

N-HYDROXYPYRIDINE-2-THIONE CARBAMATES. VI. FUNCTIONALIZATION OF CARBON RADICALS FORMED BY AMINIUM CATION RADICAL CYCLIZATIONS

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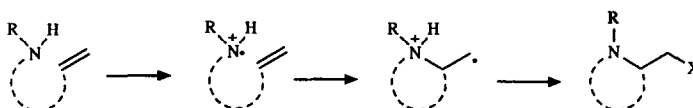
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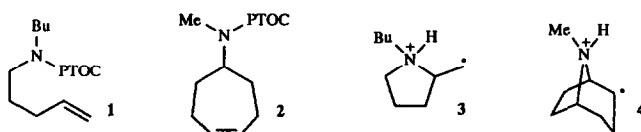
Abstract: A variety of reagents have been evaluated for trapping carbon radicals formed from aminium cation radical cyclizations. Rapid "self-trapping" of these radicals by their PTOC carbamate precursors requires highly reactive trapping agents. Synthetically useful trapping reagents include *t*-BuSH, CBr₄, phenyl vinyl sulfone and Ph₂Se₂ in addition to the PTOC carbamate radical precursors.

In the preceding papers,^{1,2} we demonstrated that high yields of cyclic products could be obtained from δ,ϵ -unsaturated aminium cation radicals formed from *N*-hydroxypyridine-2-thione (PTOC) carbamates. The variety of alkaloid skeletons produced from relatively simple amines suggests that the method can be of synthetic value. Further, the mild conditions necessary for production of the aminium cation radicals are compatible with several functional groups on the substrate, and a variety of radical trapping agents will be stable in the reaction medium. In this paper we explore functionalizations of the carbon radicals formed by aminium cation radical cyclizations. In general, we have tested reagents that Barton and co-workers have shown to be useful for functionalization of alkyl radicals produced from PTOC esters,³ and we present examples of both successful and unsuccessful trapping procedures that broadly define the limits of the reagents that can be employed. The overall reaction sequence is illustrated in Scheme 1. A δ,ϵ -unsaturated amine is converted to an aminium cation radical via reaction of its PTOC carbamate in the presence of a weak acid, cyclization of the aminium cation radical gives the β -ammonium substituted carbon radical that can then react with the trapping agent to give the cyclic, functionalized product.

Scheme 1

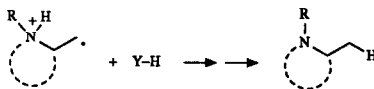


Most of the studies reported here employed PTOC carbamates **1** and **2** which give aminium radical cations that cyclize to carbon radicals **3** and **4**, respectively. Standard conditions for aminium cation radical formation and cyclization (room temperature, acetonitrile solvent, malonic acid, tungsten lamp irradiation)² were employed; the trapping agents were simply added before the reactions were initiated.



Radical Reduction Reactions

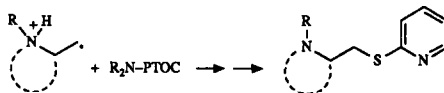
When a reactive hydrogen atom donor is present in the reaction medium, the carbon radical is reduced. Simple reduction to give an unsubstituted product represents a loss in functionality, but reduced products might nevertheless be desired. Conditions for reductions were reported in the preceding papers.^{1,2} In most cases, cyclizations of δ,ϵ -unsaturated aminium cation radicals were successful when *t*-BuSH was present as a hydrogen atom donor, and subsequent reaction of the carbon radicals thus formed with *t*-BuSH gave the reduced product. Bu_3SnH was found to react with the aminium cation radical more rapidly than did *t*-BuSH, and this resulted in formation of uncyclized product due to competition between the cyclization and trapping reactions; therefore, Bu_3SnH should be avoided in reactions of PTOC carbamates.¹



An alternative procedure for production of reduced products involving isolation of the self-trapped product and subsequent reduction is discussed below. This procedure has the advantage that the self-trapped products are often formed in higher yields than the reduction products, and, thus, a reluctant cyclization can be driven by the absence of competing reaction channels for the aminium cation radical.¹ However, it has the disadvantage that other reducible functional groups cannot be present in the self-trapped product.

