(22), 75 (100), 73 (100), 55 (18); HRMS calcd for $C_{11}H_{22}OSi$ 198.1440, found 198.1458.

(*E*)-(5-Hexadecenoyl)trimethylsilane: 1.05 g (87%); TLC R_f 0.88 (hexane/ethyl acetate, 19:1); VPC t_R 13.5 min (100–230 °C, 20 °C/min); ^1H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 0.7–1.0 (m, 3 H), 1.10–2.25 (m, 22 H), 2.57 (t, J = 7.0 Hz, 2 H), 5.3 (m, 2 H); IR (neat) 2900 (s), 2850 (m), 1640 (m), 1460 (w), 1250 (m), 840 (s) cm^{-1}; MS m/e (%) 310 (4.2), 183 (38), 169 (100), 101 (14), 73 (72); HRMS calcd for $C_{19}H_{38}OSi$ 310.2692, found 310.2719.

1-Methoxy-1-(trimethylsilyl)-1-undecene (3). To a solution of methoxybis(trimethylsilyl)methane (1.762 g, 9.25 mmol) in 20 mL of THF was added *n*-butyllithium/hexane (6.3 mL, 10.1 mmol) at −78 °C. The mixture was warmed up to 0 °C and stirred at this temperature for 0.5 h. After being recooled to −78 °C, decanal (1.569 g, 10.04 mmol) was added dropwise. The mixture was stirred at −78 °C for 0.5 h and warmed to room temperature. Aqueous saturated $NaHCO_3$ was added, and the organic materials were extracted with ether and dried ($MgSO_4$). After evaporation of the solvent flash chromatography (hexane/ethyl acetate, 19:1, containing 1% triethylamine) of the residue yielded the title compound (1.569 g, 84% yield). ^1H NMR spectral analysis indicated that essentially one isomer was obtained with respect to the geometry of the carbon–carbon double bond, although it was difficult to determine whether it is *E* or *Z*: TLC R_f 0.68 (hexane/ethyl acetate, 19:1); VPC t_R 7.9 min (100–230 °C, 20 °C/min); ^1H NMR ($CDCl_3$) δ 0.17 (s, 9 H), 0.7–1.0 (m, 3 H), 1.1–1.5 (m, 14 H), 1.85–2.2 (m, 2 H), 3.45 (s, 3 H), 5.15 (t, J = 7.9 Hz, 1 H); IR (neat) 2930 (s), 2850 (m), 1610 (m), 1460 (m), 1250 (s), 1190 (m), 1110 (s), 840 (s), 760 (m) cm^{-1}; MS m/e (%) 257 (1.2), 256 (5), 241 (45), 183 (22), 143 (29), 129 (16), 109 (12), 95 (45), 89 (100); HRMS calcd for $C_{15}H_{32}OSi$ 256.2222, found 256.2194.

(2-Bromoundecanoyl)trimethylsilane (4a). To a solution of *N*-bromosuccinimide (0.098 g, 0.55 mmol) in THF (1 mL) was added water (0.020 mL, 1.1 mmol). Then enol ether **3** (0.149 g, 0.57 mmol) was added at −78 °C. The mixture was stirred at this temperature for 10 min and at 0 °C for 20 min. To the resulting yellow solution was added brine. The organic materials were extracted with ether and dried ($MgSO_4$). After evaporation of the solvent the residue was purified via flash chromatography (hexane/ethyl acetate, 39:1) to obtain the title compound (0.126 g, 71%): TLC R_f 0.33 (hexane/ethyl acetate, 39:1); VPC t_R 7.9 min (100–230 °C, 20 °C/min); ^1H NMR ($CDCl_3$) δ 0.29 (s, 9 H), 0.7–1.0 (m, 3 H), 1.1–2.1 (m, 16 H), 4.44 (dd, J = 6.4 and 7.7 Hz, 1 H); IR (neat) 2950 (s), 2900 (s), 2850 (s), 1640 (m), 1460 (m), 1250 (m), 850 (s), 760 (m) cm^{-1}; MS m/e (%) 305 (5), 271 (2), 241 (41), 225 (5), 207 (8), 193 (19), 183 (11), 167 (30), 139 (7), 129 (2), 101 (27), 73 (100); HRMS calcd for $C_{13}H_{26}BrOSi$ 305.0937, found 305.0955; calcd for $C_{13}H_{26}{}^*BrOSi$ 307.0916, found 307.0929.

(2-Chloroundecanoyl)trimethylsilane (4b). To a solution of *N*-chlorosuccinimide (0.141 g, 1.06 mmol) in 5 mL of THF was added water (0.030 ml, 1.66 mmol). Then **3** (0.270 g, 1.04 mmol) was added at 0 °C, and the mixture was stirred at this temperature for 0.5 h and at room temperatue for 5 h. Brine was added, and the organic materials were extracted with ether and dried ($MgSO_4$). After evaporation of the solvent the residue was purified via flash chromatography (hexane/ethyl acetate, 39:1) to obtain the title compound (0.16 g, 56%): TLC R_f 0.44 (hexane/ethyl acetate, 19:1); VPC t_R 7.1 min (100–230 °C, 20 °C/min); ^1H NMR ($CDCl_3$) δ 0.28 (s, 9 H), 0.7–1.0 (m, 3 H), 1.1–2.0 (m, 16 H), 4.23 (dd, J = 5.5 and 7.8 Hz, 1 H); IR (neat) 2925 (s), 2850 (s), 1645 (s), 1470 (m), 1250 (s), 850 (s), 760 (m) cm^{-1}; MS m/e (%) 276 (0.5), 261 (1.0), 241 (1.6), 149 (7), 140 (43), 101 (100), 93 (76), 74 (100), 73 (100); HRMS calcd for $C_{14}H_{29}OSi^*Cl$ 278.1647, found 278.1658; calcd for $C_{14}H_{29}OSiCl$: 276.1676, found 276.1660.

