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N-HYDROXYPYRIDINE-2-THIONE CARBAMATES. V. SYNTHESES OF ALKALOID SKELETONS BY AMINIUM CATION RADICAL CYCLIZATIONS

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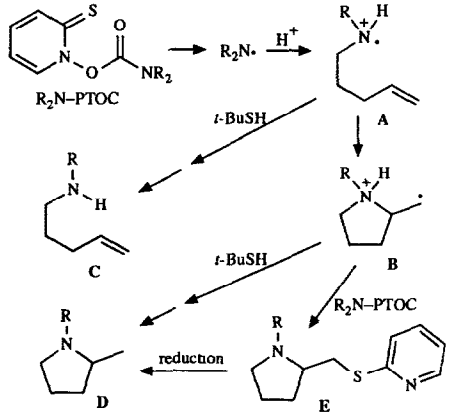
Abstract: The title radical precursors (PTOC carbamates) were employed as sources of a variety of 5,6-unsaturated aminium cation radicals. 5-*Exo* radical cyclization followed by trapping by *t*-BuSH or the PTOC carbamate gave a variety of aklaloid skeletons, typically in good to excellent yields, including pyrrolidines, perhydroindoles, pyrrolizidines, tropanes, 9-azabicyclo[4.2.1]nonanes, 6-azabicyclo[3.2.1]octanes. 6-*Exo* and 7-*endo* cyclizations competed in a 6,7-unsaturated system.

In the preceding paper we showed that *N*-hydroxypyridine-2-thione carbamates (PTOC carbamates) were useful precursors for aminyl radicals and aminium cation radicals.[1] The simple δ,ε-unsaturated radicals from a 4-pentenylamine were found to cyclize in a 5-*exo* fashion, and the aminium cation radical was shown to be significantly more efficient in cyclization than the neutral aminyl radical. In this paper we report the results of studies aimed at determining the general utility of PTOC carbamates as precursors for aminium cation radicals that can cyclize to give nitrogen-containing heterocycles. PTOC carbamates have been prepared from a variety of amines so that several "types" of cyclizations could be explored. Some of these cyclizations have been reported previously for aminium cation radicals prepared from *N*-chloramines or *N*-nitrosamines, and, in these cases, our results permit a direct comparison of the PTOC carbamate route to aminium cation radicals with alternate routes.

Most of the PTOC carbamates employed in this study were prepared from simple amines that were synthesized according to literature procedures with minor variations. For the more unusual amines, a brief description of the preparation is given, and details of the preparations are presented in the experimental section. The PTOC carbamate precursors were prepared in 68 to 85% yields as pure compounds after recrystallization or chromatography. Generally, the PTOC carbamates were obtained as crystalline solids. We have found that acetonitrile solvent containing malonic acid was a good medium for the cyclization of the *N*-butyl-4-pentenaminyl system.[1] For most of the cyclizations studied here, we used this solvent–acid system although acetic acid and trifluroacetic acid were employed for protonations in some cases. Radical chain reactions were initiated by photolysis with a tungsten filament lamp, and reactions were typically run at room temperature.

Scheme 1



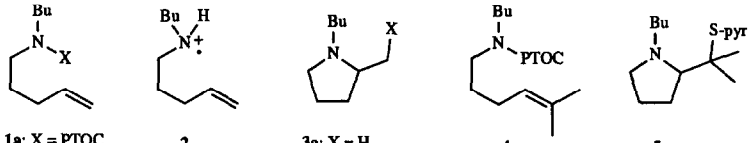
The general course of the reactions is illustrated in Scheme 1. A dialkylaminyl radical formed from the

PTOC carbamate precursor in a radical chain reaction was protonated to give an aminium cation radical (**A**). This radical cyclized to give carbon-centered radical **B**. When *t*-BuSH was present in the reaction medium, it served to trap radical **B** giving **D**, and, in some cases, the thiol also reacted with the aminium cation radical in competition with the cyclization to give amine **C**. In the absence of thiol, the carbon radical **B** reacted with the PTOC precursor to give a 2-pyridyl alkyl sulfide, the so-called "self-trapped" product (**E**). Because the nitrogen-centered radicals do not react with the PTOC carbamate precursors, good yields of self-trapped products often could be obtained in the absence of thiol even in cases where poor yields of cyclic products were obtained when the thiol was present. The thiopyridyl group can be removed by reduction,[2] so, in principle, the two protocols can give the same product **D**.

Below we discuss details of the cyclization reactions and, for most of the systems, optimized conditions for obtaining cyclic products. Wherever possible, comparisons are made with the results of previous studies that employed other routes to aminium cation radicals. The results are summarized in a table that appears at the end of the discussion.

Preparation of Pyrrolidines

Several examples of cyclizations of 4-pentenaminyl radicals and the corresponding aminium cation radicals to give, ultimately, simple pyrrolidines have been reported. Aminyl radicals have been produced by thermolysis or photolysis of symmetrical tetrazenes[3] and by anodic oxidation of lithium dialkylamides.[4] *N*-Chloramines[5] and *N*-nitrosamines[6] have been employed as aminium cation radical precursors. The best yields of cyclic products were obtained from the *N*-chloramines.



1a: X = PTOC
b: X = H

2

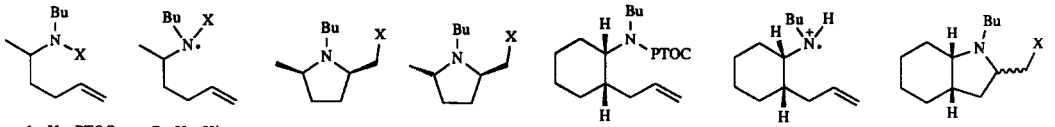
3a: X = H
b: X = S-pyr

4

5

The 5-*exo* cyclization of the *N*-butyl-4-pentenaminium cation radical (**2**) formed from carbamate **1a** was extensively studied in the preceding paper.[1] Radical **2** cyclized efficiently, and no acyclic amine **1b** was detected by GC analysis of the reaction products. The isolated yields of pyrrolidine **3a** (73%) from reaction in the presence of *t*-BuSH and pyrrolidine **3b** (92%) from reaction in the absence of *t*-BuSH can be compared to the reported 70-81% yields of *N*-propyl-2-(chloromethyl)pyrrolidine obtained from the corresponding acyclic *N*-chloramine[7] and the 82% yield of *N*-methylpyrrolidine-2-carboxaldehyde oxime obtained from the corresponding acyclic *N*-nitrosamine. The present conditions are milder than those employed with the chloramine (50% aqueous acetic acid, $TiCl_3$ or hν) and the nitrosamine (HCl, MeOH, hν), and the yield of substituted product **3b** is greater. Our yield of the unsubstituted pyrrolidine **3a** probably suffered to some degree due to the volatility and water solubility of the product.

The addition of alkyl groups to the terminus of the alkene moiety in the aminium cation radical apparently has little effect on the efficacy of the cyclization reaction. PTOC precursor **4** reacted in the absence of *t*-BuSH to give a 64% isolated yield of pyrrolidine **5** in a reaction that was not optimized.



The stereoselectivity of the pyrrolidine forming reaction was studied with *N*-butyl-2-methyl-4-pentenaminium cation radical (**7a**) produced from PTOC carbamate **6a**. As was the case of the unsubstituted analog **1a**,[1] radical chain reactions of carbamate **6a** in the absence of an acid typically gave complex product mixtures containing acyclic amine and pyrrolidines **8** and **9**.[8] However, when PTOC carbamate **6a** was allowed to react in the presence of acids, good yields of pyrrolidines **8** and **9** were obtained.

We have found that cyclization of the simple aminium cation radical **2** in the presence of Bu_3SnH was essentially irreversible.[1] It is also likely that cyclizations of radical **2** (and thus also radical **7a**) in the presence of *t*-BuSH or even in the absence of a hydrogen atom donor were not appreciably reversible. In the latter case, fast self-trapping of the cyclic carbon radical by the PTOC carbamate occurs. Therefore, the products **8** and **9** from radical **7a** probably were the kinetic products.

The reaction of PTOC carbamate **6a** in benzene in the presence of *t*-BuSH and CF_3CO_2H at 25 °C gave pyrrolidines **8a** and **9a** in 72% yield by GC and in a ratio of 1:3. The stereochemistry of the products was established by correlation to authentic materials.[9] The preferential formation of the *trans* product **9a** in the kinetically controlled cyclization of **7a** is noteworthy. Such stereoselectivity is predicted by the transition state models for radical cyclizations proposed by Beckwith[11] and Houk,[12] but aminyl radicals formed by anodic oxidation of lithium 2-substituted alkenylamides, including the aminyl radical **7b**, gave only *cis*-2,5-dialkylpyrrolidines.[4] The electrode surface might have had an effect on the stereoselectivity of these cyclization reactions, but we would speculate that the reversible nature of the aminyl radical cyclizations[1] also could have been an important factor in the observed stereoselectivity.[13]

The temperature dependence of the product ratio from cyclization of radical **7a** was determined in a series of reactions conducted in the absence of thiol. The thiopyridyl substituted products **8b** and **9b** were correlated to their analogs **8a** and **9a** by reduction under non-equilibrating conditions.[2] The results are collected in Table 1. Formation of the *trans* product was favored with a $\Delta\Delta G^{\ddagger}$ of about 0.5 kcal/mol. In the all-carbon analog, 2-methyl-5-hexenyl radical, formation of the *trans* product is favored by 0.4 kcal/mol.[11]

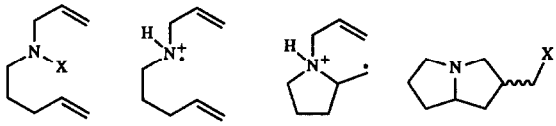
Similar low stereoselectivity was observed in the cyclization of aminium cation radical **11** formed from PTOC carbamate **10a**. Cyclizations in the presence and absence of *t*-BuSH gave comparable results. In the presence of *t*-BuSH, a 75% GC yield of

Table 1. Effect of Temperature on the Stereoselectivity of Radical 7a Cyclization[a]

Temp °C	Relative % Yield 8b	9b	Isolated Yield[b]	$\Delta\Delta G^{\ddagger}$[c]
80[d]	33	67		0.50
50	33	67		0.45
25[d,e]	25	75		0.65
20	30	70	73%	0.49
–23	40	60		0.20
–42	25	75		0.50
–78	20	80	63%	0.54

[a]Conditions: THF solvent, 0.1 M **6a**, 0.3 M CF_3CO_2H. [b]Isolated yield of a mixture of **8b** and **8a**. [c]Kcal/mol. [d]Benzene solvent. [e]*t*-BuSH added; the products were **8a** and **9a**.

a 2:1 mixture of the two isomers of perhydroindole **12a** was obtained. In the absence of *t*-BuSH, we isolated **12b** in 50% yield as a 2:1 mixture of isomers from an unoptimized reaction. Due to the low stereoselectivity, stereochemical assignments to the isomers of **12a** and **12b** were not attempted.