Self-Trapping Reactions

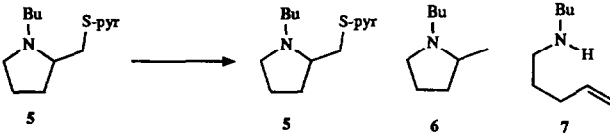
In the absence of a hydrogen atom donor or other radical trapping agents, the PTOC carbamates react with the cyclic carbon radicals (but not with their aminium cation radical precursors) to give an alkyl 2-pyridyl sulfide product. As we have shown, the facility of this reaction and the relative simplicity of the product isolation typically resulted in 80-95% yields when cyclization conditions were optimized.¹ Because of these high yields, we have investigated reactions of the alkyl pyridyl sulfides in some detail.



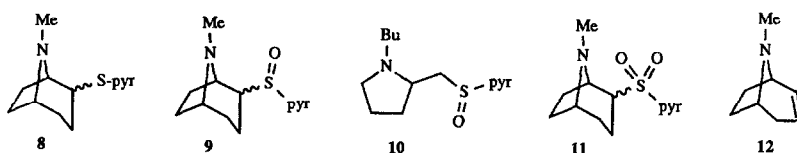
A variety of reduction conditions were studied for conversion of pyrrolidine **5** to its reduced counterpart **6**. Reduction of alkyl pyridyl sulfides by Bu_3SnH in refluxing toluene via a radical chain reaction has been reported by Barton,^{3a} but the reaction proceeded slowly when the alkyl group was primary. When sulfide **5** was treated with 2 equivalents of Bu_3SnH in benzene at 50 °C for 8 h with AIBN initiation, less than 1% conversion of **5** to **6** occurred. One may note that the alkyl phenyl selenides discussed later can be efficiently reduced by Bu_3SnH at 50 °C,² although this sequence is rather circuitous.

Nickel reducing agents (Ra-Ni or nickel boride⁴) successfully reduced pyridyl sulfide **5**, but ring opened product **7** was formed in addition to the desired reduction product **6**. Apparently, an intermediate radical formed in the nickel reductions can ring open to the aminyl radical in competition with a hydrogen transfer step. The ring opening would appear to be similar to the opening of the neutral β -amino, carbon-centered radical we have observed,² and the nickel reagents apparently do not deliver hydrogen rapidly to a radical.

Reduction of pyridyl sulfide **5** with the reagent⁵ prepared from CuCl_2 and LiAlH_4 was successful in refluxing THF; the pyrrolidine **6** was obtained in 63% yield, and ring opened products were not detected in the reaction. This powerful reducing agent precludes the presence of polar functional groups, however.

	
Conditions	Percent Composition
Bu_3SnH (2 equiv), cat. AIBN, 50 °C, 8 h	99 <1
Ra-Ni (20 equiv), EtOH, reflux, 2 h, 63%	75 25
NiCl (10 equiv), NaBH_4 (30 equiv), EtOH, reflux	25 75
$\text{CuCl}_2/\text{LiAlH}_4$ (4 equiv), THF, 25 °C, 4h	50 50
$\text{CuCl}_2/\text{LiAlH}_4$ (4equiv), THF, reflux, 4 h, 63%	100

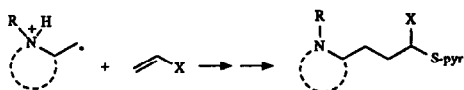
Oxidation of the pyridyl sulfide followed by elimination has precedent in Barton's work,⁶ although activated groups favored these eliminations. In our work, oxidations were achieved with MCPBA in the presence of camphor sulfonic acid which was added as a precautionary measure to prevent amine oxidation. Thus, sulfide **8** was oxidized to sulfoxide **9** in good yield by one equivalent of MCPBA. Similarly, sulfoxide **10** was prepared from sulfide **5**. Treatment of sulfide **8** with two equivalents of MCPBA gave sulfone **11** in high yield.⁷ Attempted eliminations of sulfoxide **9** in refluxing toluene failed to give olefinic products. However, elimination did occur in refluxing toluene when DBU was added; tropidine (**12**) was isolated in 74% yield from this reaction.