(2-(Phenylseleno)undecanoyl)trimethylsilane (5). To a solution of enol ether **3** (0.506 g, 1.9 mmol) in 6 mL of CH_2Cl_2 were added methanol (0.089 mL, 2.2 mmol) and triethylamine (0.31 mL, 2.2 mmol). The mixture was cooled to −78 °C, and a solution of phenylselenenyl chloride (0.408 g, 2.1 mmol) in 4 mL of CH_2Cl_2 was added dropwise. The mixture was warmed to room temperature and stirred at this temperature overnight. Water was added, and the organic materials were extracted with ether and dried ($MgSO_4$). After evaporation of the solvent the residue was purified via flash chromatography (hexane to hexane/ethyl acetate, 9:1) to obtain the title compound (0.545 g, 72%): TLC R_f 0.48 (hexane/ethyl acetate, 19:1); VPC t_R 15.8 min (100–240 °C, 10 °C/min); ^1H NMR ($CDCl_3$) δ 0.20 (s, 9 H), 0.7–1.0 (m, 3 H), 1.1–1.7 (m, 16 H), 3.90 (t, J = 6.8 Hz, 1 H), 7.23 (m, 5 H); IR (neat) 2920 (s), 2850 (s), 1735 (w), 1635 (s), 1580 (w), 1460 (m), 1440 (m), 1250 (s), 850 (s), 740 (s), 690 (m) cm^{-1}; MS m/e (%) 398 (4.2), 383 (1.6), 321 (1.4), 310 (3.2), 285 (14), 241 (97), 230 (8), 129 (100), 103 (24), 95 (66); HRMS calcd for $C_{20}H_{34}OSiSe$ 398.1544, found 398.1550.

(*E*)-(2-Undecenoyl)trimethylsilane (6). To a solution of acylsilane **5** (0.335 g, 0.84 mmol) in 5 mL of methanol was added $NaIO_4$ (0.201 g, 0.94 mmol) at room temperature, and the mixture was stirred at this temperature for 2 h. Aqueous saturated NH_4Cl was added, and the organic materials were extracted with ether and dried ($MgSO_4$). After evaporation of the solvent the residue was purified via flash chromatography (hexane to hexane/ethyl acetate, 9:1) to obtain the title compound (0.205 g, quantitative): TLC R_f 0.40 (hexane/ethyl acetate, 19:1); VPC t_R 6.7 min (100–230 °C, 20 °C/min); ^1H NMR ($CDCl_3$) δ 0.25 (s, 9 H), 0.7–1.0 (m, 3 H), 1.1–1.65 (m, 12 H), 2.05–2.4 (m, 2 H), 6.20 (dt, J = 16.3 and 1.3 Hz, 1 H), 6.59–6.93 (m, 1 H); IR (neat) 2920 (s), 2850 (m), 1580 (m), 1250 (m), 1195 (m), 980 (w), 845 (s) cm^{-1}; MS m/e (%) 240 (2), 225 (4), 197 (4), 169 (5), 155 (26), 142 (16), 127 (15), 73 (100); HRMS calcd for $C_{14}H_{28}OSi$ 240.1910, found 240.1919.

Acknowledgment. We thank the Ministry of Education, Science and Culture, Japan, for a Grant-in-Aid for Scientific Research (No.63540408).

Supplementary Material Available: ^1H NMR spectra of methoxybis(trimethylsilyl)methane, 1-methoxy-1-(trimethylsilyl)-1-undecene, and the acylsilanes synthesized in this study (11 pages). Ordering information is given on any current masthead page.

3-Hydroxy-4-methylthiazole-2(3*H*)-thione Carbamates (TTOC Carbamates). Useful Precursors for Monoalkylaminium Cation Radicals

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Received June 13, 1990

Our group has demonstrated that Barton's powerful methodology for the production of carbon-centered radicals[1] from PTOC esters (**1**)[2] can be extended to dialkyl nitrogen-centered radicals.[3] Either neutral dialkylaminyl radicals or protonated dialkylaminium cation radicals can be produced from PTOC carbamates **2**.[2] The more reactive dialkylaminium cation radicals are synthetically useful, and good yields of products resulting from intramolecular 5-exo additions to unactivated double bonds[3b–d] or from intermolecular additions to electron-rich olefins[3e] can be realized under mild reaction conditions. We now report that nitrogen-centered radicals also can be produced from the title precursors, TTOC carbamates (**3**).[4] Dialkylaminium cation radicals are available from TTOC carbamates, but, more importantly, these precursors can be used for the

(1) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901.