13a: X = PTOC
b: X = H
c: X = Cl

14 **15**

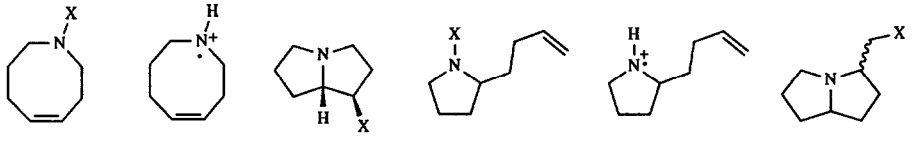
16a: X = H
b: X = S-pyr
c: X = Cl

Syntheses of Pyrrolizidines

An allyl group on nitrogen (radical **14** from PTOC carbamate **13a**) served as an internal trap for the carbon radical (**15**) formed in the initial cyclization step. The resulting tandem cyclization produced, ultimately, 2-substituted pyrrolizidines **16** in good to excellent yields. The tandem cyclization of **14** has been reported previously; the *N*-chloramine **13c** reacted with $TiCl_3$ to give pyrrolizidine **16c** in 66% yield.[14]

When *t*-BuSH was present in reactions of **13a**, two isomers of **16a** (as identified by ^{13}C NMR spectroscopy and mass spectral fragmentation patterns) in an approximate 2:1 ratio were obtained. The isomers were poorly resolved by GC, and the ^1H NMR spectrum of the mixture was not informative. In the absence of thiol, an isomeric mixture of pyrrolizidines **16b** was obtained in 90% yield. The ^1H NMR spectrum of this mixture contained signals from the pyridyl group that were sufficiently resolved to permit integration; the isomer ratio was 2.5:1.

Because the second cyclization of radical **15** is a good trapping reaction, the conditions necessary for efficient cyclization of radical **14** were not as limited as we had found for other aminium cation radical cyclizations. For example, acetic acid could be used in the reaction of PTOC **13a** in the presence of *t*-BuSH to give products **16a** in 60% yield by GC whereas these conditions were found to give low yields of cyclic products from radical **2**.[1]



17a: X = PTOC
b: X = H

18

19a: X = H
b: X = S-pyr

20a: X = PTOC
b: X = H

21

22a: X = H
b: X = S-pyr

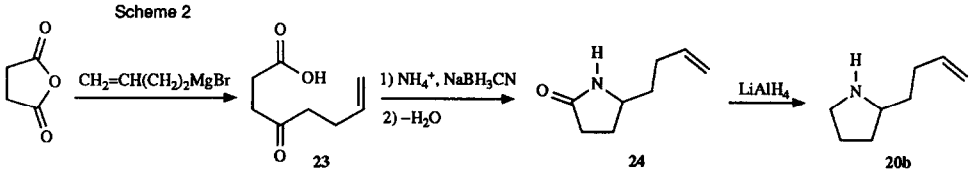
Pyrrolizidine systems substituted at different positions were available from other aminium cation radical cyclizations. PTOC carbamate **17**, for example, gave radical **18** that, ultimately, produced the 1-substituted pyrrolizidine **19b**. This reaction provides an example of a transannular cyclization. Transannular cyclizations of cycloalkenyl-substituted aminium radicals are known,[5a] but cyclizations of a nitrogen radical across a ring in which it is contained appear to have been overlooked. Such cyclizations necessarily result in bicyclic (or polycyclic) compounds with bridgehead nitrogen.

1-Azacyclooct-4-ene (**17b**) was prepared by the method of Wilson and Sawicki[15] and converted into carbamate **17a** in 68% yield. Reaction of **17a** in the presence of *t*-BuSH gave a mixture of the precursor amine (**17b**), pyrrolizidine (**19a**) and the 1-substituted pyrrolizidine **19b** in an approximate 2:1:1 ratio by GC. Product **19a** was the major product detected when the reaction was run at higher dilution, but it was not isolated. Rather, the product was identified by its mass spectrum. That **19a** was formed at all is noteworthy because the system is reluctant to cyclize; the all-carbon analog, 4-cyclooctenyl radical, apparently cyclizes less rapidly than simple acyclic 5-hexenyl radicals.[16] Based on this fact and our previous conclusion that 5-*exo* aminium cation cyclizations are irreversible,[1] we conclude that the rate of cyclization of aminium radical **18** relative to its rate of reaction with *t*-BuSH is enhanced in comparison to the all-carbon case. This is consistent with a reduction in the rate constant of the *t*-BuSH reaction due to the electrophilic nature of the aminium cation radical.[1]

In order to optimize the yield of cyclic products from aminium cation radical **18**, we took advantage of the fact that the nitrogen-centered radicals do not react with their PTOC carbamate precursors. In the absence of a hydrogen atom donor, radical **18** gave pyrrolizidine **19b** as the only significant product (82% isolated yield). This product was judged to be a single diastereomer based on GC and ^1H and ^{13}C NMR spectral analyses. The most informative NMR signal was that of the proton adjacent to sulfur which appeared as a relatively clean quartet (J = 6 Hz) indicating that its coupling constants to all three of the neighboring protons were quite similar. This information, however, was not helpful in assigning the stereochemistry of product **19b**. We tentatively assign the structure of **19b** as the *exo* isomer based on the fact that stereospecific trapping on the unhindered *exo* face of similar radicals in fused 5,5-ring systems has been found previously.[17]

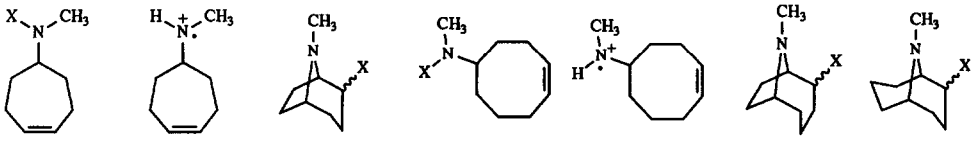
Pyrrolizidines **22** with carbon substitution at the 3 position were obtained from PTOC carbamate **20a**. The requisite amine (**20b**) was prepared as shown in Scheme 2. Addition of 3-butenylmagnesium bromide to succinic anhydride at –78 °C gave the keto acid **23**. Reductive amination[18] of **23** and *in situ* cyclization of the resulting amino acid produced lactam **24** that was reduced to the desired amine **20b**.

Scheme 2



PTOC carbamate **20a** gave 3-methylpyrrolizidine (**22a**) from reactions conducted in the presence of *t*-BuSH. The cyclization apparently was facile because no acyclic amine **20b** was detected when the concentration of *t*-BuSH was quite high, a condition necessary to limit the formation of the self-trapped product **22b**. The cyclization of radical **21** might be accelerated by the ring which limits the degrees of rotational freedom of the side chain, but radical **2** also cyclized efficiently in the presence of high concentrations of *t*-BuSH. In the absence of the thiol trap, carbamate **20a** gave pyrrolizidine **22b** in nearly quantitative yield. Again, the cyclization reactions proceeded with low stereoselectivity; both **22a** and **22b** were obtained as isomeric mixtures with a 1.7:1 isomer ratio. The isomers of **22b** could be separated, but no attempt was made to assign the stereochemistry to the isomers. We suspect that the *exo* isomer predominated.

The cyclizations of radicals **14**, **18** and **21** provide an interesting set of reactions in that three different pyrrolizidine substitution patterns were produced. In addition, each reaction represents a somewhat different type of cyclization. As noted above, cyclization of radical cation **14** was known,[14] but the cyclizations of **18** and **21** apparently are new.



25a: X = PTOC
b: X = H
c: X = Cl

26

27a: X = H
b: X = S-pyr
c: X = Cl

28a: X = PTOC
b: X = H
c: X = Cl

29

30a: X = H
b: X = S-pyr
c: X = Cl

31a: X = H
b: X = S-pyr
c: X = Cl

Syntheses of Aza Bridged Bicycles

In order to explore the syntheses of aza bridged bicycles from cycloalkenylamines, cyclizations of radicals **26** and **29** were studied. Apart from the fact that the anticipated bicyclic products are important alkaloid skeletons, we were interested in these cyclizations because *N*-chloramines **25c** and **28c** have been studied, and **25c** was found to give only low yields of cyclized products.[19] In addition, radical **29** provides a competition between 5-*exo* and 6-*exo* cyclization modes that would result in bicyclo[4.2.1] and bicyclo[3.3.1] systems, respectively.

Studies of reactions of PTOC carbamate **25a** have been reported in preliminary form.[20] The cyclization was quite facile, and it could be achieved in solvent benzene with acetic acid, conditions known to lead to low yields of pyrrolidines from the simple radical **2**.[1] Although the cyclization was equally facile in solvent acetonitrile with malonic acid, the acetic acid protocol was preferred when *t*-BuSH was present because it resulted in lower yields of the sulfide product **27b**. Tropane (**27a**) was isolated in good yield from the reaction of carbamate **25a**; the product was identified by its ^1H and ^{13}C NMR spectra which matched those previously reported.[21] In the absence of *t*-BuSH, either acetic acid or malonic acid could be used as the acid source; the sulfide product **27b** was isolated in nearly quantitative yield as a 1.5:1 mixture of the *exo* and *endo* isomers, respectively.

Given that the cyclization of radical **26** was facile when acetic acid was the proton source and that there is no internal trap in **26** comparable to that which is present in radical **14**, the cyclization of **26** represents the most facile aminium cation radical cyclization we have studied to date. For comparison, the simple radical **2** gave low yields of cyclic products under the conditions used to form tropane (acetic acid, *t*-BuSH).[1] The all-carbon analog, cyclohept-4-enylmethyl radical, also cyclizes efficiently.[22] However, only a 7.5% yield of 2-chlorotropane (**27c**) was realized when the *N*-chloramine **25c** was the source of radical **26**.[19] It is difficult to assess the origin of the low yield in the chloramine study, but there are several possible complications: (1) the product **27c** is a nitrogen mustard that might have decomposed during the isolation, (2) competing ionic reactions of **25b** might have occurred, (3) reactions involving chlorine radicals might have produced side products.