Mukaiyama and co-workers⁸ have demonstrated α -lithiation and alkylation of benzyl and allyl 2-pyridyl sulfides. Given the potential utility of this type of conversion for pyridyl sulfides like **5** and **8**, especially coupled with oxidation and elimination of the resulting sulfoxide, we explored several possible deprotonation-alkylation conditions. However, numerous attempts to deprotonate and alkylate either sulfide **5** or sulfoxide **10** failed. Typically, starting materials were recovered from reactions run at low temperatures. At higher temperatures, LDA reacted with sulfoxide **10** to give unidentified products. Apparently, Mukaiyama's successful deprotonations required the activation of the benzylic and allylic groups.

Olefin Trapping Reactions

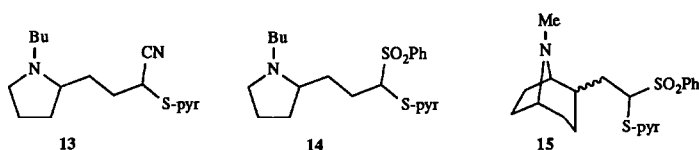
Olefin trapping agents were tested with the expectation that electron deficient olefins would readily discriminate between the



electrophilic aminium cation radical and the less electrophilic² cyclic carbon radical. For these reactions to be successful, the β -ammonium carbon radical must react with the trapping agent at least as fast as it reacts with the PTOC carbamate precursor. This addition reaction gives a new electrophilic radical that will either react with the PTOC carbamate precursor to give a thiopyridyl substituted addition product or will add to another molecule of the olefin to give, ultimately, telomers.

A variety of olefin trapping agents have been exploited by Barton for functionalization of carbon radicals formed from PTOC esters,^{3,6,9,10} but our results show that a more limited set of olefin trapping agents are available for functionalization of carbon radicals formed by aminium cation radical cyclizations. The major problem appears to be that the self trapping reaction of the cyclic radical by the PTOC carbamate is faster than the self-trapping reaction of a simple carbon radical by its PTOC ester precursor. This is consistent with our previous observation that the β -ammonium radical shows an inverted order of reactivity (relative to that of a simple alkyl radical) with the hydrogen atom donors *t*-BuSH and Bu₃SnH.² Specifically, an electrophilic radical would be expected to add more rapidly to the polarized thione group of the PTOC precursor than does a simple carbon radical. However, it is also possible that the β -ammonium radicals suffered a reduced rate of addition to the electron deficient olefins.

In practice, trapping of radical **3** by acrylonitrile to give product **13** was achieved in only low yield from the reaction of PTOC carbamate **1**. Even when 10 equivalents of the olefin were present, the ratio of self-trapped product **5** to adduct product **13** was 2:1. Radical telomerization products also were formed in this reaction, so it is clear that acrylonitrile is not a useful trapping agent for our radicals even though acrylonitrile and acrylates successfully trap alkyl radicals from PTOC esters.⁹



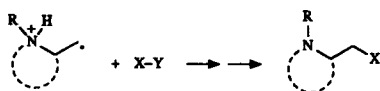
The highly reactive olefin, phenyl vinyl sulfone, gave better results. Reactions of PTOC carbamates **1** and **2** in the presence of 10 equivalents of this olefin gave products **14** and **15**, respectively, along with comparable amounts of sulfides **5** and **8**. However, the absence of telomers in these reactions suggested an experimental modification that optimized the yield of product **14**. The PTOC carbamate **1** was added in small portions to a reaction mixture containing excess phenyl vinyl sulfone. Effectively, the concentration of the trapping agent was at least 100 times that of **1** at any time. From this reaction, product **14** was isolated in 56% yield, and a small amount of sulfide **5** was also detected. Barton *et al.*¹⁰ have shown that the geminal sulfone and sulfide groups in compounds like **14** are subject to a variety of useful synthetic conversions.