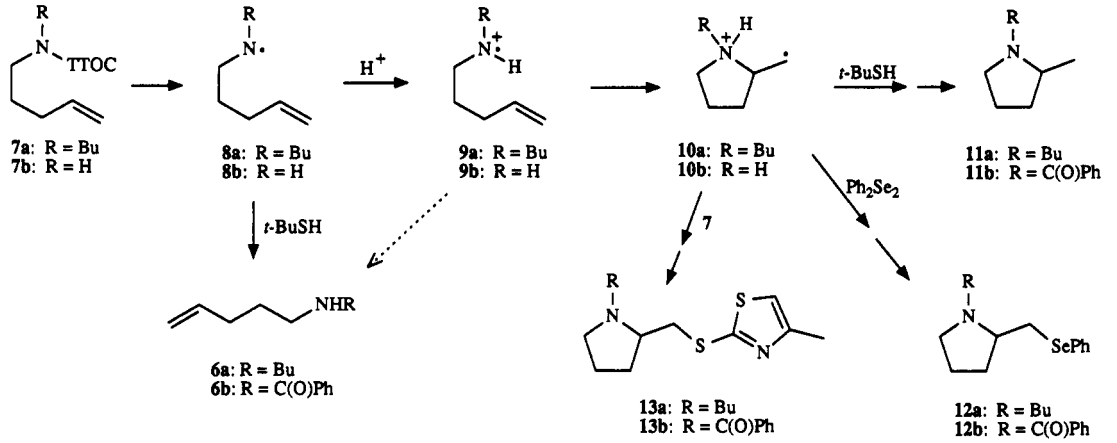
(2) PTOC is the acronym for 2-thioxopyridinyloxycarbonyl. PTOC esters and PTOC carbamates are actually mixed anhydrides of the thiohydroxamic acid with a carboxylic acid and a carbamic acid, respectively.

(3) (a) Newcomb, M.; Deeb, T. M. *J. Am. Chem. Soc.* **1987**, *109*, 3163. (b) Newcomb, M.; Deeb, T. M.; Marquardt, D. J. *Tetrahedron* **1990**, *46*, 2317. (c) Newcomb, M.; Marquardt, D. J.; Deeb, T. M. *Ibid.* **1990**, *46*, 2329. (d) Newcomb, M.; Marquardt, D. J.; Kumar, M. U. *Ibid.* **1990**, *46*, 2345. (e) Newcomb, M.; Kumar, M. U. *Tetrahedron Lett.* **1990**, *31*, 1675.

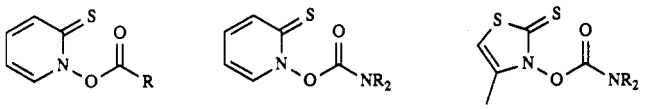
(4) TTOC for thioxothiazolyloxycarbonyl.

0022-3263/91/1956-1309$02.50/0

Scheme I



production of monoalkylaminium cation radicals, a class of reactive intermediates that cannot be prepared from PTOC carbamates.

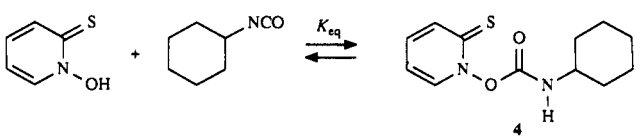


1 2 (PTOC-NR_2) 3 (TTOC-NR_2)

Monoalkylaminium cation radicals have not been studied extensively. Neale and Marcus[5] showed that monoalkylchloramines reacted in UV-initiated radical chain reactions under strongly acidic conditions (H_2SO_4, AcOH) to give monoalkylaminium cation radicals that added to simple olefins. The ultimate products of the reactions, β-chloro amines, were obtained in fair to good yields. The products and yields were comparable to those obtained when dialkylchloramines were allowed to react (via dialkylaminium cation radicals) under similar conditions.[6] Thus, one might expect that monoalkylaminium cation radicals should typically react in a manner similar to the dialkylaminium cation radicals; for example, cyclizations of δ,ϵ-unsaturated monoalkylaminium cation radicals would be expected to occur even though, apparently, none have been reported previously.

Results and Discussion

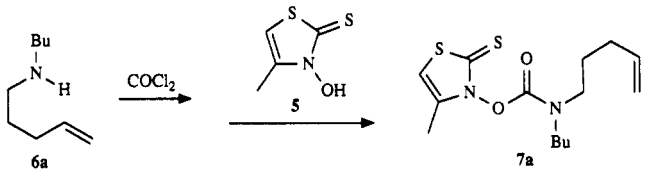
Attempts to extend the PTOC carbamate chemistry to primary aminyl systems were thwarted by the instability of the precursors. For example, PTOC carbamate **4**, which could be isolated as a crystalline solid from the reaction of cyclohexyl isocyanate with *N*-hydroxypyridine-2-thione in benzene, partially dissociated to its constituent components when dissolved in chloroform. The equilibrium constant for formation of **4** in $CDCl_3$ at 25 °C was ca. 2 M^{-1} as determined by NMR spectroscopy. With the expectation that other, less aromatic, thiohydroxamic acid derivatives would form more stable mixed anhydrides of primary carbamic acids, we have explored the use of TTOC carbamates that incorporate 3-hydroxy-4-methylthiazole-2(3*H*)-thione (**5**).[7]



4

(5) Neale, R. S.; Marcus, N. L. *J. Org. Chem.* **1963**, *33*, 3457.
(6) Neale, R. S. *Synthesis* **1971**, 1.

Dialkylaminyl Radicals and Dialkylaminium Cation Radicals. Insight into the general properties of TTOC carbamates was obtained from reactions of a TTOC precursor that provided a dialkylaminyl radical that can also be produced by other methods. Treatment of amine **6a** with phosgene gave the corresponding carbamoyl chloride in 87% yield after distillation. Subsequent reaction of the carbamoyl chloride with thione **5** gave TTOC carbamate **7a** in 89% yield.