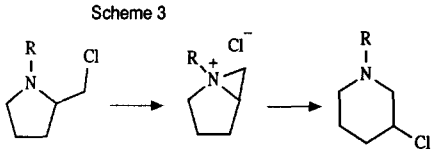
The one-carbon homolog of radical **26**, radical **29**, appears to represent the other extreme in reactivity. Poor yields of cyclic products were obtained when *t*-BuSH was present in the reaction medium. The recalcitrance of radical **29** towards cyclization was apparent when PTOC carbamate was allowed to react in the

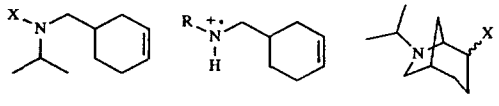
absence of any hydrogen atom donor; a fair yield of sulfides **30b** and **31b** were obtained along with a significant amount of the precursor amine **28b**. The aminium cation radical **29** apparently was reasonably persistent in this reaction, and amine **28b** was produced by radical disproportionation or reaction of the radical with the solvent or malonic acid. That some radical disproportionation of **29** occurred was indicated by the detection of small amounts of 4-cyclooctenone (from hydrolysis of the corresponding imine) by GC analysis of the product mixture.

The reaction of carbamate **28a** in the absence of thiol gave four pyridyl sulfide products (*endo*- and *exo*-**30b** and *endo*- and *exo*-**31b**) in 61% isolated yield and in a ratio of 24:8:2:1 according to GC analysis. These isomers could not be separated by simple LC techniques. The three most abundant isomers gave distinct ^{1}H NMR signals for the C-1 protons (adjacent to sulfur), and these signals integrated in a ratio similar to that found by GC; the minor isomer was not detected by ^{1}H NMR spectroscopy. The two major isomers were identified as the two isomers of **30b** based on their mass spectral fragmentation patterns. For the major isomer, the base peak was at m/e = 82, and for the second most abundant isomer, the intensity of the peak at m/e = 82 was 95% that of the base peak. The peak at m/e = 82 was nearly absent in the mass spectrum of the third most prevalent product, and analysis of the minor product by GC-mass spectroscopy was not possible due to its low concentration in the product mixture. Because large peaks at m/e = 82 are known to be characteristic of azabicyclic compounds that contain the *N*-methylpyrrolidine moiety,[19,23] we assign the bicyclo[4.2.1] ring system to the two most abundant products. No attempt was made to assign *exo* and *endo* stereochemistry to products **30b**. The assignment of the two major products as the stereoisomers of **30b** rather than as two regioisomers was further supported by DBU activated elimination of the sulfoxides formed by oxidation of the product mixture with MCPBA.[2] GC analysis of the product mixture revealed only one elimination product in addition to a considerable amount of sulfones from overoxidation.

Again, one can compare the results from PTOC precursor **28a** to its *N*-chloramine analog (**28c**). Bastable *et al.*[19] have reported that reaction of **28c** gave mainly bicyclo[3.3.1] products **31c** and smaller amounts of bicyclo[4.2.1] products **30c**. In addition, they[19] reported that the yields of cyclic products from chloramine **28c** were significantly greater than those obtained from chloramine **25c**, in contrast to the results we obtained with the PTOC precursors **28a** and **25a**. We would speculate that ionic reactions occurred in the chloramine studies. For example, rearrangement of **30c** to **31c** via the aziridinium ion is similar to the known pathway for rearrangements of 2-(chloromethyl)pyrrolidines to 3-chloropiperidines (Scheme 3).[25,26]

Scheme 3





32a: X = PTOC
b: X = H

33a: R = *i*-Pr
b: R = Me
c: R = Pr

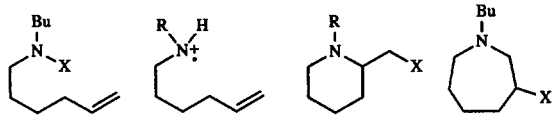
34a: X = H
b: X = S-pyr

Another type of transannular aminium cation radical cyclization is represented by the reaction of radical **33a**. Here the aminium center is one-carbon removed from direct attachment to the ring. Aminium cation radical cyclizations of the *N*-methyl (**33b**) and *N*-propyl (**33c**) analogs of **33a** have been reported using the *N*-nitrosamine[25] and *N*-chloramine[26] precursors, respectively. Again a 6-*exo* cyclization of radicals **33** is possible in principle, but only products from 5-*exo* cyclizations have been reported. Aminium cation radical

33b from the nitrosamine gave an 80% yield of the bicyclic oximes and corresponding ketone related to **34**,[25] and 50-77% yield of bicyclic products were reported from reactions of radical **33c**.[26]

PTOC carbamate **32a** was prepared from amine **32b** which was obtained by reductive amination of 1,2,3,6-tetrahydrobenzadehyde by isopropylamine in the presence of $NaBH_3CN$. Reaction of carbamate **32a** in the presence of *t*-BuSH gave a mixture of the precursor amine **32b** and cyclic products **34a** and **34b**. It is possible that the acyclic product could be avoided by using low concentrations of thiol, but this would also result in increased yields of the sulfide **34b** at the expense of reduced product **34a**.

In the absence of *t*-BuSH, bicyclic products **34b** were isolated in 86% yield. GC-mass spectral analysis showed that the product mixture contained two isomers in a 6:1 ratio, and these two products were judged to be stereoisomers rather than regioisomers based on their virtually identical mass spectra. A large peak at *m/e* = 110 in the mass spectra suggested the presence of an *N*-isopropylpyrrolidine moiety. The ^1H NMR spectrum of the isolated products also indicated a 5:1 mixture of isomers. The major product was isolated in pure form; the bicyclo[3.2.1] skeleton of **34b** was confirmed for this isomer via a proton COSY spectrum in which all of the protons could be assigned from their coupling patterns.



35a: X = PTOC
b: X = H

36a: R = Bu
b: R = Pr

37a: R = Bu, X = H
b: R = Bu, X = S-pyr
c: R = Pr, X = Cl

38a: X = H
b: X = S-pyr

6-*exo* Aminium Radical Cation Cyclizations

For aminium cation radicals **29** and **33**, 6-*exo* cyclizations were possible, but 5-*exo* cyclizations predominated. Similar behavior is well known for carbon radical cyclizations where the 5-*exo* mode of cyclization is by far the most facile.[27] However, 6-*exo* cyclizations of carbon radicals are known to occur when 5-*exo* cyclization pathways do not exist, and 6-*exo* aminium cation radical cyclizations have been reported.[28] Thus, it was of interest to determine whether or not a 6-*exo* mode for aminium cation radical cyclization was possible when a PTOC carbamate precursor was employed to give a radical in which the 5-*exo* mode was not an option.

Amine **35b** was prepared from 5-hexenoic acid via the *N*-butylcarboxamide, and PTOC carbamate **36a** was prepared from this amine. Reaction of precursor **36a** under conditions that typically resulted in good yields of pyrrolidine products gave mainly the acyclic amine precursor although low yields of cyclic products **37a** and **38a** and their corresponding pyridylsulfides were indicated by GC mass spectral analysis of the product mixture.

In the absence of thiol, radical **36a** gave cyclic sulfides **37b** and **38b** in 42% yield by GC and in a ratio of 2.5:1 along with amine **35b** (31%). Due to the low yield, the products were not isolated, but the identity of the sulfides was apparent from their mass spectral fragmentation patterns. Specifically, the only significant peak in the mass spectrum of sulfide **37b** was at *m/e* = 140 resulting from loss of the pyridyl-S-CH_2 group; this fragmentation is characteristic of the 2-[(2-pyridylthio)methyl] substituted heterocycles. The mass spectrum of **38b** contained a large peak at *m/e* = 153 from loss of pyridyl-S. The 7-*endo* mode of cyclization was

Table 2. Yields from PTOC Carbamate Reactions

	Self-trapping Reactions			Thiol Trapping Reactions				
Precursor	Details	Product	Yield[a]	Details	[*t*-BuSH][b]	Products, Yield[a]		
1a	A	**3b**	92%	A	2.2		**3a** 75%	**3b** (5%)
4	B	**5**	64%[c]					
6a	C	**8b** + **9b**[d]	73%	D	0.05		**8a** + **9a**[e] (72%)	
10	E	**12b**[f]	50%[c]	D	0.05		**12a**[f] (75%)[c]	
13a	A	**16b**[g]	90%	A	0.28		**16a**[g] 56%	**16b**, (2%)
17a	A	**19b**[h]	82%	A	0.10	**17b** (45%)	**19a** (28%)	**19b** (24%)
20a	A	**22b**[i]	96%	A	2.0		**22a**[i] 68%	**22b** (6%)
25a	A	**27b**[j]	92%					
	F	**27b**[j]	94%	F	0.30		**27a** 68%	**27b** (3%)
28a	A	**30b**[k]	60%[l]	A	0.10	**28b** (45%)	**30a** (9%)	**30b**, (7%)
32a	A	**34b**[m]	86%	A	0.10	**32b** (10%)	**34a** (34%)	**34b** (42%)
35a	A	**37b** + **38b**[n]	(42%)[o]	A	0.10	**35b** (60%)	**37a** + **38a**[n] (17%)	

Key for Details: A, solvent CH_3CN, 25 °C, 0.05 M PTOC, 0.15 M $CH_2(CO_2H)_2$; B, solvent benzene, 25 °C, 0.1 M PTOC, 0.3 M CF_3CO_2H; C, solvent THF, 20 °C, 0.1 M PTOC, 0.3 M CF_3CO_2H; D, solvent benzene, 25 °C, 0.04 M PTOC, 0.13 M CF_3CO_2H; E, solvent THF, 25 °C, 0.1 M PTOC, 0.3 M CF_3CO_2H; F, solvent CH_3CN, 25 °C, 0.05 M PTOC, 0.15 M CH_3CO_2H. [a]Isolated yield of products; GC yields are in parentheses. [b]Initial molar concentration. [c]Yield not optimized. [d]**8b**:**9b** = 1:4. [e]**8a**:**9a** = 1:3. [f]2:1 mixture of isomers. [g]2.5:1 mixture of isomers. [h]One isomer. [i]1.7:1 mixture of isomers. [j]*exo*:*endo* = 1.5:1. [k]3:1 mixture of isomers. [l]20% yield of **28b** detected by GC. [m]6:1 mixture of isomers. [n]**37**:**38** = 3:1. [o]31% yield of **35b** detected by GC.

nearly as efficient as the 6-*exo* mode. For comparison, cyclization of the *N*-propyl aminium cation radical **36b** from the corresponding *N*-chloramine has been reported to give piperidine product **37c** in 50% yield.[28b]

Conclusion

Table 2 is a collection of the yields of products formed by aminium cation radical cyclizations. Reactions run in the absence and presence of *t*-BuSH are reported. Most of the reactions were run under optimized conditions, and those that were not are noted. Products generally were isolated from reactions unless complicated product mixtures were observed by GC.