Other, less active, olefins did not trap radical **3** to any appreciable extent. A reaction of PTOC carbamate **1** in the presence of 10 equivalents of ethyl vinyl ether resulted in formation only of sulfide **5** despite the fact that ethyl vinyl ether traps electrophilic perfluoroalkyl radicals produced by the PTOC ester

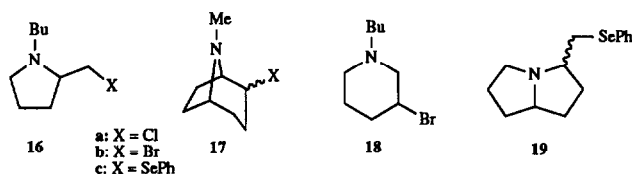
protocol.¹¹ A similar reaction in the presence of tributylallylstannane¹² gave a complex product mixture that did not appear to contain any of the desired allylated product.

Group Transfer Reactions

Group transfer reactions occurring by a radical chain sequence that involves an S_H2 process are among the most useful radical functionalization reactions because a stable product is formed directly from the radical and because a variety of readily transformed functional groups can be added to the radical center. In addition, several group transfer reagents are highly reactive. We have tested a variety of simple S_H2 trapping reagents with varying results; reactive group transfer agents successfully competed with the fast self-trapping reaction.



Reactions of PTOC esters in the presence of CCl_4 or $CBrCl_3$ result in excellent yields of alkyl halides in a facile equivalent of the Hunsdiecker reaction.^{3a,13} However, reactions of PTOC carbamates **1** and **2** in the presence of large excesses of CCl_4 (up to 50% of the solvent) led to formation of sulfides **5** and **8** and no detectable amounts of chlorine substituted products **16a** and **17a**. These results again suggest an enhanced reactivity of the β -ammonium carbon radical with the PTOC carbamate. Similarly, only a small amount of bromine substituted products were obtained when $CBrCl_3$ was used as a trapping agent. However, CBr_4 was found to trap the intermediate carbon radicals efficiently. The reaction of PTOC carbamate **2** in the presence of 10 equivalents of CBr_4 resulted in a 60% yield of bromide **17b**. A similar reaction of PTOC carbamate **1** gave a 64% yield of piperidine **18**. The piperidine presumably resulted from a rearrangement of the 2-(bromomethyl)pyrrolidine **16b** via an aziridinium ion intermediate; similar rearrangements of 2-(chloromethyl)pyrrolidines are well known.¹⁴



Diphenyl diselenide is a good trapping agent for radicals formed from PTOC esters,¹⁵ and it also proved to be a superb trapping agent for the β -ammonium radicals from the PTOC carbamates. A reaction of carbamate **1** in the presence of two equivalents of Ph_2Se_2 resulted in an 85% isolated yield of phenylseleno product **16c**. Similarly, an 82% yield of product **17c** was realized from a reaction of carbamate **2**, and product **19** was isolated in 86% yield from a reaction of its corresponding PTOC carbamate.¹ The high yields of the phenylseleno substituted products combined with the reactivity imparted to these compounds upon oxidation of the selenides¹⁶ shows that the diselenide trapping has excellent synthetic potential. One should also note that the 2-(phenylselenomethyl) substituted amine products are not subject to the rearrangements of their 2-(halomethyl) counterparts (*i.e.* rearrangement of **16b** to **18**).

Given the results with Ph_2Se_2 trapping, we expected that disulfides also might trap the intermediate β -ammonium carbon radicals. However, in practice, reactions of **1** with both dimethyl disulfide and diphenyl

disulfide in large (10-fold) excess gave only small amounts of sulfide products **16** ($X = \text{SMe}$) and **16** ($X = \text{SPh}$) along with the ubiquitous 2-pyridyl sulfide **5**.