6a 5 7a

TTOC **7a** is a precursor to the *N*-butyl-4-pentenaminyl radical (**8a**), and reactions of this system, produced from the corresponding PTOC precursor, have been studied extensively by our group.[3a-d] The chain reaction steps for radical **8a** are shown in Scheme I. Under neutral conditions, aminyl radical **8a** reacts with *t*-BuSH to give acyclic amine **6a**. However, under mildly acidic conditions, the aminyl radical is protonated to give aminium cation radical **9a** that cyclizes in a 5-exo fashion to give radical **10a**. In the presence of the trapping agents *t*-BuSH or Ph_2Se_2, the cyclic radical **10a** reacts by group transfer to give, ultimately, *N*-butyl-2-methylpyrrolidine (**11a**) or *N*-butyl-2-(phenylselenomethyl)pyrrolidine (**12a**), respectively. In these cases, the *t*-BuS$^\bullet$ and PhSe$^\bullet$ radicals can react with the precursor in a chain propagation step. In the absence of trapping agents, cyclic radical **10a** will react with its PTOC precursor to give, ultimately, a substituted pyrrolidine product; based on Barton's results,[8] one should expect that cyclic radical **10a** also will react with its TTOC precursor to give the substituted pyrrolidine **13a**.

Reactions of TTOC **7a** in CH_3CN in the presence of malonic acid and either *t*-BuSH or Ph_2Se_2 were conducted. Product yields, determined by GC, are collected in Table I. For comparison, the product yields obtained from reactions of the PTOC precursor **14** under similar conditions[3b-e] are included in Table I. A notable difference in the reaction procedures for the two precursors is the me-

(7) Mixed anhydrides of a carboxylic acid and thiohydroxamic acid **5** comprise another class of Barton's carbon radical precursors.[8] They react in a manner similar to the PTOC esters **1**, although the absence of an absorbance in the visible region precludes visible light initiation of radical chain reactions.
(8) Barton, D. H. R.; Crich, D.; Kretzschmar, G. *J. Chem. Soc., Perkin Trans. 1*, **1986**, 39.

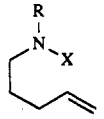
Table I. Products from Reactions of TTOC 7a and PTOC 14[a]

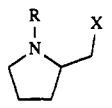
entry	precursor	conc[b] (M)	[t-BuSH] (M)	[Ph_2Se_2] (M)	% yield 6a	11a	12a	13a (15)
1	7a	0.1	0.5		<2	70		7
2	14	0.05	0.7			84		12
3	14	0.05	2.2			92		5
4	7a	0.1	0					53
5	7a	0.1	0.01			10		80
6	14	0.05	0					92
7	7a	0.1		0.2	0		48	0
8	14	0.1		0.2			85	

[a] All reactions were run at 25 °C in CH_3CN containing 3 equiv of malonic acid. Reactions of 7a are from this work; reactions of 14 are from refs 3b–d. [b] Initial concentration of precursor.

thod of radical initiation. UV irradiation was required to initiate reactions of the TTOC precursor whereas visible irradiation served to initiate reactions of the PTOC precursor. Another apparent difference involved the reaction times; typically, PTOC precursors have been found to be consumed within minutes, but the TTOC precursor appeared to be consumed less rapidly. We do not know the quantum efficiency of the processes, but, qualitatively, reactions of TTOC precursors seem to be less efficient than those of PTOC precursors. This observation, and other evidence discussed below, suggests that propagation reactions involving radical attack of the TTOC precursor are not as facile as those for the PTOC precursors.

From Table I, one can see that the TTOC and PTOC precursor gave comparable results when t-BuSH was present. In the absence of t-BuSH, the highly efficient self-trapping of radical **10a** by PTOC precursor **14** to give sulfide **15** (entry 6) was not paralleled by TTOC **7a** (entry 4); however, a good yield of self-trapped product **13a** was obtained when a small amount of t-BuSH was present (entry 5). The origin of this effect is not clear, but we suspect that radical chain lengths with the TTOC precursor were not long and that the thiol might promote radical reactions by scavenging (or preventing the formation of) UV absorbing byproducts.





14: R = Bu, X = PTOC
16: R = Pr, X = Cl
17: R = Me, X = NO

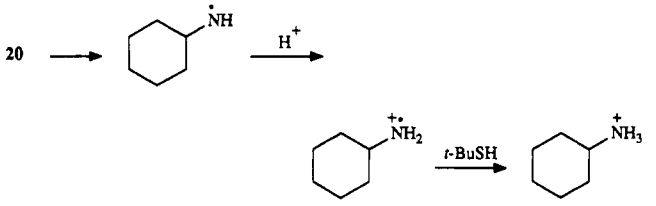
15: R = Bu, X = S-2-pyridyl
18: R = Pr, X = Cl
19: R = Me, X = (=NOH)

The Ph_2Se_2 results also suggest that the chain lengths were short in the TTOC reactions. Ph_2Se_2 is known to capture cyclic radical **10a** quite efficiently, and the PhSe• radical readily propagates chain reactions with PTOC carbamate precursors.[3d] Ultimately, excellent yields of phenylseleno-substituted products can result from the PTOC reactions[3d] (cf. entry 8). The reduced yield of **12a** from the reaction of TTOC **7a** (entry 7) most likely resulted from an inefficent chain propagation step involving attack of PhSe• on the precursor.