PTOC carbamate precursors can be employed for a variety of aminium cation radicals that will subsequently cyclize. In general, the yields of cyclic products are greater when the radicals are formed from the PTOC precursors than when they are produced from analogous *N*-chloramines or *N*-nitrosamines. In addition, the use of PTOC precursors permits milder reaction conditions than the alternative aminium sources, and, in principle, some functional groups can be maintained in the PTOC route that would not be stable in the more acidic conditions employed with the other radical precursors. When no hydrogen atom donor is present in the reaction medium, 2-thiopyridyl substituted products are formed by the self-trapping reaction, and this group offers some potential for further functional group conversions. In the following paper, we report studies of such conversions and alternative carbon radical trapping reactions.

Experimental Section

General. Reagents were purchased from Aldrich Chemical Co. unless noted. Commercial amines were distilled from CaH_2 and stored over KOH. All solvents used for reactions of PTOC carbamates were dried and deoxygenated before use. Benzene was distilled from CaH_2 and then purged with a nitrogen stream for at least 30 min before use. Acetonitrile was stored over molecular sieves and similarly purged before use. THF was distilled from benzophenone and potassium.

Melting points were determined on either a Fischer-Johns hot stage or a Thomas-Hoover melting point apparatus; temperatures are not corrected. ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on a Varian XL-200 spectrometer at 200 and 50 MHz, respectively; chemical shifts are reported in ppm upfield of internal Me_4Si. GC analyses were performed on a variety of instruments equipped with flame ionization detectors using low polarity, large bore capillary columns (0.53 mm ID, 15 m). GC-mass spectrometry was accomplished on a Hewlett-Packard (HP) 5790 GC interfaced to an HP 5970-A mass selective detector. Analyses were performed by Galbraith Laboratories.

Preparations of PTOC Carbamates were accomplished by two similar methods. In Method A, a stirred suspension of the salt (1.1 molar equiv) prepared from the reaction of *N*-hyroxypyridine-2-thione and phosgene[1,29] in benzene under nitrogen was cooled in an ice bath in a flask wrapped in aluminum foil to exclude light. To this mixture was added dropwise a solution of the dialkylamine (1.0 molar equiv) and Et_3N (1.1 molar equiv) in benzene. After the addition, the stirred reaction mixture was maintained at 0 °C for 2-3 h and then at 25 °C for 1-2 h. Water was added, and the organic layer was separated and washed with saturated aqueous NaCl solution. After drying ($MgSO_4$), the solutions were concentrated to give crude PTOC carbamates as heavy yellow oils or yellow solids. Most of the products were crystallized by dissolving the crude product in benzene, toluene or ether, diluting the resulting solution with 5 volumes of hexanes, and cooling to ca. –20 °C. Products that did not crystallize were purified by chromatography on silica gel (EtOAc--hexanes elution).

In Method B, a solution of the dialkylamine (1.0 molar equiv) and Et_3N (1.1 molar equiv) in benzene under nitrogen was stirred in a shielded flask. To this solution was added in one portion the above salt (1.2-1.5 molar equiv) as a solid. The mixture was stirred for 2-3 h at 25 °C, and water was added. The organic phase was washed with saturated aqueous $NaHCO_3$ solution. The remainder of the product work-up and isolation was the same as that described above.

As noted in the accompanying paper,[1] the NMR spectra of the PTOC carbamates were complicated due to the presence of two conformers.

1-[(Butyl(4-pentenyl)carbamoyl)oxy]-2(1H)-pyridinethione (1a) was prepared by Method A as described in the accompanying paper.[1]

1-[(Butyl(5-methyl-4-hexenyl)carbamoyl)oxy]-2(1H)-pyridinethione (4) was prepared in 72% yield (oil) as previously reported:[3b] ^1H NMR, δ 0.91 (t, 3 H), 1.2-1.5 (m, 2 H), 1.5-1.85 (m, 4 H), 1.58 (s, 3 H), 1.72 (s, 3 H), 1.9-2.1 (m, 2 H), 3.3 (t, 2 H), 3.45 (t, 2 H), 5.1 (broad s, 1 H), 6.65 (dt, 1 H), 7.15 (dt, 1 H), 7.55-7.68 (m, 2 H); ^{13}C NMR, δ 13.76, 13.82, 17.77, 19.90, 20.04, 25.23, 25.34, 25.68, 27.59, 28.74, 29.58, 30.74, 47.49, 47.65, 48.87, 112.16, 123.25, 123.35, 132.31, 132.48, 133.41, 137.09, 138.74, 151.62, 176.37.

1-[(Butyl(1-methyl-4-pentenyl)carbamoyl)oxy]-2(1H)-pyridinethione (6a). *N*-Butyl-1-methyl-4-pentenamine (**6b**) was prepared as follows. Freshly distilled 5-hexene-2-one (10 g, 0.10 mol) in 500 mL of dry benzene was placed in a dry flask equipped with a Dean-Stark trap and a condenser. Butylamine (14.9 g, 0.20 mol) was added, and the mixture was heated at reflux for 24 h. Solvent and excess amine were distilled at reduced pressure. The residue was dissolved in 100 mL of ethanol, and the resulting solution was placed in a flask containing a stir bar. The mixture was cooled in an ice bath, and $NaBH_4$ (7.8 g, 0.20 mol) was added in portions. The resulting mixture was stirred and allowed to warm to 25 °C. After 18 h, 15 mL of a 25% aqueous NaOH solution was added, and the mixture was stirred vigorously for 1 h. The phases were separated, and the aqueous phase was extracted with ether (3 x 25 mL). The combined organic phases were extracted with saturated aqueous NaCl solution (3 x 25 mL) and dried over K_2CO_3. Distillation gave 11.7 g (75%) of **6b** as an oil: bp 82 °C (12 Torr) (lit.[4b] bp 82-84 °C (15 Torr)).

PTOC carbamate **6a** was obtained by Method A from a reaction of 20 mmol of **6b**. Recrystallization of the crude product from toluene--hexanes gave **6a** in 79% yield: mp 43-45 °C (dec); ^1H NMR, δ 0.9 (broad t, 3 H), 1.3 (d, 3 H), 1.2-1.5 (m, 2 H), 1.5-2.0 (m, 4 H), 2.0-2.3 (m, 2 H), 3.4-3.5 (m, 1.5 H), 3.1-3.2 (m, 0.5 H), 3.8-4.0 (m, 0.75 H), 4.3-4.5 (m, 0.25 H), 4.9-5.2 (m, 2 H), 5.7-6.0 (m, 1 H), 6.65 (t, 1 H), 7.2 (t, 1 H), 7.65 (broad d, 2 H); ^{13}C NMR, δ 13.99, 18.84, (19.65), 20.45, 31.00, (31.13), 32.34, 33.49, (34.11), (44.43), 45.13, (53.07), (54.92), 55.06, 112.38, (112.54), 115.14, 133.62, 137.00, (137.95), 138.93, 151.46, 176.22, (176.38). *Anal.* Calcd for $C_{16}H_{24}N_2O_2S$: C, 62.31; H, 7.84. Found: C, 62.27; H, 7.87.

1-[(Butyl(2-allylcyclohexyl)carbamoyl)oxy]-2(1H)-pyridinethione (10a). An 8:1 mixture of *cis*- and *trans*-*N*-butyl-2-allylcyclohexylamine (**10b**) was prepared by a procedure similar to that used for amine **6b**. Thus, the imine was made from 10 g (78 mmol) of freshly distilled 2-allylcyclohexanone[30] and 6.0 g (155 mmol) of butylamine (6.0 g, 155 mmol) in 120 mL of benzene, and the crude imine was treated with 4.2 g (1.5 mol) of $NaBH_4$. Distillation gave 9.4 g (67%) of amine **10b** as a colorless oil: bp 85-90 °C (2 Torr). The *cis* to *trans* ratio was determined to be 8:1 by GC analysis (J&W Scientific, DB-Wax); the major isomer eluted first. ^1H NMR (of the mixture), δ 0.85 (t, 3 H), 1.2-1.8 (m, 14 H), 1.8-2.2 (m, 2 H), 2.3-2.7 (m, 3 H), 4.8-5.0 (m, 2 H), 5.6-5.7 (m, 1 H); ^{13}C NMR, major (minor), δ 13.91, 20.49, 22.65, 23.08, (25.26), (25.72), 27.18, 28.81, (30.92), 32.60, (32.69), (32.79), 33.38,

(37.44), 39.09, (42.36), (46.57), 46.95, 57.17, (60.53), 115.11, (115.63), (137.29), 138.17; mass spectrum, *m/e* (intensity); major isomer, 195 (9), 180 (21), 152 (100), 96 (11); minor isomer, 195 (11), 180 (13), 152 (100), 96 (10).

A 1:5 mixture of *cis*- and *trans*-**10b** resulted when 2-allylcyclohexanone was converted to its oxime which was then reduced with sodium metal, and the resulting 2-allylcyclohexylamine was treated with butyraldehyde and then $NaBH_4$.

PTOC carbamate **10a** was prepared from 11.5 mmol of the 8:1 mixture of **10b** by Method A. Recrystallization from toluene--hexanes gave 3.4 g (85%) of **10a** as a yellow solid: mp 88.5-91 °C; ^{1}H NMR, δ 0.9 (broad t, 3 H), 1.1-2.6 (m, 15 H), 2.95-4.5 (m, 3 H), 4.95-5.15 (m, 2 H), 5.6-5.9 (m, 1 H), 6.6 (t, 1 H), 7.15 (t, 1 H), 7.65 (d, 2 H); ^{13}C NMR, major (minor) δ (13.67), 13.80, 19.33, 20.20, 24.92, (25.15), 26.24, 27.31, 30.21, (31.27), (31.55), 33.07, 36.59, (38.12), 46.24, (46.89), (59.29), 61.66, 112.21, 115.89, (116.27), (121.87), 133.47, 136.99, (137.19), (137.29), 137.50, 138.81, (138.94), 151.54, 176.19, (176.34). *Anal.* Calcd for $C_{19}H_{28}N_2O_2S$: C, 65.48; H, 8.10. Found: C, 65.42; H, 8.12.