Conclusions

Cyclizations of aminium cation radicals produced from PTOC carbamates can be followed by synthetically useful radical trapping reactions, and some limits of the reagents that can be applied have been defined by this work. In general, the trapping reagents must be highly reactive to compete successfully with the self-trapping reaction, and the number of useful trapping reagents for the β -aminium carbon radicals is appreciably smaller than the set of reagents that can be employed to functionalize alkyl radicals produced by PTOC ester protocols. The overall sequences we have demonstrated in this work and in the previous paper¹ result in conversion of a δ,ϵ -unsaturated amine into a heterocycle with substitution adjacent to the newly formed N–C bond as shown in Scheme 1 where X is H, Br, SePh, 2-pyridylthio, or $\text{CH}_2\text{CH}(\text{S-pyr})\text{SO}_2\text{Ph}$, and other, reactive radical trapping agents should also prove to be successful traps for carbon radicals formed by aminium cation radical cyclizations. That most of the radical trapping reactions could even be attempted in the aminium cation radical cyclization procedures illustrates the utility of the PTOC carbamates. Other routes to aminium cation radicals involve substantially more severe reaction conditions (strong Brønsted or Lewis acids) that would not tolerate many of the trapping agents we have employed.

Experimental Section

General. Melting points and boiling points were uncorrected. All ^1H and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer at 200 MHz and 50 MHz, respectively, for solutions in CDCl_3 with Me_4Si as internal standard. GC analyses were accomplished on various instruments equipped with FID detectors using wide bore capillary columns (J&W Scientific DB-5 or DB-1). GC-mass spectral analyses were performed on a Hewlett-Packard (HP) 5790 GC interfaced with an HP 5970 mass selective detector. Commercial amines were distilled from CaH_2 and stored over KOH. All solvents used in photolyses of carbamates were dried and deoxygenated before use. Benzene was distilled from CaH_2 and purged of oxygen by bubbling nitrogen through it at least for 30 minutes. Acetonitrile was distilled and stored over 4A molecular sieves. THF was distilled from a solution containing potassium and benzophenone under N_2 .

The preparation of PTOC carbamates **1** and **2** and alkyl pyridyl sulfide products **5** and **8** and reactions of the carbamates in the presence of hydrogen atom donors were described in the preceding papers.^{1,2}

Reduction of **5 with Mukaiyama's reagent.** To a slurry of dry CuCl_2 (1.0 g, 7.54 mmol) in dry THF (20 mL) cooled to 0–5 °C was added dropwise LiAlH_4 (0.6 g, 15.8 mmol) in dry THF (40 mL). During the addition, a black

solid was formed. After the addition of LAH, **5** (0.47 g, 1.89 mmol) in THF (5 mL) was added dropwise. The reaction mixture was heated at reflux for about 4 h. A standard LAH work up afforded the product **6** (0.17 g) after distillation in 63% yield.

Tropidine (12). To a solution of **8** (0.25 g, 1.07 mmol) and camphor sulphonic acid (0.3 g, 1.3 mmol) in CH_2Cl_2 (25 mL) at 0° C was added 85% MCPBA (0.24 g, 1.2 mmol). The reaction mixture was stirred for 20 min and poured into a solution of 10% NaOH (25 mL). The two layers were separated, and the aqueous portion was extracted with an additional 25 mL of CH_2Cl_2 . The combined organic layers were washed with brine and dried. The solvent was removed under reduced pressure to afford sulfoxide **9** (0.22 g, 84%) as a mixture of 4 diastereomers: ^1H NMR, δ 1.2–2.2 (m, 8 H), 2.2–2.36 (m, 3 H), 2.8–3.18 (m, 1 H), 3.2–3.45 (m, 1 H), 3.8–3.95 (m, 1 H), 7.2–7.55 (m, 1 H); ^{13}C NMR, δ 21.59, 21.87, 22.21, 25.21, 26.00, 26.77, 32.09, 33.81, 35.73, 35.86, 44.96, 62.31, 62.58, 63.02, 66.22, 66.70, 68.06, 70.63, 120.70, 121.27, 123.51, 124.93, 127.16, 137.71, 137.97, 149.82, 150.44.