Other routes to dialkylaminium cation radicals related to **10a** include reactions of the N-chloramine **16** and the N-nitrosamine **17**. These precursors react under strongly acidic conditions to give, ultimately, pyrrolidines **18** (70–81%)[9a,b] and **19** (82%),[9c] respectively. It would appear that the various dialkylaminium cation radical precursors are nearly equally efficient radical sources, but the PTOC ad

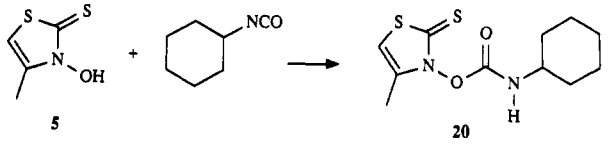
(9) (a) Surzur, J.-M.; Stella, L.; Tordo, P. *Tetrahedron Lett.* **1970**, 3107. (b) Surzur, J.-M.; Stella, L.; Tordo, P. *Bull. Soc. Chim. Fr.* **1970**, 115. (c) Chow, Y. L.; Perry, R. A.; Menon, B. C.; Chen, S. C. *Tetrahedron Lett.* **1971**, 1545.

Scheme II



TTOC derivatives offer the advantages of significantly milder reaction conditions and selection from a variety of radical trapping agents. For dialkylaminyl radicals or dialkylaminium cation radicals, the TTOC precursors should be considered to be generally inferior to the PTOC precursors primarily because chain reactions of the PTOC precursors can be initiated by visible irradiation; in addition, chain propagation steps involving attack of the PTOC precursor appear to be more facile than those of the TTOC precursor.

Monoalkylaminium Cation Radicals. As noted in the introduction, the PTOC methodology could not be extended to primary nitrogen radical systems due to instability of the precursors. However, TTOC precursors to primary nitrogen radicals were substantially more stable. Reaction of cyclohexyl isocyanate with thione **5** gave TTOC carbamate **20** in 74% yield. Unlike PTOC **4**, TTOC **20** appeared to be stable in chloroform solutions as judged by IR and NMR spectroscopy and even survived a mild base workup.



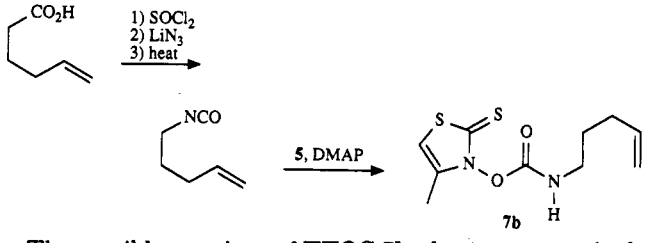
5 20

Despite its stability toward mild base, when TTOC **20** was treated with cyclohexylamine, dicyclohexylurea was obtained in 72% yield. Presumably, a simple base-catalyzed elimination reaction gave cyclohexyl isocyanate that reacted with the amine to give the urea. This result indicates that attempts to produce monoalkylaminyl radicals from reactions of TTOC precursors under neutral conditions will be complicated by secondary reactions of the product amines with the TTOC precursors. Indeed, the expectation was confirmed; when TTOC was allowed to react in the presence of t-BuSH, dicyclohexylurea was the major product.

However, the protonated aminium cation radicals are significantly more attractive synthetic intermediates than aminyl radicals due to their high reactivity.[3b] When TTOC **20** was allowed to react in CH_3CN in the presence of malonic acid and t-BuSH, cyclohexylamine (identified as its benzamide derivative) was produced in 85% yield as determined by GC. We have firmly established that di-

alkylaminyl radicals are completely protonated under these reaction conditions,[3b] so the most likely course of the reaction involves protonation of the cyclohexylaminyl radical gave the cyclohexylaminium cation radical that reacted with *t*-BuSH to give cyclohexylammonium ion. The *t*-BuS• thus formed added to TTOC **20** in a chain propagation step (Scheme II).

A primary aminium cation radical capable of cyclizing also was studied. 5-Hexenoic acid was converted to its acid chloride and then to 4-pentenyl isocyanate via a Curtius rearrangement. The isocyanate was then treated with thione **5** and a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) to give TTOC carbamate **7b** in 67% yield from the carboxylic acid.



7b

The possible reactions of TTOC **7b**, the 4-pentenaminyl radical (**8b**), and the 4-pentenaminium cation radical (**9b**) are the same as those shown in Scheme I for the dialkylaminyl case. Protonation of the neutral radical **8b** by malonic acid was expected to be complete based on the results with dialkylaminyl radicals.[3b] The cyclization of the primary aminium cation radical **9b** was expected to be efficient, again based on analogy to the reactions of dialkylaminium cation radicals,[3a-d] although, to the best of our knowledge, no such reaction of a monoalkylaminium cation radical has been reported.

A mixture of TTOC carbamate **7b**, malonic acid, and *t*-BuSH in dry CH_3CN at 25 °C was irradiated with a low-power UV lamp, and the crude product mixture obtained on workup was treated with benzoyl chloride. Chromatography gave the benzamide of 2-methylpyrrolidine (**11b**) in 78% isolated yield; small amounts of products **6b** and **13b** were detected in the product mixture by GC. The isolation of pyrrolidine **11b** in high yield confirms the expected reaction sequence in Scheme I and demonstrates the utility of TTOC carbamates as precursors for primary aminium cation radicals.