1-[(Allyl(4-pentenyl)carbamoyl)oxy]-2(1H)-pyridinethione (13a). *N*-Allyl-4-pentenamide was prepared from 4-pentenoic acid. To 1.5 g (15 mmol) of the acid in 20 mL of benzene was added 1.3 mL of thionyl chloride. The solution was heated at reflux for 3 h. Benzene and excess thionyl chloride were distilled. An additional 10 mL of benzene was added and then distilled from the reaction mixture. The residue was dissolved in 20 mL of ether, and 3 mL of allylamine was added dropwise at 0 °C. The reaction mixture was allowed to warm to 25 °C, and 15 mL of water was added. The layers were separated, and the aqueous layer was extracted with 15 mL of ether. The combined ethereal phase was extracted with 10 mL of 1 M HCl solution and saturated $NaHCO_3$ solution and then dried ($MgSO_4$). Distillation of the solvent at reduced pressure gave 1.5 g (10.8 mmol, 72%) of the desired amide as a white solid: ^{1}H NMR, δ 2.30 (m, 4 H), 3.81 (m, 2 H), 4.9-5.2 (m, 4 H), 5.65-5.9 (m, 2 H), 5.91 (broad s, 1 H); ^{13}C NMR, δ 29.82, 36.00, 42.12, 116.00, 116.69, 134.81, 137.58, 172.82.

N-Allyl-4-pentenamine (**13b**) was prepared by reduction of the amide. A solution of 1.5 g (10.8 mmol) of the amide in 50 mL of THF was added dropwise to a stirred suspension of 0.9 g of $LiAlH_4$ in 100 mL of THF. The reaction was heated at reflux for 48 h. The mixture was cooled and treated sequentially with 1.5 mL of water, 1.5 mL of 20% aqueous NaOH solution, and 4.5 mL of water. The mixture was stirred for 3 h and then filtered. The salts were triturated with ether (2 x 25 mL). The combined ethereal solution was dried with $MgSO_4$. Distillation from CaH_2 gave 0.88 g (65%) of **13b** as a colorless liquid: bp 149-150 °C (lit.[14] bp 148 °C); ^{1}H NMR, δ 0.95 (broad s, 1 H), 1.5 (quin, 2 H), 2.0 (q, 2 H), 2.54 (t, 2 H), 3.18 (d, 2 H), 4.7-5.1 (m, 4 H), 5.5-5.9 (m, 2 H); ^{13}C NMR, δ 28.86, 31.08, 48.40, 52.10, 114.14, 115.08, 136.60, 137.94.

PTOC carbamate **13a** was prepared by Method B from 0.88 g (7.04 mmol) of amine **13b**. Recrystallization from benzene--hexanes gave 1.5 g (5.4 mmol, 77%) of **13a** in three crops as a pale yellow solid: mp 70.5-71 °C; ^{1}H NMR, δ 1.6-1.9 (m, 2 H), 2.08 (q, 2 H), 3.31 and 3.49 (pair of t, 2 H), 3.93 and 4.16 (pair of d, 2 H), 4.98 (m, 2 H), 5.27 (m, 2 H), 5.7-6.1 (m, 2 H), 6.68 (dt, 1 H), 7.15 (dt, 1 H), 7.62 (m, 2 H); ^{13}C NMR, δ 26.63, 27.71, 30.94, 31.07, 47.22, 48.34, 50.56, 51.51, 112.64, 115.73, 115.84, 117.94, 118.75, 132.12, 133.88, 134.01, 137.65, 137.72, 138.00, 139.23, (carbonyls not observed). *Anal.* Calcd for $C_{14}H_{18}N_2O_2S$: C, 60.41; H, 6.52. Found: C, 60.68; H, 6.57.

1-Aza-1-[carbonyloxy(1-pyridyl-2(1H)-thione)]-4-cyclooctene (17a). 4-Cycloheptenol was obtained by oxidative decarboxylation of 4-cycloheptene-1-carboxylic acid which was prepared by a modification[31] of the method of Stork and Landesman.[32] A mixture of 8.0 g (57 mmol) of the acid, 47 g of NaOAc and 200 mL of acetic acid was heated to 70 °C in an oil bath. Addition of 39 g of $Pb(OAc)_4$ in 5 portions resulted in the evolution of CO_2. The reaction was stirred for an additional 2 h at 70 °C after the gas evolution had ceased. The mixture was cooled to 25 °C, 150 mL of water was added, and the resulting solution was extracted with pentane (5 x 80 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ solution until the washings were neutral. GC-mass spectral analysis indicated a 1:6 mixture of the desired alcohol and its acetate. Pentane was distilled at reduced pressure, and 100 mL of 10% aqueous NaOH solution was added to the residue. Following a 6 h reflux, the cooled reaction mixture was extracted with ether (4 x 50 mL). The combined ethereal phase was washed with saturated NaCl solution and dried ($MgSO_4$). Concentration and distillation gave 5.6 g (50 mmol, 89%) of the desired alcohol: bp 72-74 °C (10 Torr); ^{1}H NMR, δ 1.39 (m, 2 H), 1.70 (broad s, 1 H), 1.90 (m, 4 H), 2.22 (m, 2 H), 3.78 (hep, 1 H), 5.74 (m, 2 H); ^{13}C NMR, δ 23.14, 35.40, 74.35, 132.33.

4-Cycloheptenone was prepared by oxidation of 4-cycloheptenol. To a solution of 2.5 g (22 mmol) of the alcohol in 50 mL of CH_2Cl_2 was added 2.0 g of NaOAc and 26 g of powdered 4A molecular sieves. The resulting mixture was stirred, and 5.3 g of pyridinium chlorochromate was added in 4 portions. After stirring at room temperature for 10 h, the reaction mixture was diluted with 50 mL of ether and then filtered through Celite. Distillation gave 1.8 g (16.4 mmol, 74%) of the desired ketone:[33] bp 80 °C (20 Torr); ^{1}H NMR, δ 2.34 (m, 4 H), 2.63 (m, 4 H), 5.76 (m, 2 H); ^{13}C NMR, δ 24.28, 42.70, 130.00, (carbonyl not observed).

1-Aza-4-cyclooctene (**17b**) was prepared from the above ketone in 32% yield by the method of Wilson and Sawicki.[15]

PTOC carbamate **17a** was prepared by Method A from 0.22 g (2.0 mmol) of amine **17b**. Recrystallization from benzene--hexanes gave 0.39 g (1.48 mmol, 74%) of **17a** as a yellow solid: mp 110-111 °C; ^{1}H NMR, δ 1.8-2.0 (m, 2 H), 2.29 (m, 3 H), 2.52 (m, 1 H), 3.39 (t, 1 H), 3.60 (m, 2 H), 5.78 (m, 2 H), 6.69 (dt, 1 H), 7.17 (dt, 1 H), 7.63 (m, 2 H); ^{13}C NMR, δ 23.37, 23.67, 25.48, 26.46, 26.94, 27.39, 47.59, 49.29,

50.81, 112.23, 128.39, 128.75, 131.42, 131.46, 133.44, 137.19, 137.25, 138.67, 138.81 (carbonyls not observed). *Anal.* Calcd for $C_{13}H_{16}N_2O_2S$: C, 59.07; H, 6.10. Found: C, 59.19; H, 6.08.

1-[Carbonyloxy(1-pyridyl-2(1H)thione)]-2-(3-butenyl)pyrrolidine (20a). 3-Butenylmagnesium bromide was prepared from 10.2 mL of 4-bromo-1-butene (ca. 100 mmol) and 2.68 g of Mg in 50 mL of THF. The Grignard reagent was added to a mixture of 30 g (300 mmol) of succinic anhydride in 300 mL of THF and 50 mL of HMPA at –78 °C. The mixture was stirred for 6 h and allowed to warm to room temperature. HCl (150 mL of a 10% solution) was added, and most of the THF was removed at reduced pressure. An additional 100 mL of water was added, and the mixture was extracted with EtOAc (4 x 100 mL). The combined organic extracts were washed with 50 mL of water and 50 mL of saturated NaCl solution. Drying ($MgSO_4$) and distillation of the solvent gave a dark yellow oil. The oil was dissolved in 200 mL of CH_2Cl_2, and the solution was extracted with NaOH solution. The basic wash was acidified (HCl), and the resulting solution was extracted with CH_2Cl_2. Drying ($MgSO_4$) and distillation of the solvent at reduced pressure gave 6.2 g (40 mmol, 40%) of crude keto acid **23** as a light yellow oil: ^{1}H NMR, δ 2.28 (q, 2 H), 2.45-2.6 (m, 6 H), 4.94 (m, 2 H), 5.74 (m, 1 H), 10.95 (broad s, 1 H); ^{13}C NMR, δ 27.86, 28.05, 37.25, 41.95, 115.73, 137.47, 177.97, 208.94.

To 5.5 g (35 mmol) of acid **23** and 30 g of ammonium acetate was added 110 mL of MeOH followed by 1.6 g of $NaBH_3CN$. The reaction mixture was stirred at room temperature for 48 h and then acidified to pH < 2 (conc HCl). The MeOH was removed at reduced pressure, and the resulting solution was adjusted to pH 6 with 5% aqueous NaOH solution. Benzene (200 mL) was added, and the resulting mixture was heated at reflux in a flask fitted with a Dean-Stark trap until water no longer distilled. Removal of the benzene at reduced pressure gave a heavy oil. Distillation gave 3.0 g (21.6 mmol, 62%) of pyrrolidinone **24**: bp 140-145 °C (5 Torr); ^{1}H NMR, δ 1.60 (m, 3 H), 2.0-2.4 (m, 5 H), 3.61 (quin, 1 H), 4.98 (m, 2 H), 5.66 (m, 1 H), 7.13 (broad s, 1 H); ^{13}C NMR, δ 27.19, 30.20, 30.26, 35.78, 54.18, 115.35, 137.50, 178.55.