The mixture of sulfoxides was dissolved in toluene (25 mL), DBU (0.5 mL, 3.35 mmol) was added, and the resulting mixture was heated at reflux for 6 h. The solution was cooled, and water was added. The layers were separated, and the aqueous portion was extracted with ether (2 x 25 mL).

The combined organic extracts was basified (15% NaOH) and extracted with ether. After drying (MgSO_4), the solvent was removed, and tropidine (**12**) (69 mg, 67% from crude **9**) was obtained after bulb-to-bulb distillation (75°C, 35 Torr) (lit.¹⁷ bp 25°C, 0.6 Torr) as a colorless oil: ^1H NMR, δ 1.3–2.2 (m, 6 H), 2.30 (s, 3 H), 3.16 (m, 1 H), 3.24 (m, 1 H) and 5.62 (m, 2 H).

N-Butyl-2-[(2-pyridylsulfoxide)methyl]pyrrolidine (11). Oxidation of **5** (0.2 g, 0.8 mmol) with MCPBA (0.8 mmol) as described above afforded **6** as a mixture of diastereomers in 1:1.5 ratio (0.19 g, 0.71 mmol) in 90% yield: ^1H NMR, δ 0.79 (q, 3 H), 1.08–1.58 (m, 4 H), 1.6–1.95 (m, 2 H), 1.96–2.3 (m, 2 H), 2.4–3.1 (m, 6 H), 3.2–3.4 (d, 1 H), 7.24–7.36 (m, 1 H), 7.8–8.05 (m, 2 H), 8.05 (d, 1 H); ^{13}C NMR, δ 13.67, 13.77, 20.35, 22.39, 22.64, 30.43, 30.53, 30.73, 30.89, 53.24, 53.34, 53.88, 54.57, 59.24, 59.88, 61.00, 119.77, 119.80, 124.37, 137.93, 137.97, 149.55, 149.59.

N-Butyl-2-[3-(phenylsulfonyl)-3-(2-pyridylthio)propyl]pyrrolidine (14). To a 10 mL round bottom flask containing phenyl vinyl sulfone (0.60 g, 3.57 mmol) and malonic acid (0.10 g, 0.96 mmol) was added acetonitrile (20 mL). A solution of **1** (0.10 g, 0.34 mmol) in acetonitrile (2 mL) was prepared and kept under nitrogen in the dark. A 0.2 mL portion of PTOC carbamate was added to the solution of phenyl vinyl sulfone, and the mixture was irradiated with a 150 W tungsten lamp at a distance of 0.5 m. At 10 min intervals, the lamp was turned off, another 0.2 mL of the carbamate solution was added, and the lamp was turned on. After the final addition of carbamate solution, the reaction mixture was irradiated for an additional 0.5 h. Solvent was removed at reduced pressure, and the residue was partitioned between ether and 10% HCl. The layers were separated. The aqueous portion was basified and extracted with ether (2 x 30 mL). The combined ether extracts was dried (MgSO_4), filtered and concentrated. Preparative TLC (silica gel, 1:1 hexane–EtOAc) yielded the addition adduct **14** (80 mg, 56%) as a mixture of diastereomers: ^1H NMR, δ 0.82 (m, 3 H), 1.1–2.5 (m, 15 H), 2.64 (m, 1 H) 3.07 (m, 1 H), 5.68 (dd, 1 H), 6.88 (m, 2 H), 7.32 (m, 4 H), 7.85 (d, 2 H), 8.14 (d, 1 H); ^{13}C NMR, δ 14.19, 14.24, 21.01, 22.34, 22.44, 30.30, 30.47, 31.02, 31.15, 54.30, 54.60, 54.80, 64.15, 65.81, 66.24, 120.83, 122.81, 128.72, 130.15, 133.93, 136.72, 149.50.

Reaction of 1 with ethyl vinyl ether (10 equiv) was attempted by the procedure described above with the exception that all of the PTOC carbamate was added in one portion. GC analysis of the product mixture showed it to contain amine **7** (12%) and sulfide **5** (37%) as the major products.

