Amines by Carbon Dioxide in the Presence of an Organoantimony Catalyst[1]

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1,3-Dialkylureas (RNHCONHR; where R = Bu, *i*-Bu, *s*-Bu, *t*-Bu, allyl, Ph) and tetramethylurea were successfully prepared at 80 °C under an initial CO_2 pressure of 4.9 MPa, from the corresponding amines and carbon dioxide with catalysis by triphenylstibine oxide and assistance from tetraphosphorus decasulfide (Ph_3SbO/P_4S_{10}). Monitoring of the reaction by ^{13}C NMR revealed that the successive thiolation of carbamic acid to an intermediate antimony carbamate species and aminolysis of the carbamothioic acid thus formed constitute the reaction course. Cyclic ureas can also be synthesized by similar carbonylations of diamines ($RNHCH_2CH_2NHR'$; where R, R' = H, H; Me, H; Ph, H; $HOCH_2CH_2$, H; $HOCHMeCH_2$, H; Me, Me). Furthermore, the Ph_3SbO/P_4S_{10} catalyst system enabled the preparation of trisubstituted ureas such as 1-butyl-3,3-diethylurea by a selective cocarbonylation of butylamine and diethylamine.

Ureas have found widespread use as pesticides, pharmaceuticals, and resin precursors.[2-4] Although several synthetic routes to ureas have been studied, including carbonylation by carbon monoxide[5] and by activated carbonic derivatives[6] such as isocyanates,[7] urea,[8] phosgene,[9] carbamates,[10] and carbonates,[11] the method of direct carbonylation of amines by carbon dioxide is particularly interesting from the standpoint of environmental considerations.[6,12] It is well-known that CO_2 readily adds to amines to give the corresponding carbamic acids, even at room temperature and under ambient pressure.[12] The formation of ureas from carbamic acids, however, requires high reaction temperatures near 200 °C and pressures of CO_2 higher than 10 MPa, because the degradation of carbamic acids to isocyanates, the active intermediates, occurs only under such conditions.[2a] Although the use of certain dehydrating agents such as carbodiimides[13] and diorganophosphites[14] converts this method into a direct condensation, thus supplying a new synthetic process under mild conditions, no successful catalytic system has thus far been developed. Exceptional claims have been made regarding certain available Ru complexes,[15] but these require even higher reaction temperatures (>120 °C). Thus, we set out to develop a more effective catalyst for the carbonylation reaction and found that triphenylstibine oxide (Ph_3SbO) with assistance from tetraphosphorus decasulfide (P_4S_{10}) is an outstanding catalytic system.

Table I. Synthesis of 1,3-Dialkylureas from Amines and Carbon Dioxide[a]

starting amines (RR'NH)			
R	R'	T/°C	% yield of ureas $(RR'N)_2CO$[b]
Bu	H	80	88 (100)
i-Bu	H	80	89
s-Bu	H	80	73
t-Bu	H	80	30[c]
allyl	H	80	62[d]
Ph	H	120	48[d]
Me	Me	120	33[d-f]

[a] General reaction conditions: amine/Ph_3SbO/P_4S_{10} = 40/1.0/2.0 mmol, benzene, 20 mL, CO_2, 4.9 MPa, period, 12 h. [b] Isolated yield (HPLC yield). [c] Resinous byproduct was obtained. [d] Ph_3SbO (2.0 mmol) and P_4S_{10} (4.0 mmol) was employed. [e] Reaction period is 3 h. [f] Prolonged reaction period and higher reaction temperatures like 24 h and 160 °C, respectively, caused thionation of the ureas.