In another reaction of TTOC carbamate **7b**, Ph_2Se_2 was employed as a radical trapping agent. Treatment of the crude products with benzoyl chloride and GC analysis indicated the formation of the 4-pentenamide **6b** in 30% yield and *N*-benzoyl-2-[(phenylseleno)methyl]pyrrolidine (**12b**) in 40% yield. Apparently, the poor yield of cyclic product **12b** obtained in this reaction reflects an inefficient radical propagation reaction similar to that seen in the reaction of TTOC **7a** with Ph_2Se_2. We presume that the acyclic product arose mainly from decomposition of the precursor at extended reaction times.

TTOC carbamates containing a primary amine group would appear to be the most useful precursors for monoalkylaminium cation radicals now available. The corresponding PTOC carbamates are not stable, and the reaction conditions necessary for the production of chloramines from amines and for the generation of monoalkylaminium cation radicals from chloramines are substantially more severe than those required for production and reactions of TTOC carbamates. The TTOC carbamate precursors to monoalkylaminium cation radicals are readily prepared from isocyanates, and 5-exo cyclizations of δ,ε-unsaturated monoalkylaminium cation radicals can be realized using the TTOC protocol.

Experimental Section

General. Reagents were purchased from Aldrich Chemical Co. and used as received unless noted. *N*-Hydroxypyridine-2-thione was obtained from the corresponding sodium salt (Olin, sodium Omadine) as previously described.[3b] Thione **5** was prepared by the method of Barton.[8] Benzene and Et_3N were distilled from CaH_2 under N_2. THF was distilled from sodium benzophenone under N_2. Toluene, acetonitrile, pentane, and hexanes were dried over 4A molecular sieves. GC analysis were performed with a flame ionization detector equipped instrument on a 15 m J&B Scientific DB-17 wide bore capillary column. ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions containing Me_4Si were obtained at 200 and 50 MHz, respectively. Melting points are uncorrected.

1-[(Cyclohexylcarbamoyl)oxy]-2(1*H*)-pyridinethione (4). To a stirred solution of *N*-hydroxypyridine-2-thione (252 mg, 1.98 mmol) and ca. 5 mg of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) in 20 mL of dry benzene was added cyclohexyl isocyanate (250 μL, 2.0 mmol). The solution was allowed to stir at 25 °C for 5 h, and the light yellow precipitate that formed was isolated by filtration and washed with pentane to give 288 mg (57%) of **4**: mp 118–119 °C. Anal. Calcd for $C_{12}H_{16}N_2O_2S$: C, 57.12; H, 6.39. Found: C, 57.42; H, 6.43.

IR and NMR spectra of solutions of **4** in $CDCl_3$ contained signals from **4**, cyclohexyl isocyanate, and *N*-hydroxypyridine-2-thione.

3-[[Butyl(4-pentenyl)carbamoyl]oxy]-4-methylthiazole-2(3*H*)-thione (7a). The carbamoyl chloride was prepared by a modification of the method of Boon.[10] A solution containing 40 mL of 1.9 M phosgene (76 mmol) in toluene and an additional 200 mL of toluene was cooled to ca. −15 °C. To this was added over 15 min a solution of 5.31 g (37.6 mmol) of *N*-butyl-4-pentenamine[3b] and 5.3 mL (38 mmol) of Et_3N in 40 mL of toluene. The mixture was allowed to warm to room temperature, and the reaction was stirred for 18 h. Toluene and excess phosgene were distilled. The residue was distilled to give 6.67 g (32.7 mmol, 87%) of the carbamoyl chloride as a colorless liquid: bp 98 °C (0.1 Torr). NMR spectra were complicated by the presence of two rotamers. ^1H NMR: δ 5.8 (m, 1 H), 5.0 (m, 2 H), 3.40 (t, 2 H, J = 5 Hz), 3.32 (t, 2 H, J = 5 Hz), 2.1 (br d, 2 H, $J \approx 8$ Hz), 1.72 (quin, 2 H, J = 5 Hz), 1.59 (quin, 2 H, J = 5 Hz), 1.32 (m, 2 H), 0.92 and 0.96 (2 overlapping t, 3 H, $J \sim 7$ Hz). ^{13}C NMR: δ 148.8, 137.1, 136.9, 115.4, 115.2, 51.0, 50.5, 49.6, 49.3, 30.6, 30.4, 29.4, 27.3, 26.4, 19.7, 13.6. Exact mass: calcd for $C_{10}H_{18}NOCl$ m/e 203.10769, found m/e 203.10784.

The above sample of carbamoyl chloride was added to a stirred solution of thione **5** (4.97 g, 33.8 mmol), DMAP (0.2 g), and Et_3N (8.4 mL, 60.3 mmol) in 240 mL of CH_3CN. After 12 h at 25 °C, the CH_3CN was distilled at reduced pressure, and the residue was dissolved in 200 mL of CH_2Cl_2. The resulting solution was extracted with 150 mL of 10% aqueous $KHSO_4$, 150 mL of saturated aqueous $NaHCO_3$, and 100 mL of saturated aqueous NaCl. The solution was dried ($MgSO_4$), and the solvent was distilled to give a green oil. Filtration chromatography through a 30 × 25 mm column of silica gel (CH_2Cl_2 elution) and distillation of the solvent in vacuo gave 9.18 g (29.2 mmol, 89%) of carbamate **7a** as a light yellow oil. IR ($CDCl_3$): 1724, 1594, 1636 cm^{-1}. NMR spectra were complicated by the the presence of two rotamers. ^1H NMR: δ 6.25 (s, 1 H), 5.81 (m, 1 H), 5.06 (m, 2 H), 3.21–3.77 (m, 4 H), 2.20 (s, 3 H), 2.12 (m, 2 H), 1.70 (m, 4 H), 1.37 (m, 2 H), 0.94 and 0.97 (2 overlapping t, 3 H, $J \sim 7$ Hz). ^{13}C NMR: δ 180.6, 151.1, 137.6, 137.2, 137.1, 115.1, 115.0, 101.7, 48.6, 48.3, 47.4, 47.0, 30.6, 30.4, 29.4, 27.4, 26.4, 19.7, 19.5, 13.6, 13.5, 13.1. Anal. Calcd for $C_{14}H_{22}N_2O_2S_2$: C, 53.47; H, 7.05. Found: C, 53.66, 52.90; H, 7.23, 7.14. The scatter in analytical results on repeat analyses of one sample suggests that the compound might have decomposed in handling.