A solution of 2.0 g (14.4 mmol) of pyrrolidinone **24** in 20 mL of THF was added dropwise to a stirred suspension of 1.1 g of $LiAlH_4$ in 100 mL of THF. The mixture was heated at reflux for 72 h. The cooled reaction mixture was treated sequentially with 1.1 mL of water, 1.1 mL of 20% NaOH solution, and 3.3 mL of water with stirring. The mixture was filtered, and the filtrate was triturated with ether (4 x 20 mL). The combined organic phases were dried (K_2CO_3), and the solvent was distilled at reduced pressure to give a yellow liquid. Distillation from CaH_2 have 1.5 g (12 mmol, 83%) of pyrrolidine **20b** as a colorless liquid: bp 67-69 °C (15 Torr); ^{1}H NMR, δ 1.18 (m, 1 H), 1.4-1.9 (m, 5 H), 2.34 (m, 2 H), 2.7-3.0 (m, 3 H), 4.92 (m, 2 H), 5.78 (m, 1 H); ^{13}C NMR, δ 25.57, 31.69, 32.00, 35.92, 46.81, 59.04, 114.83, 139.24. Compound **20b** has been reported without physical data.[34]

PTOC carbamate **20a** was prepared by Method A from 1.5 g (12 mmol) of pyrrolidine **20b**. Attempts to crystallize the product from benzene--hexanes and from ether--hexanes failed. The product (2.48 g, 8.9 mmol, 74%) was obtained as a heavy yellow oil: ^{1}H NMR, δ 1.50 (m, 1 H), 1.65-2.2 (m, 7 H), 3.4-3.7 (m, 1.6 H), 3.90 (m, 1.2 H), 4.34 (m, 0.2 H), 4.97 (m, 2 H), 5.77 (m, 1 H), 6.68 (dt, 1 H), 7.14 (dt, 1 H), 7.62 (m, 2 H); ^{13}C NMR, δ 23.07, 24.26, 30.10, 30.54, 30.70, 32.57, 33.70, 47.16, 48.05, 58.60, 59.55, 112.69, 115.39, 134.03, 137.55, 137.67, 138.31, 139.30, 176.88. *Anal.* Calcd for $C_{14}H_{18}N_2O_2S$: C, 60.41; H, 6.52. Found: C, 60.17; H, 6.61.

1-[(Methyl(4-cycloheptenyl)carbamoyl)oxy]-2(1H)-pyridinethione (25a). *N*-Methyl-4-cycloheptenamine (**25b**) was prepared from 4-cyclohepten-1-carboxylic acid[31,32] in 65% yield by the method of Bastable:[19] bp 65 °C (18 Torr) (lit.[19] bp 55-57 °C (18 Torr)); ^{1}H NMR, δ 1.27 (m, 3 H), 1.82 (m, 2 H), 1.98 (m, 2 H), 2.16 (m, 2 H), 2.39 (s, 3 H), 2.53 (hep, 1 H), 5.73 (m, 2 H); ^{13}C NMR, δ 24.76, 33.08, 34.24, 62.70, 132.32.

PTOC carbamate **25a** was prepared by Method A from 1.7 g (13.6 mmol) of amine **25b**. Recrystallization from ether--hexanes gave 3.0 g (10.8 mmol, 79%) of **25a** in two crops as a yellow solid: mp 64 °C; ^{1}H NMR, δ 1.52 (m, 2 H), 1.8-2.4 (m, 6 H), 2.90 (s, 1 H), 3.05 (s, 2 H), 4.06 (tt, 0.66 H), 4.38 (tt, 0.33 H), 5.81 (m, 2 H), 6.59 (dt, 1 H), 7.16 (dt, 1 H), 7.64 (m, 2 H); ^{13}C NMR, δ 25.32, 31.14, 31.80, 61.08, 62.32, 112.65, 113.47, 134.01, 137.56, 139.26, (carbonyls not observed). *Anal.* Calcd for $C_{14}H_{18}N_2O_2S$: C, 60.41; H, 6.52. Found: C, 60.08; H, 6.55.

1-[(Methyl(4-cyclooctenyl)carbamoyl)oxy]-2(1H)-pyridinethione (28a). 4-Cyclooctene-1-carboxylic acid was prepared by the method of Stork and Landesman[32] in 33% yield from cyclohexanone. The acid was obtained as a colorless liquid after distillation: bp 94-97 °C (0.15 Torr) (lit.[32] bp 118-120 °C (0.4 Torr)); ^{1}H NMR, δ 1.2-2.6 (m, 11 H), 5.59 (m, 2 H), 11.4 (broad s, 1 H); ^{13}C NMR, δ 23.99, 25.83, 27.73, 29.18, 31.37, 43.15, 119.42, 130.56, 184.33.

N-Methyl-4-cyclooctenamine (**28b**) was prepared in 59% yield from the above acid by the method used for the preparation of amine **25b**.[19] Amine **28b** had the following properties: bp 80 °C (8 Torr) (lit.[19] bp 84-85 °C (8 Torr)); ^{1}H NMR, δ 1.32 (m, 3 H), 1.5-1.8 (m, 4 H), 2.07 (m, 3 H), 2.2-2.5 (m, 5 H), 5.58 (m, 2 H); ^{13}C NMR, δ 23.67, 25.90, 26.65, 33.34, 33.99, 35.24, 60.11, 129.58, 130.14.

PTOC carbamate **28a** was prepared by Method A from 1.0 g (7.2 mmol) of amine **28b**. Recrystallization from ether--hexanes gave 1.4 g (4.8 mmol, 67%) of **28a** as a yellow solid: mp 55 °C; ^{1}H NMR, δ 1.5-1.9 (m, 6 H), 2.0-2.4 (m, 4 H), 2.88 (s, 1.1 H), 3.04 (s, 1.9 H), 4.03 (m, 0.65 H), 4.40 (m, 0.35 H), 5.62 (m, 2 H), 6.57 (t, 1 H), 7.16 (d, 1 H), 7.62 (d, 2 H); ^{13}C NMR, δ 23.44, 25.81, 26.52, 30.46, 32.22, 32.84, 33.01, 33.14, 57.38, 58.66, 112.60, 129.12, 129.72, 130.86, 134.03, 137.52, 139.33. *Anal.* Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.62; H, 6.89. Found: C, 61.91; H, 6.97.

1-[(Isopropyl(3-cyclohexenylmethyl)carbamoyl)oxy]-2(1H)-pyridinethione (32a). *N*-Isopropyl-4-(aminomethyl)-

cyclohexene (**32b**) was prepared by reductive amination of 1,2,3,6-tetrahydrobenzaldehyde. To a solution of 6.0 mL (ca. 51 mmol) of the aldehyde, 44 mL of isopropylamine and 29 mL of acetic acid in 150 mL of MeOH was added 2.0 g of $NaBH_3CN$. The mixture was stirred at room temperature for 96 h. The pH was adjusted to < 2 with conc HCl, and the MeOH was distilled at reduced pressure. Water (75 mL) was added, and the pH was adjusted to > 10 with NaOH. The mixture was extracted with ether (2 x 100 mL). The combined ethereal phase was washed with water and saturated NaCl solution and dried ($MgSO_4$). Ether was distilled at reduced pressure. Distillation of the residue from CaH_2 afforded 6.9 g (45 mmol, 88%) of **32b** as a clear liquid: bp 86-90 °C (14 Torr); ^{1}H NMR, δ 0.80 (broad s, 1 H), 0.98 (d, 6 H), 1.16 (m, 1 H), 1.67 (m, 3 H), 2.0 (m, 3 H), 2.46 (m, 2 H), 2.71 (hep, 1 H), 5.60 (m, 2 H); ^{13}C NMR, δ 23.22, 25.07, 27.27, 30.37, 34.34, 49.01, 53.83, 126.62, 127.57

PTOC carbamate **32a** was prepared from 1.53 g (10 mmol) of amine **32b** by Method B. Recrystallization from benzene--hexanes gave 2.6 g (8.5 mmol, 85%) of **32a** as a yellow solid: mp 138 °C; ^{1}H NMR, δ 1.30 (m, 7 H), 1.81 (m, 2 H), 2.08 (m, 4 H), 3.21 (d, 0.8 H), 3.42 (d, 1.2 H), 3.85 (m, 0.6 H), 4.49 (m, 0.4 H), 5.63 (m, 2 H), 6.67 (dt, 1 H), 7.14 (dt, 1 H), 7.61 (m, 2 H); ^{13}C NMR, δ 19.96, 21.44, 25.13, 26.78, 29.75, 33.93, 34.04, 49.76, 50.49, 52.36, 53.17, 112.60, 126.19, 127.61, 133.89, 137.65, 139.34. *Anal.* Calcd for $C_{16}H_{22}N_2O_2S$: C, 62.72; H, 7.24. Found: C, 62.94; H, 7.28.

1-[(Butyl(5-hexenyl)carbamoyl)oxy]-2(1H)-pyridinethione (35a) *N*-Butyl-5-hexenamide was prepared from 5-hexenoic acid. To 2.28 g (20 mmol) of 5-hexenoic acid in 50 mL of benzene was added 2.40 g of thionyl chloride and a drop of DMF. The reaction was stirred for 12 h at room temperature. The solution was cooled to 0 °C, and 4.5 g of butylamine in 50 mL of benzene was added dropwise. After stirring for 1 h, the reaction was warmed to room temperature, and 50 mL of water was added. The layers were separated, and the organic portion was washed once with 5% aqueous HCl and once with saturated $NaHCO_3$. After drying ($MgSO_4$), the benzene was removed at reduced pressure to give 3.0 g (89%) of the desired amide as a white solid which was pure by NMR: ^{1}H NMR, δ 0.84 (t, 3 H), 1.2-1.5 (m, 4 H), 1.68 (quin, 2 H), 1.95-2.15 (m, 4 H), 3.17 (2t, 2 H), 4.94 (m, 2 H), 5.70 (m, 2 H); ^{13}C NMR, δ 13.90, 20.24, 25.03, 31.95, 33.39, 36.19, 39.42, 115.65, 138.49, 173.43.

N-Butyl-5-hexenamine (**35b**) was prepared by reduction of the amide. A solution of 2.9 g (17 mmol) of *N*-butyl-5-hexenamide in 50 mL of THF was added dropwise to a stirred suspension of 1.5 g of $LiAlH_4$ in 50 mL of THF. The mixture was heated at reflux for 48 h and then quenched by the addition of 1.5 mL of water in 15 mL of THF followed by 1.5 mL of 20% aqueous NaOH and 4.5 mL of water. After filtration, the salts were washed with ether (3 x 50 mL). The combined filtrates were dried ($MgSO_4$). Distillation from CaH_2 gave 2.0 g (75%) of amine **35b** as a colorless liquid: bp 74-76 °C (7 Torr); ^{1}H NMR, δ 0.86 (t, 3 H), 1.38 (m, 9 H), 2.01 (q, 2 H), 2.63 (t, 4 H), 4.92 (m, 2 H), 5.76 (m, 1 H); ^{13}C NMR, δ 13.99, 20.50, 26.67, 29.67, 32.32, 33.64, 49.80, 49.94, 114.37, 138.76.