Scheme I

$$2\ RR'NH \xrightarrow[Ph_3SbO/P_4S_{10}]{CO_2} RR'NCONRR'$$

where R, R' = Bu, H; *i*-Bu, H; *s*-Bu, H; *t*-Bu, H; allyl, H; Ph, H; Me, Me

Results and Discussion

In previous papers, we reported the high catalytic activity of the Ph_3SbO/P_4S_{10} system toward direct amidation and esterification of carboxylic acids.[16] Giving the structural similarity between carboxylic and carbamic acids, it seemed reasonable to assume that the Ph_3SbO/P_4S_{10} system could act as a catalyst to promote the amidation of carbamic acid. The carbonylation of primary amines by CO_2 in the presence of Ph_3SbO/P_4S_{10} did, in fact proceed smoothly, and the corresponding 1,3-disubstituted ureas were obtained in good yields even at 80 °C (Table I). Some less basic amines such as allylamine and aniline gave the corresponding ureas in somewhat lower yields at 120 °C. Furthermore, the carbonylation of secondary amines is also accessible by increasing the amount

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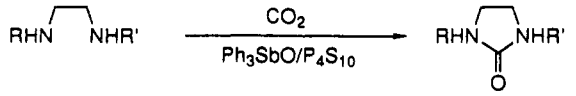
Table II. Synthesis of Cyclic Ureas from Diamines and Carbon Dioxide[a]



starting diamines R	R'	T/°C	t/h	% yield of cyclic ureas[b]
H	H	150	12	85
		150	24	0[c]
		80	24	17
Me	H	80	12	60
Ph	H	80	24	40
$HOCH_2CH_2$-	H	150	24	95
$HOCH(CH_3)CH_2$-	H	150	24	54
Me	Me	150	24	75

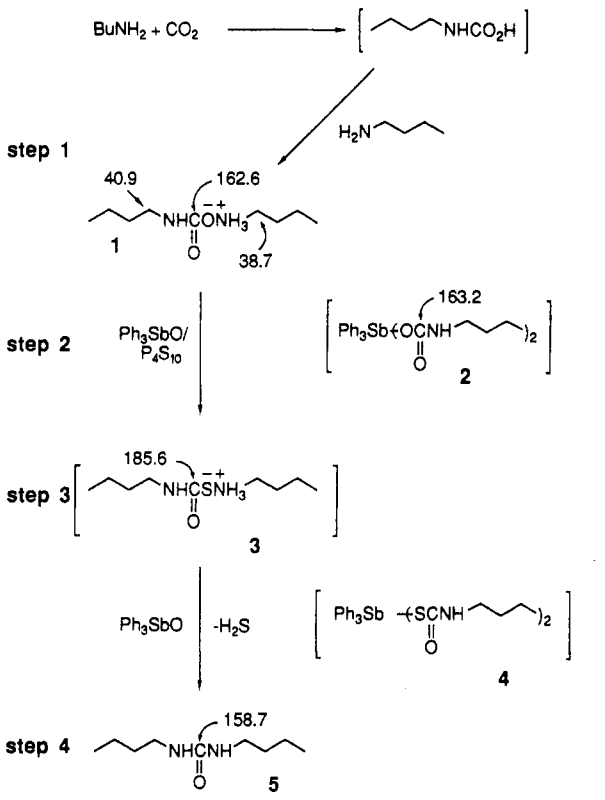
[a] Reaction conditions: diamine/Ph_3SbO/P_4S_{10} = 20/1.0/2.0 mmol, benzene 20 mL, CO_2 4.9 MPa. [b] Isolated yields. [c] Absence of the catalyst system.

of catalyst employed and shortening the reaction period in order to prevent undesirable thiolation.[1,17] For example, tetramethylurea was obtained in 33% yield at 120 °C, while the formation of thionation products such as thiourea became predominant at reaction temperatures higher than 130 °C.

We next examined the carbonylation of ethylene diamines by CO_2, with a view toward cyclic urea formation. In our earlier paper, we reported that cyclic ureas were readily prepared from *N*-methylethylenediamine or hydroxyalkylated ethylenediamines in the presence of Ph_3SbO as a catalyst,[4] but that ethylenediamine, *N*-phenylethylenediamine, and *N,N'*-dimethylethylenediamine would not react with CO_2. We now report that the modified catalyst Ph_3SbO/P_4S_{10} is highly active for the carbonylation of these diamines, and the corresponding 2-imidazolidinones were obtained at 80–150 °C (Table II). In these runs, it is interesting to note that tri- and tetrasubstituted ureas were readily obtained without thionation even at 150 °C.