3-[(Cyclohexylcarbamoyl)oxy]-4-methylthiazole-2(3*H*)-thione (20). To a stirred solution of 100 mg (0.68 mmol) of thione **5** and ca. 5 mg of DMAP in 10 mL of benzene was added 86 μL (0.67 mmol) of cyclohexyl isocyanate. A precipitate formed. The mixture was stirred at 25 °C for 18 h. CH_2Cl_3 (20 mL) was added to give a solution. The mixture was extracted with 20 mL of 10% aqueous $KHSO_4$, 20 mL of saturated aqueous $NaHCO_3$, and 15

(10) Boon, W. R. *J. Chem. Soc.* **1947**, 307.

mL of saturated aqueous NaCl. The solution was dried ($MgSO_4$), and the solvent was distilled at reduced pressure to give 137 mg (0.5 mmol, 74%) of carbamate **20** as a residue that solidified on standing to give an off-white solid. Mp: 124–125 °C. IR ($CDCl_3$): 3424, 1768, 1600 cm^{-1}. ^1H NMR: δ 6.23 (s, 1 H), 5.50 (br d, 1 H, $J \sim 6$ Hz), 3.50–3.77 (m, 1 H), 2.22 (s, 3 H), 1.1–2.1 (m, 10 H). ^{13}C NMR: δ 181.4, 150.6, 138.1, 102.0, 51.3, 32.5, 24.9, 24.3, 13.0. Anal. Calcd for $C_{11}H_{16}N_2O_2S_2$: C, 48.51; H, 5.92. Found: C, 49.20, 49.34; H, 6.14, 6.15. We note the high value for carbon in the analysis.

3-[[(4-Pentenyl)carbamoyl]oxy]-4-methylthiazole-2-(3*H*)-thione (7b). To a stirred solution of 2.14 g (21.6 mmol) of 5-hexenoic acid[11] in 250 mL of benzene were added 2.34 mL (32.1 mmol) of thionyl chloride and 0.1 mL of DMF. The solution was stirred at 25 °C for 18 h. Most of the benzene was distilled to give a light brown residual oil. The residue was dissolved in 250 mL of THF, and 1.11 g (20.4 mmol) of LiN_3 was added to the solution. The mixture was stirred at 25 °C for 18 h and then heated at reflux for 0.5 h. To the cooled solution was added 3.00 g (20.4 mmol) of thione **5** and 25 mg of DMAP. Stirring was continued for 18 h; the solution developed a faint blue color. Solvent was distilled at reduced pressure, and the residue was dissolved in 100 mL of CH_2Cl_2. The solution was extracted with 70 mL of 10% aqueous $KHSO_4$, 50 mL of saturated aqueous $NaHCO_3$, and 50 mL of saturated aqueous NaCl. The solution was dried ($MgSO_4$), and the solvent was distilled at reduced pressure to give a light blue oil as a residue. Pentane (25 mL) and ether (5 mL) were added to the residual oil, and the mixture was stirred vigorously; carbamate **7b** precipitated. Filtration gave 3.30 g (12.8 mmol, 67%) of **7b** as a light blue solid. Mp: 62–63 °C. IR ($CDCl_3$): 3439, 1768, 1644, 1598 cm^{-1}. ^1H NMR: δ 6.26 (s, 1 H), 5.7–6.0 (m, 2 H), 5.04 (m, 2 H), 3.33 and 3.30 (2 overlapping t, 2 H, $J \sim 6$ Hz), 2.22 (s, 3 H), 2.17 and 2.13 (2 overlapping t, 2 H, $J \sim 7$ Hz), 1.70 (m, 2 H). ^{13}C NMR: δ 181.3, 151.5, 138.1, 137.4, 115.6, 102.3, 41.5, 30.7, 28.6, 13.5. Anal. Calcd for $C_{10}H_{14}N_2O_2S_2$: C, 46.49; H, 5.46. Found: C, 47.05, 47.03; H, 5.38, 5.53. We note the high value for carbon in the analysis.