Reactions with CBr_4 . A solution of the PTOC carbamate (0.7 mmol), malonic acid (2.0 mmol) and CBr_4 (8.0 mmol) in acetonitrile (30 mL) was irradiated (5 h). An acid-base extraction as described above afforded the products. **2-Bromotropane (17b)** was obtained in 61% yield as an oil: ^1H NMR, δ 1.3–2.2 (m, 8 H), 2.34 (s, 3 H), 3.25 (m, 2 H), 4.35 (m, 1 H); ^{13}C NMR, δ 22.08, 25.55, 28.21, 32.39, 40.43, 52.72, 60.51, 68.04. **N-Butyl-3-bromopiperidine (18)** was obtained in 68% yield as an oil: ^1H NMR, δ 0.89 (t, 3 H), 1.2–2.85 (m, 7 H), 1.95–2.25 (m, 3 H), 2.33 (t, 2 H), 2.75 (m, 1 H), 4.15 (m, 1 H); ^{13}C NMR, δ 14.00, 20.67, 25.96, 28.96, 35.81, 48.36, 53.04, 58.13, 62.12.

Reactions with Ph_2Se_2 . A solution of PTOC carbamate (1.0 mmol), malonic acid (3.0 mmol) and Ph_2Se_2 (2.0 mmol) in acetonitrile (10 mL) was irradiated (2 h) at room temperature. Solvent was removed at reduced pressure, the residue was partitioned between ether and 10% HCl, and the ethereal layer was extracted with an additional portion of HCl. The combined aqueous phase was basified with 15% NaOH and extracted with ether. After solvent removal at reduced pressure, the crude product was dissolved in ethanol (5 mL), and NaBH_4 was added until the solution became colorless. Ether and 10% NaOH were added, and the phases were quickly separated. The ethereal layer was dried and concentrated to afford the phenylseleno products. **2-[(Phenylseleno)methyl]pyrrolidine (16c)** was obtained as a pale yellow oil (85 % yield): ^1H NMR, δ 0.87 (t, 3 H), 1.2–1.5 (m, 4 H), 1.6–1.85 (m, 3 H), 1.85–2.20 (m, 3 H), 2.65 (m, 1 H), 2.72 (m, 1 H), 2.96 (m, 1 H), 3.11 (m, 2 H), 7.21 (m, 3 H), 7.47 (m, 2 H); ^{13}C NMR, δ 13.85, 20.58, 22.21, 30.74, 32.99, 54.19, 54.34, 63.98, 126.56, 129.04, 132.34, (quaternary carbon not observed). **2-(Phenylseleno)tropane (17c)** was obtained as a 1.5:1 mixture of diastereomers in 82% yield: ^1H NMR, δ 1.30–2.15 (m, 8 H), 2.21 (s, 1.2 H), 2.24 (s, 1.6 H), 3.11 (m, 1.6 H), 3.27 (m, 0.4 H), 3.42 (m, 0.4 H), 3.60 (m, 0.6 H), 7.21 (m, 3 H), 7.50 (m, 2 H); ^{13}C NMR, δ 23.07, 23.28, 24.35, 24.69, 25.94, 26.82, 29.70, 32.47, 40.79, 42.33, 46.04, 49.68, 60.86, 62.36, 66.01, 67.57, 126.56, 127.11, 128.85, 128.99, 133.13, 133.78. **3-[(Phenylseleno)methyl]pyrrolizidine (18)**¹⁸ was obtained as a 1.7:1 mixture of diastereomers (86% yield): ^1H NMR, δ 1.2–1.6 (m, 3 H), 1.6–1.9 (m, 4 H), 2.05 (m, 1 H), 2.51 (m, 1 H), 2.7–3.3 (m, 4 H), 3.4–3.6 (m, 1 H), 7.20 (m, 2 H), 7.48 (m, 2 H); ^{13}C NMR, δ 25.63, 25.83, 29.12, 29.30, 31.76, 32.00, 32.25, 33.78, 34.33, 45.76, 54.29, 62.63, 64.69, 65.40, 67.20, 126.49, 126.74, 129.01, 129.08, 132.09, 132.35.

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