By analogy to the direct amidation,[16] the carbonylation was expected to proceed through two successive steps: thiolation of carbamic acid followed by aminolysis of the carbamothioic acid thus formed. The reaction was monitored by ^{13}C NMR using a CO_2 pressure of 0.2 MPa. Absorption of CO_2 into a benzene-d_6 solution of butylamine resulted in the quantitative formation of butylammonium *N*-butylcarbamate (**1**) as shown in step 1 of Scheme II. After gentle warming of this solution at 30 °C over the catalyst, a set of signals assignable to triphenylantimony bis(butylcarbamate) (**2**), which should behave as an activated ester toward thiolation by P_4S_{10} (as did triphenylantimony dicarboxylates in the amidation process),[16a] appeared amidst those of the carbamate (step 2). Continuous heating of the mixture at 60 °C triggered the thiolation, and the signals of butylammonium *N*-butylcarbamothioate (**3**) appeared while those of **2** disappeared (step 3). The P_4S_{10} was gradually converted into partially thiolated phosphoric acid as the thiolation (or amidation) proceeded.[16a,18] Finally, the mixture was heated at 80 °C, and the intensities of the 1,3-dibutylurea signals increased (step 4). Although we could not prove from the spectra the formation of the antimony butylcarbamothioate species (**4**), the aminolysis of **3** perhaps occurs via the intermediate

Scheme II[a]



[a] Chemical shift ($\delta(^{13}C)$). Details for steps 1–4 are described in the Experimental Section.

4, as is the case in the amidation from carboxylic acids.[16] In contrast, no change was detected in the similar carbamate solution without the catalyst at 80 °C for 48 h.

These ^{13}C NMR spectral observations give support to the above-mentioned thiolation-aminolysis sequence. The catalyst Ph_3SbO should activate both the carbamic and carbamothioic acids by forming antimony esters **2** and **4**. It was indicated that carbamothioic acids are more reactive to nucleophilic attack by amines than the corresponding carbamic acid. Similarly, some thio derivatives of carboxylic and carbonic acid have been postulated to be reactive to nucleophilic substitution.[18,19]

Free isocyanate generation by the degradation of carbamate salts under severe conditions is thought to give rise to the high temperature requirement of the uncatalyzed carbonylation of amines by CO_2.[3a] In contrast, our catalytic reaction establishes a convenient urea synthesis under mild conditions and bypasses this difficulty by exploiting the aminolysis of thiol carbamic acids. Additionally, two different amines can be permitted to form the carbamate salt and thereby be incorporated into the urea. Consequently, we approached the synthesis of trisubstituted ureas by utilizing a combination of primary and secondary amines. A hypothetical reaction path is illustrated in Scheme III, wherein the formation of a mixed carbamate salt leading to the trisubstituted urea is proposed.

Scheme III. Basic Concept of Synthesis of Trisubstituted Urea

$$BuNH_2 + Et_2NH \xrightarrow{CO_2} BuNHCO_2NH_2Et_2$$

$$BuNHCO_2NH_2Et_2 \xrightarrow[Ph_3SbO/P_4S_{10}]{} BuNHCONEt_2$$

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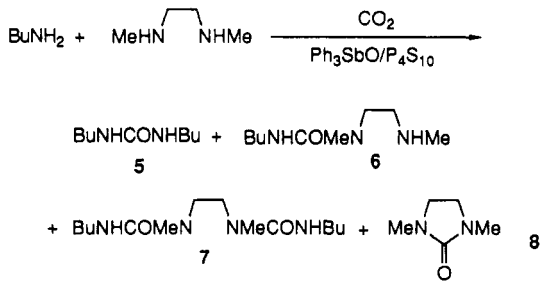
Table III. Synthesis of Trisubstituted Ureas from Butylamine and Diethylamine[a]