Reactions of TTOC Carbamate 7a. Carbamate **7a** (314 mg, 1.0 mmol), malonic acid (320 mg, 3 mmol), and the appropriate amount of Ph_2Se_2 (if desired) were placed in a quartz tube. The tube was sealed with a septum and flushed with N_2, and 10 mL of CH_3CN and the appropriate amount of *t*-BuSH (if desired) were added. The resulting solution was irradiated with a 6-W UV lamp (thiol reactions) or a 450-W high-pressure Hg lamp (Ph_2Se_2 reaction) at a distance of ca. 12 cm for 48 h (thiol) or 3.5 h (Ph_2Se_2). The resulting mixture was diluted with 10 mL of THF. Solid KOH (ca. 25 mg) and 0.3 mL of 50% aqueous NaOH were added, and the mixture was stirred for ca. 0.2 h. $MgSO_4$ was added, and the mixture was filtered through a 25 × 10 mm column containing basic alumina (THF elution). Hexadecane (75 μL) was added, and the yields of products in the resulting solution were determined by quantitative GC. The identities of **6a**, **11a**, and **12a** were determined by co-injection with authentic samples.[3b,d]

***N*-Butyl-2-[[(4-methylthiazol-2-yl)thio]methyl]pyrrolidine (13a)** was obtained in 80% yield from a reaction as a described above with 0.1 equiv of *t*-BuSH. The product mixture was subjected to high vacuum to remove **11a**; product **13a** remained as a light brown oil. ^1H NMR: δ 6.72 (s, 1 H), 3.48 (dd, 1 H, J = 3, 13 Hz), 3.14 (dd, 2 H, J = 8, 13 Hz), 2.40 (s, 3 H), 2.20 (m, 2 H), 1.74 (m, 4 H), 1.42 (m, 4 H), 0.93 (t, 3 H, J = 7 Hz). ^{13}C NMR: δ 164.7, 152.9, 112.8, 63.1, 54.5, 54.3, 39.3, 31.0, 30.3, 22.7, 20.8, 17.2, 14.1. Exact mass: calcd for $C_{13}H_{22}N_2S_2$ m/e 270.1224, found m/e 270.1201.

Reactions of TTOC Carbamates 7b and 20. The reactions were run by the same methods as described above for reactions of **7a** to the point of product isolation. The reaction was extracted with 25 mL of 10% aqueous $KHSO_4$. Excess 50% aqueous NaOH was added to the crude reaction mixtures in CH_2Cl_2. The mixtures were cooled to 0 °C, and benzoyl chloride (1.1–1.5 equiv) was added. After 12 h, the phases were separated, and the solvent was distilled from the organic phase. The residual oil was analyzed by quantitative GC; product yields were calculated from predetermined response factors or, for **13b**, with an estimated response factor. *N*-cyclohexylbenzamide (from **20**) was identified by comparison to an authentic sample.

***N*-Benzoyl-2-methylpyrrolidine (11b).** The residual product mixture from the reaction of **7b** in the presence of *t*-BuSH was purified by preparative TLC on silica gel with a 6:1 (v:v) mixture of CCl_4 and ethyl acetate as developing solvent. Amide **11b** was obtained as an oil in 78% yield. The identity of the product was confirmed by comparison to an authentic sample prepared from commercial 5-methyl-2-pyrrolidinone by $LiAlH_4$ reduction and treatment of the crude amine product with benzoyl chloride. ^1H NMR: δ 7.44 (m, 5 H), 3.9–4.4 (complex m, 1 H), 1.5–2.2 (complex m, 4 H), 1.37 (d, 3 H, J = 7 Hz). ^{13}C NMR: δ 169.9, 129.7, 128.3, 128.2, 127.2, 53.0, 49.7, 32.6, 24.7, 19.6.

***N*-Benzoyl-2-[(phenylseleno)methyl]pyrrolidine (12b).** The residual product mixture from the reaction of **7b** in the presence of Ph_2Se_2 was purified by chromatography as above. Product **12b** was obtained in 25% yield as an oil. ^{13}C NMR: δ 170.4, 137.1, 131.6, 130.2, 129.3, 128.3, 127.5, 126.6, 57.3, 50.9, 30.6, 30.5, 25.0. Exact mass: calcd for $C_{18}H_{19}NOSe$ m/e 345.0632, found m/e 345.0636.

2-[[(4-Methylthiazol-2-yl)thio]methyl]pyrrolidine. A pure sample of the benzamide **13b** was not obtained, but the product identity was confirmed for the benzyloxycarbonyl (CBZ) derivative. A reaction of TTOC **7b** conducted in the presence of 0.1 equiv of *t*-BuSH was worked up as described above. The crude product mixture was treated with benzyl chloroformate in a reaction similar to that described above for benzoyl chloride functionalization. Preparative TLC (silica gel, 10:1 hexanes–ethyl acetate development) gave the CBZ derivative in 20% yield. ^1H NMR: δ 7.35 (m, 5 H), 6.7 and 6.8 (2 br s, 1 H), 5.14 (s, 2 H), 4.19 (m, 1 H), 3.1–3.7 (complex m, 4 H), 2.37 (d, 3 H, J = 5 Hz), 1.91 (complex m, 4 H). ^{13}C NMR: δ 154.8, 153.0, 136.7, 130.9, 128.8, 128.5, 128.2, 128.0, 127.8, 113.7, 67.0, 66.8, 57.4, 56.6, 47.2, 38.0, 37.4, 30.3, 29.6, 23.8, 22.9, 17.2. Exact mass: calcd for $C_{17}H_{20}N_2O_{S2}$: m/e 348.0966. Found: m/e 348.0952.

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of compounds **12b**, **13a**, and the CBZ derivative of 2-[[(4-methylthiazolyl-2-yl)thio]methyl]pyrrolidine (6 pages). Ordering information is given on any current masthead page.

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The Influence of Microwaves on the Rate of Reaction of Propan-1-ol with Ethanoic Acid

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Recent reports have suggested that the rates of some chemical reactions are accelerated by microwave irradiation. Rate enhancement factors between five and over one thousand, in comparison to classical methods of heating, have been recorded.[1-4] The majority of the reactions where rate enhancement has been observed were carried out in sealed polytetrafluoroethylene vessels. From the information published, it is not possible to separate the

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