PTOC carbamate **35a** was prepared by Method B using 1.9 g (12.3 mmol) of amine **35b**. Recrystallization from ether--hexanes gave 3.3 g (10.7 mmol, 87%) of carbamate **35a** as a yellow solid: mp 72 °C; ^{1}H NMR, δ 0.90 (2t, 3 H), 1.37 (m, 4 H), 1.66 (m, 4 H), 2.06 (quin, 2 H), 3.29 (t, 2 H), 3.48 (t, 2 H), 4.92 (m, 2 H), 5.76 (m, 1 H), 6.67 (dt, 1 H), 7.13 (dt, 1 H), 7.61 (dd, 2 H); ^{13}C NMR, δ 13.77, 13.84, 19.89, 20.04, 25.84, 25.99, 26.82, 27.96, 29.52, 30.67, 33.31, 47.54, 48.82, 112.24, 114.77, 114.87, 133.48, 137.06, 138.29, 138.40, 138.75, 151.62, 176.30. *Anal.* Calcd for $C_{16}H_{24}N_2O_2S$: C, 62.31; H, 7.84. Found: C, 62.57; H, 7.89.

General Procedure for Reaction of PTOC Carbamates in the Presence of *t*-BuSH (Method C). The PTOC carbamate and acid were weighed into an appropriately sized round-bottom flask containing a small stir bar. The flask was sealed with a septum, wrapped with aluminum foil to exclude light, and purged with nitrogen. Solvent was then added via syringe followed by *t*-BuSH. The shield was removed, and the mixture was stirred and irradiated with a 100 or 150 W, tungsten filament bulb from a distance of about 0.5 m. The reactions were monitored for dissappearance of the PTOC carbamate by TLC. When the reactions were judged to be complete (10-30 min), a small amount of 20% aqueous HCl was added, and the solvent was removed at reduced pressure. Ether (ca 25 mL) was added, and the resulting solution was basified with 20% aqueous NaOH solution. The layers were separated, and the aqueous layer was extracted with ca. 25 mL of ether. The combined ethereal layers were dried (K_2CO_3) and analyzed by GC and GC-mass spectrometry. If a large amount of acyclic product was detected, no attempt was made to isolate the cyclic products. When no acyclic amine was detected but large amounts of pyridyl sulfide products were present, the reactions were repeated with a higher concentration of *t*-BuSH. When the product mixture contained a large amount of cyclized amine by GC, the products were isolated by bulb-to-bulb distillation. Detailed conditions are given in Table 2.

General Procedure for Reaction of PTOC Carbamates in the Absence of *t*-BuSH (Method D). Reactions were run as in Method C but without thiol. When the reaction was judged to be complete, solvent was removed at reduced pressure. The residue was partitioned between ether and 10% aqueous HCl. The aqueous portion was basified and extracted with several portions of ether. The combined ethereal extract was washed with saturated NaCl solution and dried (K_2CO_3). The alkyl pyridyl sulfide products typically were purified by chromatography; small amounts of dipyridyl disulfide byproducts eluted before the alkyl pyridyl sulfides.

***N*-Butyl-2-methylpyrrolidine (3a).** Method C was employed for reaction of PTOC carbamate **1a** (0.59 g, 2.0 mmol). Bulb-to-bulb distillation of the products (85 °C, 35 Torr) gave 0.21 g of 90:10 mixture of **3a** and **1b** as a colorless oil; the yield of **3b** was 0.19 g (1.34 mmol, 67%). Product **3a**

was identified by comparison of its GC retention, mass spectrum and NMR spectra with those of an authentic sample.[1]

N-**Butyl-2-[(2-pyridylthio)methyl]pyrrolidine (3b).** Method D was employed for reaction of PTOC carbamate **1a** (0.30 g, 1.0 mmol). Chromatography (silica gel, ether elution) gave 0.23 g (0.92 mmol, 92%) of **3b** as a heavy oil: ^{1}H NMR, δ 0.88 (t, 3 H), 1.2-2.0 (m, 8 H), 2.14 (m, 2 H), 2.60 (m, 1 H), 2.8-3.0 (m, 2 H), 3.13 (dt, 1 H), 3.59 (dd, 1 H), 6.90 (dt, 1 H), 7.13 (dd, 1 H), 7.40 (dt, 1 H), 8.37 (dd, 1 H); ^{13}C NMR, δ 14.28, 21.03, 22.73, 30.43, 31.17, 34.40, 54.63, 54.84, 63.86, 119.61, 122.73, 136.21, 149.81, 160.07; mass spectrum, *m/e* (intensity), 139 (15), 126 (100), 96 (17).

N-**Butyl-2-[1-(2-pyridylthio)-1-methylethyl]pyrrolidine (5).** Method D was employed for reaction of PTOC carbamate **4** (0.92 g, 2.86 mmol). Chromatography (neutral alumina, EtOAc--hexanes elution) gave 0.51 g (1.8 mmol, 64%) of **5** as an oil: ^{1}H NMR, δ 0.85 (t, 3 H), 1.3 (s, 3 H), 1.45 (s, 3 H), 1.2-1.5 (m, 4 H), 1.6-2.1 (m, 4 H), 2.2-2.5 (m, 2 H), 2.7-2.9 (m, 1 H), 3.0-3.1 (m, 2 H), 7.0 (dt, 1 H), 7.3-7.5 (m, 2 H), 8.45 (broad d, 1 H); ^{13}C NMR, δ 14.21, 20.47, 24.64, 25.37, 26.89, 28.35, 31.60, 55.39, 56.84, 58.97, 72.00, 120.74, 128.04, 135.79, 149.33, 158.56; mass spectrum, *m/e* (intensity), 263 (0.4), 235 (3), 168 (6), 167 (6), 126 (100), 84 (8), 70 (20).

N-**Butyl-2-methyl-5-[(2-pyridylthio)methyl]pyrrolidines (8b and 9b).** Method D was employed for reaction of PTOC carbamate **6a** (0.25 g, 0.81 mmol). Chromatography (neutral alumina, EtOAc--hexanes elution) gave 0.157 g (0.59 mmol, 73%) of **8b** and **9b** as an oil. The isomer ratio was determined by GC; the major isomer eluted second on a nonpolar column. ^{1}H NMR (of a 1:4 mixture), δ 0.9 (m, 6 H), 1.2-2.2 (m, 8 H), 2.4-2.7 (m , 2 H), 2.9 (dd, 1 H), 3.0-3.3 (m, 2 H), 3.6 (dd, 1 H), 6.95 (dt, 1 H), 7.15 (d, 1 H), 7.45 (dt, 1 H), 8.4 (d, 1 H); ^{13}C NMR, major, (minor), δ 14.13, 15.73, (20.84), 20.91, 28.01, (29.05), (29.72), 30.76 (2 C), 32.12, (35.88), 47.35, (52.30), 55.47, 59.75, (60.29), (63.59), (119.06), 119.12, (112.17), 112.25, 135.65, 149.20, 159.40, (159.52); mass spectrum (major isomer), *m/e* (intensity), 249 (0.2), 207 (4), 153 (10), 140 (100), 138 (12), 111 (8), 110 (8), 98 (9), 84 (12). Reduction of the product mixture with $CuCl_2$--$LiAlH_4$[2] gave a mixture of amines **8a** and **9a** that were identical to authentic samples.[9]

N-**Butyl-2-[(2-pyridylthio)methyl]octahydroindoles (12b).** Method D was employed for reaction of PTOC carbamate **10** (1.0 g). Chromatography (neutral alumina, EtOAc--hexanes elution) gave a mixture of isomers of **12b** as an oil. The isomer ratio was determined by GC. ^{1}H NMR (of the mixture), δ 0.85 (t, 3 H), 1.0-3.0 (m, 19 H), 3.0-3.6 (m, 2 H), 6.85 (t, 1 H), 7.2 (m, 1 H), 7.4 (t, 1 H), 8.3 (d, 1 H); ^{13}C NMR (of the major isomer), δ 14.13, 20.76, 21.88, 24.06, 28.93, 29.29, 30.37, 35.44, 36.42, 36.90, 53.00, 63.36, 63.54, 118.90, 122.10, 135.50, 149.14, 159.71.

2-Methylpyrrolizidine (16a). Method C was employed for reaction of PTOC carbamate **13a** (0.56 g, 2.0 mmol). Bulb-to-bulb distillation (87 °C, 40 Torr) gave 0.16 g of a 1:1 mixture of isomers of **16a** contaminated with ca. 10% of amine **13b** (yield 0.14 g, 1.12 mmol, 56%) as a colorless oil: ^{1}H NMR, δ 0.94 (dd, 3 H), 1.2-2.3 (m, 8 H), 2.35-2.6 (m, 1.5 H), 2.8-3.2 (m, 1.5 H), 3.48 (m, 1 H); ^{13}C NMR, δ 17.31, 17.79, 25.96, 26.38, 31.99, 32.56, 33.18, 36.66, 40.16, 41.94, 54.96, 55.99, 62.45, 63.51, 63.82, 64.94; mass spectrum, *m/e* (intensity), 125 (21), 97 (24), 83 (100).

2-[(2-Pyridylthio)methyl]pyrrolizidine (16b). Method D was employed for reaction of 0.26 g (0.94 mmol) of PTOC carbamate **13a**. Chromatography (silica gel, ether elution) gave 0.21 g (0.90 mmol, 96%) of a 1:1 mixture of isomers of **16b** as an oil: ^{1}H NMR, δ 1.0-1.5 (m, 1 H), 1.5-2.0 (m, 4 H), 2.17 (m, 1 H), 2.5-3.1 (m, 5 H), 3.19 (m, 2 H), 3.50 (m, 1 H), 6.89 (dt, 1 H), 7.09 (d, 1 H), 7.38 (dt, 1 H), 8.33 (d, 1 H); ^{13}C NMR, δ 25.94, 26.22, 32.46, 32.94, 33.03, 33.18, 38.09, 38.31, 39.24, 41.64, 55.00, 55.73, 60.11, 60.85, 63.66, 64.66, 119.22, 119.27, 122.10, 122.20, 135.76, 149.30, 159.03.; mass spectrum, *m/e* (intensity), 124 (100), 111 (66).

Photolysis of 17a in the Presence of *t*-BuSH. Method C eas employed for reaction of PTOC carbamate **17a** (30 mg). Amine **17b** was the major product as determined by GC. GC--mass spectral analysis indicated that amine **19a**[15] was also formed: mass spectrum, *m/e* (intensity), 111 (25), 110 (22), 83 (100).