		% yield[b]	
T/°C	t/h	BuNHCONEt$_2$	BuNHCONHBu
120	24	39	55
100	24	34 (23)	32 (31)
	24	31[c]	3
80	48	42	1

[a] Reaction conditions: butylamine/diethylamine = 10/10 mmol, Ph_3SbO/P_4S_{10} = 1.0/2.0 mmol, benzene, 20 mL, CO_2, 4.9 MPa. [b] Yields determined by ^{13}C NMR spectra (based on butylamine). Isolated yields are also presented in parentheses. [c] Butylamine/diethyleamine = 8.0/16 mmol, Ph_3SbO/P_4S_{10} = 0.6/1.2 mmol.

Scheme IV



Although any attempt to prepare tetraethylurea from diethylamine and CO_2 failed,[20] the cocarbonylation of butylamine and diethylamine gave trisubstituted urea in good yield as shown in Table III. At higher reaction temperatures, such as 120 °C, dibutylurea was a major product but selectivity of the trisubstituted urea enormously increased with a lowering of the reaction temperature. The formation of trisubstituted urea was predominant at 80 °C. In the control reaction, dibutylurea did not react with diethylamine in either the presence or absence of the catalyst, under the same conditions. Thus, the trisubstituted urea must arise from the mixed carbamate salt, as expected. These results strongly suggest that the carbamate salt initially formed is diethylammonium butylcarbamate[21] and that the diethylamine does not escape from the carbamate moiety during the reaction. Consequently, the cocarbonylation between butylamine and diethylamine proceeded selectively under mild conditions, while a significant degree of dissociation of the carbamate salt and/or carbamic acid occurred at 120 °C, resulting in the formation of dibutylurea.

Co-carbonylation of butylamine with *N,N'*-dimethylethylenediamine (Scheme IV) was also investigated. Unfortunately, trisubstituted ureas **6** and **7** could be obtained in only low yields and selectivities. This reaction system is, however, able to give *N,N*-dimethyl-2-imidazolidinone (**8**) in good yield under milder conditions. For example, **8** could not be obtained at reaction temperatures lower than 150 °C in the direct carbonylation of *N,N*-dimethylethylenediamine, but **8** could be obtained even at 80 °C in this cocarbonylation system. Further, the yield of **8** approached 90% at 120 °C. These results suggest that a transcarbonation[4] from the butylcarbamate to the diamine plays an important role, accelerating carbonylation of the diamine via thiolation.

(20) Carbonylation of diethylamine could occur at 160 °C, but the main product was tetraethylthiourea.[1]

(21) Separately, the formation of diethylammonium butylcarbamate prepared by an absorption of CO_2 into a mixture of diethylamine and butylamine was confirmed by ^{13}C NMR spectra. Signals assignable to the mixed carbamate are as follows: δ 163.1 (s), 41.9 (t, $^1J(^{13}C^1H)$ = 137.5 Hz, Bu), 41.2 (t, $^1J(^{13}C^1H)$ = 144.4 Hz, Et), 32.4 (t), 19.9 (t), 13.6 (q, Bu), 12.7 (q, Et).

Table IV. Synthesis of Trisubstituted Ureas from Butylamine and *N,N'*-Dimethylethylenediamine[a]

	% yield[b,c]			
T/°C	5	6	7	8
150	66			94
120	44			87
100	34		16	65
	(25)[d]	(0)[d]	(10)[d]	(35)[d]
80		20	tr	19
	(0)[d]	(12)[d]	(0)	(10)[d]

[a] Reaction conditions: butylamine/*N,N'*-dimethylethylenediamine = 10/10 mmol, Ph_3SbO/P_4S_{10} = 1.0/2.0 mmol, benzene, 20 mL, CO_2, 4.9 MPa. [b] Yields determined by ^{13}C NMR spectra (based on butylamine for **5–7** and on *N,N*-dimethylethylenediamine for **8**). [c] Blank means that any signal assignable to the corresponding urea was not detected. [d] Isolated yields in parentheses.

In summary, the high catalytic activity of the Ph_3SbO/P_4S_{10} system can promote the carbonylation of several types of amines by CO_2. Thus, the preparation of a wide variety of ureas is facile under mild conditions.

Experimental Section

General Procedures. Melting and boiling points are uncorrected. ^1H and ^{13}C NMR spectra were recorded with a Hitachi R90H FT spectrometer. IR spectra were recorded with a Hitachi 260-30 spectrophotometer using KRS-5 windows or KBr pellets. High-resolution mass spectra were recorded with a JEOL JMS-DX303 with a JMA-DA5000 data processing system (Faculty of Engineering, Osaka University). Triphenylstibine oxide (Ph_3SbO) and tetraphosphorus decasulfide (P_4S_{10}) were obtained as reported.[16,18] Other reagents and solvents were used after distillation or recrystallization. All of the previously unknown ureas that were prepared in this study gave satisfactory mass spectra and elemental analyses.

Ph_3SbO-Catalyzed Carbonylation of Amines by CO_2: 1,3-Dibutylurea (5). All of the reactions under CO_2-pressured conditions were carried out in a stainless steel reactor (SUS 304, 30 mL, TVS-5 type, Taiatsu Garasu Kogyo, Co., Ltd., Tokyo). Thus, 40 mmol of butylamine (2.9 g), 1.0 mmol of Ph_3SbO (370 mg), 2.0 mmol of P_4S_{10} (890 mg), and 20 mL of benzene were charged into the reactor, and then CO_2 was introduced under a pressure of 4.9 MPa (50 kg cm^{-2}, ca. 65 mmol) at room temperature. The reactor was heated at 80 °C in a temperature-regulated incubator (80 °C) for 12 h. The heating was given in an oil bath when a reaction temperature higher than 100 °C was necessary. After the heating, the reactor was cooled and decompressed carefully. The contents were treated with hot benzene (20 mL × 3) and filtered off to remove insoluble residue containing the catalyst and phosphoric acid derivatives. The collected benzene solution was then evaporated to dryness in vacuo with cooling. Pure 1,3-dibutylurea was isolated by recrystallization from ligroin (yield 2.99 g, 88%): colorless crystals; mp 73 °C [lit.[22] mp 67–69 °C]; IR (KBr) 3300 and 1620 cm^{-1}, ^1H NMR ($CDCl_3$) δ 4.85 (bd, 2 H, N*H*), 3.08 (t, 4 H, *J* = 5.9 Hz, NHC*H*$_2$), 1.16–1.61 (m, 8 H), 0.91 (t, 6 H, *J* = 6.2 Hz); ^{13}C NMR ($CDCl_3$) δ 158.7 (s, *C*O), 40.0 (t, NHCH$_2$, 32.5 (t, β-*C*H$_2$), 20.1 (t, γ-*C*H$_2$), 13.8 (q, *C*H$_3$). Several solvents such as toluene, methylene chloride, acetonitrile, THF, and pyridine were also examined but they lowered the yields somewhat.[1] We tentatively assumed that the solubility of P_4S_{10} to the solvent considerably influences the yields because P_4S_{10} could be recovered unchanged in these runs. Thus, the following symmetrically disubstituted ureas were prepared in benzene solution under similar conditions. **1,3-Di-*sec*-butylurea**: colorless crystals; mp 136–137 °C [lit.[22] mp 135 °C]. **1,3-Diisobutylurea**: colorless crystals; mp 135 °C [lit.[22] mp 134 °C]. **1,3-Di-*tert*-butylurea**: colorless crystals; mp 248 °C [lit.[22] mp 245 °C]. **1,3-Diallylurea**: colorless crystals; mp 92 °C [lit.[22] mp 90–93 °C]. **1,3-Diphenylurea**: colorless crystals; mp 238–239 °C [lit.[23]