1-(Pyridylthio)pyrrolizidine (19b). Method D was employed for the reaction of 49 mg (0.19 mmol) of **17a**. Chromatography (silica gel, ether elution) gave 34 mg (0.15 mmol, 79%) of one isomer of **19b** as an oil: ^{1}H NMR, δ 1.5-2.0 (m, 5 H), 2.35-2.7 (m, 3 H), 2.98 (m, 1 H), 3.20 (m, 1 H), 3.39 (q, 1 H), 3.82 (q, 1 H), 6.93 (dt, 1 H), 7.14 (dd, 1 H), 7.42 (dt, 1 H), 8.38 (dd, 1 H); ^{13}C NMR, δ 26.02, 31.60, 34.44, 48.13, 54.31, 55.51, 70.92, 119.93, 123.16, 136.34, 149.97, (quaternary not observed).

3-Methylpyrrolizidine (22a). Method C was employed for a reaction of PTOC carbamate **20a** (0.56 g, 2.0 mmol). Bulb-to-bulb distillation (70 °C, 15 Torr) gave a 1.7:1 mixture of isomers of **22a** (0.20 g, 1.6 mmol, 80%) as an oil: ^{1}H NMR, δ 1.06 (d, 1.1 H), 1.17 (d, 1.9 H), 1.36 (m, 3 H), 1.6-2.1 (m, 5 H), 2.4-2.7 (m, 2 H), 2.8-3.1 (m, 1 H), 3.35-3.6 (m, 1 H); ^{13}C NMR, δ 16.58, 21.15, 25.72, 26.23, 30.48, 32.26, 32.35, 32.74, 32.90, 35.65, 46.07, 53.33, 57.66, 62.09, 64.25, 64.90; mass spectrum, *m/e* (intensity), 125 (25), 124 (21), 110 (100), 97 (60), 82 (20). (see Don ref 62 for NMR data)

3-[(Pyridylthio)methyl]pyrrolizidine (22b). Method D was employed for a reaction of PTOC carbamate **20a** (0.28 g, 1.0 mmol). Chromatography (silica gel, ether elution) gave a 1.7:1 mixture of isomers of **22b** (0.225 g, 0.96 mmol, 96%) as an oil. Pure samples of each isomer were obtained by further chromatography (alumina, ether--THF). Stereochemical assignments were not made. For the major isomer: ^{1}H NMR, δ 1.3-1.9 (m, 7 H), 2.1 (m, 1 H), 2.21 (d, 1 H), 2.55 (m, 1 H), 2.83 (m, 1 H), 3.27 (m, 1 H), 3.44 (m, 2 H), 6.92 (m, 1 H), 7.15 (d, 1 H), 7.42 (dt, 1 H), 8.49 (d, 1 H); ^{13}C NMR, δ 26.32, 30.54, 31.68, 32.22, 32.49, 46.36, 62.45, 65.08, 119.69, 122.77, 136.27, 149.94, (quaternary not observed). For the minor isomer: ^{1}H NMR, δ 1.32 (m, 2 H), 1.5-2.2 (m, 6 H), 2.6-3.1 (m, 4 H), 3.42 (dd, 1 H), 3.56 (quin, 1 H), 6.88 (dt, 1

H), 7.12 (dd, 1 H), 7.39 (dt, 1 H), 8.34 (dd, 1 H); ^{13}C NMR, δ 25.93, 32.43, 32.67, 33.52, 36.39, 54.81, 65.75, 67.02, 119.60, 122.64, 136.23, 149.88, (quaternary not observed).

Tropane (27a). Method C was employed for the reaction of 0.28 g (1.0 mmol) of carbamate **25a**. Bulb-to-bulb distillation (85 °C, 35 Torr) gave 84 mg (0.67 mmol, 67%) of tropane as a colorless liquid. The NMR spectra agreed with those reported:[21] ^{1}H NMR, δ 1.25-1.55 (m, 6 H), 1.68 (m, 2 H), 1.95 (dt, 2 H), 2.20 (s, 3 H), 3.04 (m, 2 H); ^{13}C NMR, δ 16.36, 26.02, 31.43, 40.93, 61.68.

2-(Pyridylthio)tropane (27b). Method D was employed for reaction of 0.28 g (1.0 mmol) of carbamate **25a**. Chromatography (silica gel, ether) gave a 1.5:1 mixture of isomers of **27b** in 94% yield (0.22 g) as an oil.[35] Each diastereomer was obtained in pure form by further chromatography on silica gel using 1:1 hexane--EtOAc. The major isomer gave the following spectra: ^{1}H NMR, δ 1.45 (m, 3 H), 1.90 (m, 5 H), 2.32 (s, 3 H), 3.11 (m, 1 H), 3.26 (m, 1 H), 4.11 (dt, 1 H), 6.92 (dt, 1 H), 7.11 (d, 1 H), 7.42 (dt, 1 H), 8.39 (dd, 1 H); ^{13}C NMR, δ 23.17 (2 C), 26.01, 31.29, 40.36, 44.60, 60.61, 65.39, 119.37, 122.24, 135.86, 149.60, 158.70. The minor isomer gave: ^{1}H NMR, δ 1.35 (m, 1 H), 1.62 (m, 3 H), 2.02 (m, 4 H), 2.20 (s, 3 H), 3.14 (m, 1 H), 3.29 (m, 1 H), 4.03 (m, 1 H), 6.90 (dt, 1 H), 7.14 (d, 1 H), 7.40 (dt, 1 H), 8.37 (dd, 1 H); ^{13}C NMR, δ 22.76, 24.53, 26.41, 29.79, 42.26, 46.71, 62.22, 68.83, 118.94, 122.66, 135.62, 149.24, (quaternary carbon not observed).

Photolysis of 28a in the presence of *t*-BuSH. Method C was employed for reaction of 60 mg (0.2 mmol) of carbamate **28a**. The parent amine **28b** was produced in 83% yield by GC analysis. The presence of 9-methyl-9-azabicyclo[4.2.1]nonane (**30a**) in ca. 9% yield was indicated by GC but could not be confirmed by GC-mass spectroscopy. The presence of **30b** was indicated by GC and GC-mass spectrometry (see below); **30b** was present as a 3:1 mixture of diastereomers.

9-Aza-9-methyl-2-(2-pyridylthio)bicyclo[4.2.1]nonane (30b). Method D was employed for reaction of 0.15 g (0.5 mmol) of carbamate **28a**. Chromatography (silica gel, ether) gave an 11:1 mixture of products **30b** and **31b** in 61% yield. GC analysis before chromatography also indicated the presence of the parent amine (**28b**), but this was not isolated. By GC and ^{1}H NMR, compound **30b** was a 3:1 mixture of diastereomers, and **31b** was a 2:1 mixture of diastereomers. The four pyridyl sulfides could not be separated by chromatography; the mixture had the following spectra: ^{1}H NMR, δ 1.3-2.3 (m, 10 H), 2.38 (s, 2.1 H), 2.47 (s, 0.73 H), 2.52 (s, 0.19 H), 3.21 (m, 1 H), 3.3-3.5 (m, 1 H), 3.92 (m, 0.69 H), 4.16 (m, 0.24 H), 4.28 (m, 0.06 H), 7.90 (m, 1 H), 7.12 (m, 1 H), 7.40 (m, 1 H), 8.38 (m, 1 H); ^{13}C NMR, major (minor), δ 22.37, (23.78), (25.30), 29.46, 31.36, 31.52, (32.66), (35.33), 36.59, (42.14), 46.43, (48.39), 50.63, (63.37), 66.36, (68.72), 72.49, 119.53, (119.78), (123.12), 123.29, 136.23, (136.36), 149.96, (150.16); mass spectrum, *m/e* (intensity), (major isomer of **30b**), 248 (20), 170 (10), 137 (95), 110 (30), 96 (60), 82 (100); (major isomer of **31b**) 248 (40), 136 (55), 110 (50), 96 (100).

Photolysis of carbamate 32a in the presence of *t*-BuSH. Method C was employed for reaction of 30.6 mg (0.1 mmol) of carbamate **32a**. The desired amine (**34a**) was indicated by GC-mass spectrometry but was not isolated: mass spectrum, *m/e* (intensity), 153 (37), 138 (20), 122 (100), 110 (68).

7-Aza-7-(2-propyl)-2-(2-pyridylthio)bicyclo[3.2.1]octane (34b). Method D was employed for reaction of 0.15 g (0.5 mmol) of carbamate **32a**. Chromatography (silica gel, ether) gave 0.15 g (0.43 mmol, 86%) of a 6:1 mixture of isomers (by GC) of **34b** as an oil. Further chromatography gave a sample of the major isomer: ^{1}H NMR, δ 1.09 (d, 3 H), 1.17 (d, 3 H), 1.48 (m, 1 H), 1.55-1.73 (m, 3 H), 1.89 (d, 1 H), 2.17 (m, 1 H), 2.31 (m, 2 H), 2.66 (d, 1 H), 2.98 (m, 2 H), 3.84 (t, 1 H), 4.18 (t, 1 H), 6.90 (dt, 1 H), 7.11 (dd, 1 H), 7.42 (dt, 1 H), 8.47 (dd, 1 H); ^{13}C NMRm, δ 21.86, 22.05, 25.92, 28.29, 34.09, 34.61, 43.20, 50.15, 53.91, 58.88, 119.15, 122.34, 135.76, 149.41, 159.33; mass spectrum, *m/e* (intensity), 262 (3), 247 (6), 151 (100), 122 (96), 110 (75);

Photolysis of 35a in the presence of *t*-BuSH. Method C was employed for reaction of 31 mg (0.1 mmol) of carbamate **35a**. Amines **37a** and **38a** were identified by GC-mass spectral analysis. Amine **37a** had *m/e* (intensity), 155 (7), 140 (60), 112 (100). The large M-15 peak indicated the 2-methyl piperidine product. Amine **38a** had *m/e* (intensity), 155 (4), 112 (100).

Photolysis of 35a in the absence of a hydrogen atom donor. Method D was employed for reaction of 31 mg (0.1 mmol) of carbamate **35a**. Products were analyzed by GC and GC-mass spectrometry. Amine **35b** was formed in 31% yield, and products **37b** and **38b** were formed in 42% yield. Sulfide **37b** had *m/e* 140 as the only significant peak. Sulfide **38b** had *m/e* (intensity), 153 (45), 110 (100).

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