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mp 234-235 °C]. Similarly, tetramethylurea was prepared from dimethylamine using twice the amount of catalyst. **Tetramethylurea**: colorless oil; bp 180 °C [lit.[24] bp 176.5 °C]. **^{13}C NMR Study on the Reaction Path.** Butylamine (1.3 mmol), Ph_3SbO (0.1 mmol), P_4S_{10} (0.2 mmol), and benzene-d_6 (0.5 mL) were charged into a NMR tube, and then the tube was sealed under CO_2 (0.2 MPa at room temperature). Monitoring the carbonylation by ^{13}C NMR spectra was done in a step-by-step manner as follows: the tube was shaken in the incubator at 15 °C overnight (step 1), at 30 °C overnight (step 2), at 60 °C overnight (step 3), and at 80 °C for 24 h (step 4). Compound 1 was prepared separately by placing butylamine under CO_2 atmosphere. **Butylammonium butylcarbamate (1)**: white crystalline solid; mp dec above 80 °C; ^{13}C NMR ($CDCl_3$) δ 162.8 (s), 40.9 (t, $^1J(^{13}C^1H)$ = 133.4 Hz, CH_2NHCO_2), 38.7 (t, $^1J(^{13}C^1H)$ = 143.0 Hz, CH_2N^+), 32.2 (t, $^1J(^{13}C^1H)$ = 123.0 Hz), 30.0 (t, $^1J(^{13}C^1H)$ = 128.2 Hz), 19.5 (t, $^1J(^{13}C^1H)$ = 126.8 Hz), 13.1 (q, $^1J(^{13}C^1H)$ = 127.8 Hz). In step 1, signals of 1 were observed predominantly. New signals appeared in the mixture after step 2. These were assignable to those of triphenylantimony bis(butylcarbamate) (2) by means of the correlation of $\delta(^{13}C)$ of phenyl carbon with the nature of the ligands in triphenylantimony(V) derivatives based on the data collected by Havránek and Lyčka.[25] 2: 162.3 (s), 139.0 (s, ipso), 133.8 (d, o), 131.6 (d, p), 129.7 (d, m), 40.5 (t), 33.4 (t), 20.8 (t), 14.3 (q). Further, the generation of butylammonium *N*-butylcarbamothioate (3) was suggested by an appearance of a signal at 185.6 ppm[26] during steps 3 and 4. Finally, signals of dibutylurea were only observed after step 4.

Ph_3SbO-Catalyzed Carbonylation of Diamines by CO_2. Imidazolidinone. Ethylene diamine (20 mmol, 1.2 g) with 1.0 mmol of Ph_3SbO and 2.0 mmol of P_4S_{10} was autoclaved under pressure of CO_2 (4.9 MPa). Imidazolidinone was isolated by column chromatography (Silica gel, eluted by ethyl acetate/hexane, 1/1 in volume) (yield 1.5 g; 85%): colorless crystals; mp 130 °C [lit.[27] mp 129-131 °C]. Similarly, the following imidazolidinones were prepared from the corresponding diamines. **1-Methyl-2-imidazolidinone**: colorless crystals; mp 111-113 °C [lit.[28] mp 112 °C]. **1-Phenyl-2-imidazolidinone**: colorless crystals; mp 167 °C [lit.[29] mp 166 °C]. **1-(2-Hydroxypropyl)-2-imidazolidinone**: colorless; mp 72-73 °C; IR (KBr) 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.24 (bd, 1 H, NH), 3.88-4.07 (A_2X_3 type m, 1 H, CH), 3.30-3.80 (m, 5 H, ring CH_2 and OH), 3.17 (d, 2 H, J = 5.5 Hz), 1.17 (d, 3 H, J = 6.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 163.9 (s), 66.5 (d), 52.0 (t), 47.0 (t), 38.5 (t), 20.8 (q); MS (EI) m/z 144 (M^+). Anal. Calcd for $C_6H_{12}N_2O_2$: C, 49.99; H, 8.39; N, 19.43. Found: C, 50.00; H, 8.38; N, 19.41. **1-(2-Hydroxyethyl)-2-imidazolidinone**: colorless crystals; mp 52 °C [lit.[30] mp 53.5-57.5 °C]. **1,3-Dimethyl-2-imidazolidinone (8)**: colorless oil; bp 88 °C/1.3 kPa [lit.[31] bp 106-108 °C/2.3 kPa]; ^{13}C NMR ($CDCl_3$) δ 160.2 (s), 43.6 (t), 30.0 (q).

Synthesis of Trisubstituted Ureas. This series of reactions was carried out using 1.0 mmol of Ph_3SbO, 2.0 mmol of P_4S_{10}, 10 mmol of butylamine, and 10 mmol of diethylamine or 10 mmol of *N,N'*-dimethylethylenediamine. After the general workup the yields of the products were estimated by ^{13}C NMR spectra using benzophenone as an internal standard with respect to the predetermined calibration factors. Isolation of the ureas was accomplished by column chromatography (silica gel) eluted by hexane, ethyl acetate/hexane (1/1 in volume), ethyl acetate, methanol/ethyl acetate (1/1 in volume), and methanol, successively. **1-Butyl-3,3-diethylurea**: colorless oil; bp 150 °C/1.1 kPa; IR (KRS-5) 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.44 (bd, 1 H), 3.06-3.19 (m, 6 H), 1.32-1.43 (m, 2 H), 1.16-1.28 (m, 2 H), 1.00 (t, 6 H, J = 7.1 Hz), 0.81 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 156.7 (s), 40.1 (t), 39.8 (t), 31.9 (t), 19.4 (t), 13.1 (q); HRMS (EI) m/z 172.1562; calcd for $C_9H_{20}N_2O$ 172.1589. **1-[2-(Methylamino)ethyl]-3-butyl-1-methylurea (6)**: slightly yellow oil; bp 150-155 °C/1.3 Pa; IR (KRS-5) 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.68 (bd, 1 H), 3.07-3.31 (m, 4 H), 2.81 (s, 3 H), 2.65 (t, 2 H, J = 5.7 Hz), 2.35 (s, 3 H), 1.61 (s, 1 H), 1.15-1.45 (m, 4 H), 0.84 (t, 3 H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 158.2 (s), 50.3 (t), 49.4 (t), 40.4 (t), 36.1 (q), 34.9 (q), 32.1 (t), 19.9 (t), 13.6 (q); MS (CI) m/z 188 (M^+ + 1); Anal. Calcd for $C_9H_{21}N_3O$: C, 57.72; H, 11.30; N, 22.44. Found C, 58.00; H, 11.12; N, 22.49. ***N,N'*-Bis(butylcarbamoyl)-*N,N'*-dimethylethylenediamine (7)**: slightly yellow crystals; mp 112-114 °C: IR (KBr) 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.86 (bd, 2 H), 3.36 (s, 4 H), 3.18 (t, 4 H, J = 6.2 Hz), 2.90 (s, 6 H), 1.23-1.56 (m, 8 H), 0.92 (t, 6 H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 158.3 (s), 47.3 (t), 40.6 (t), 35.1 (q), 32.3 (t), 20.0 (t), 13.7 (q); MS (CI) m/z 287 (M^+ + 1). Anal. Calcd for $C_{14}H_{30}N_4O_2$: C, 58.74; H, 10.49; N, 19.58. Found C, 58.86; H, 10.55; N, 19.62.

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Notes

Oxidation of Aliphatic Amines by $HOF \cdot CH_3CN$ Complex Made Directly from F_2 and Water

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Recently we have developed a powerful, yet relatively stable, oxygen transfer reagent, $HOF \cdot CH_3CN$, simply by passing fluorine through aqueous acetonitrile.[1] It proved to be an effective epoxidizing agent,[2] was used for hydroxylation of tertiary unactivated C-H bonds,[3] and could convert aromatic amines into the corresponding nitroarenes.[4]

The synthesis of aliphatic nitro compounds is usually more difficult than the aromatic ones. There are a few specific methods for this purpose, some described in an

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