Organoselenium Chemistry. Dealkylation of Amines with Benzeneselenol

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Spectroscopic studies of alkylamine–benzeneselenol mixtures show that complete or almost complete proton transfer to form an ammonium selenolate salt occurs. Pyrolysis of these salts or solutions of them results in nucleophilic dealkylation of the amine if an alkyl group susceptible to S_N2 displacement is present. Products are the dealkylated amine and an alkyl phenyl selenide. Primary amines are dealkylated least and hindered tertiary amines most rapidly. Benzenethiol does not protonate alkylamines, although a salt does form with 1,8-bis(dimethylamino)naphthalene (**4**). Competitive studies show that $PhSe^-$ is at least a factor of 5 more nucleophilic than PhS^- but that PhS^- will demethylate $PhSeCH_3$ at a rate comparable to its reaction with protonated **4**.

We report here a method for the nucleophilic dealkylation of alkylamines which differs fundamentally from other available procedures[2] in that it does not involve the formation of any new bonds to nitrogen other than N–H. The procedure is thus not restricted to tertiary amines but is applicable to secondary and, in principle, primary amines as well. Furthermore, no troublesome hydrolyses are required to liberate the amine after dealkylation.

Although isolated reports of the dealkylation of primary [via the bis(*N*-sulfonamide)[2a]] and secondary amines (Al, 350 °C;[2b] RMgBr, 125–250 °C[2c]) are in the literature, most of the published amine dealkylation procedures involve treatment of amines with acylating (benzoyl chloride,[2d] acetic anhydride,[2e] iminophosgene,[2f] chloroformates[2g,h]), cyanating (von Braun reaction[2i]), and nitrosating[2j] reagents. Some aromatic amines are cleaved on treatment with HBr[2k] or HCO_2H.[2l] Most of these procedures are limited to tertiary amines, and amides or urethanes are formed as products which can be difficult to hydrolyze. The very successful vinyl chloroformate procedure introduced by Olofson, Schnur, Bunes, and Pepe[2h] has gone far in solving the latter problem. While the method outlined here has not been successful in all cases, it works well for some amines which previously could not be dealkylated in reasonable yields.

Results and Discussion

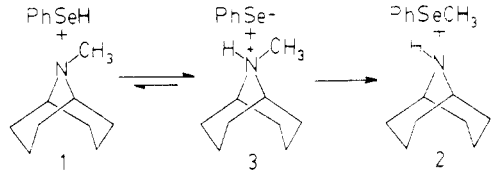
The procedure described here is based on two chemical properties of selenols: their relatively high acidity and the great nucleophilicity of their conjugate bases (selenolate anions). Table I summarizes some of the literature pK_a data available for S–H, Se–H, and Te–H bonds. These data show that thiols and selenols can protonate alkylamines in the aqueous media used for the pK_a measurement. The increased acidity of selenols over thiols (2–3 pK_a units) has the consequence that a selenol such as PhSeH[3] will protonate amines even in organic solvents,

Table I. Literature pK_a Data for Thiols and Selenols

compd	pK_a Y = S	Y = Se	Y = Te	ref
HYH	7.0	3.74	3.64	*a*
PhYH	6.5	5.9[c]		*b*
8-quinoline-YH	7.68	4.94		*d*
$HO_2CCH(NH_2)CH_2YH$	8.25	5.24		*e*
$\overset{+}{H}_3NCH_2CH_2YH$	8.3	5.0		*f*

[a] "Encyclopedia of Electrochemistry of the Elements", Vol. IV, A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1975, pp 280, 363. [b] C. L. Liotta, E. M. Perdue, and H. P. Hopkins, Jr., *J. Am. Chem. Soc.*, **96**, 7981 (1974). [c] See ref 3. [d] N. Nakamura and E. Sekido, *Talanta*, **17**, 515 (1970). [e] R. E. Huber and R. S. Criddle, *Arch. Biochem. Biophys.*, **122**, 164 (1967). [f] Y. Sugiura, Y. Hojo, Y. Tamai, and H. Tanaka, *J. Am. Chem. Soc.*, **98**, 2339 (1976).

whereas PhSH does not. This is clearly illustrated by the ^{13}C NMR spectral data presented in Figure 1.[4] The chemical shifts of the aromatic carbons of PhSH as well as the aliphatic carbons of the amine are essentially unchanged in the mixture (Figure 1b) when compared to those of each compound separately in $CDCl_3$ solution (<7% protonation). On the other hand, an equimolar solution of PhSeH and amine (Figure 1e) gives chemical shifts characteristic of the selenolate anion and the ammonium cation (>80% protonation), an ideal situation for a nucleophilic dealkylation.[5] In fact, when methylgranatanine (**1**) and excess PhSeH (1.5–3 equiv) are heated



to 150 °C without solvent and in the absence of air,[6] an essentially quantitative conversion to granatanine **2** (isolated as the hydrochloride) results. Spectroscopic measurements similar to those in Figure 1 show that here also conversion to the ionic form **3** is almost complete. Thiophenol does not significantly dealkylate **1** even after extended pyrolysis at 150 °C. This is a consequence of an unfavorable equilibrium (**1** + PhSH ⇌ **2** + PhS^-) and the

(1) A. P. Sloan Fellow, 1975–1979.

(2) (a) P. J. DeChristopher, J. P. Adamek, G. D. Lyon, J. J. Galante, H. E. Haffner, R. J. Boggio, and R. J. Baumgarten, *J. Am. Chem. Soc.*, **91**, 2384 (1969); (b) J. P. Napolitano, *Chem. Abstr.*, **79**, 126056 (1973); (c) E. C. Ashby and G. F. Willard, *J. Org. Chem.*, **43**, 4750 (1978); (d) Y. L. Gol'dfarb and R. M. Ispiryan, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 839 (1969); (e) R. P. Mariella and K. H. Brown, *Can. J. Chem.*, **49**, 3348 (1971); (f) G. Leclerc, B. Rouot, and C. G. Wermuth, *Tetrahedron Lett.*, 3765 (1974); (g) T. A. Montzka, J. D. Matiskella, and R. A. Partyka, *ibid.*, 1325 (1974); J. D. Hobson and J. G. McCluskey, *J. Chem. Soc. C*, 2015 (1967); (h) R. A. Olofson, R. C. Schnur, L. Bunes, and J. P. Pepe, *Tetrahedron Lett.*, 1567 (1977); (i) H. A. Hageman, *Org. React.*, **7**, 198 (1953); G. Fodor, S. Abidi, and T. Carpenter, *J. Org. Chem.*, **39**, 1507 (1974); (j) P. A. S. Smith and R. N. Loeppky, *J. Am. Chem. Soc.*, **89**, 1147 (1967); (k) J. Berlot and J. Renault, *Bull. Soc. Chim. Fr.*, 3175 (1973); R. A. Chambers and D. E. Pearson, *J. Org. Chem.*, **28**, 3144 (1963); (l) M. Sekiya, M. Tomie, and N. J. Leonard, *ibid.*, **33**, 318 (1968).

(3) The only literature value for the pK_a of PhSeH is one determined during an electrochemical experiment and is probably subject to considerable experimental error [F. Fagioli, F. Pulidori, C. Bighi, and A. DeBattisti, *Gazz. Chim. Ital.*, **104**, 639 (1974)].

(4) Experimental details are available as supplementary material.

(5) V. Simánek and A. Klásek [*Tetrahedron Lett.*, 3039 (1969)] reported the demethylation of quaternary ammonium salts with PhSeNa.

(6) Selenols and selenolate anions are easily oxidized by air, particularly at elevated temperatures.

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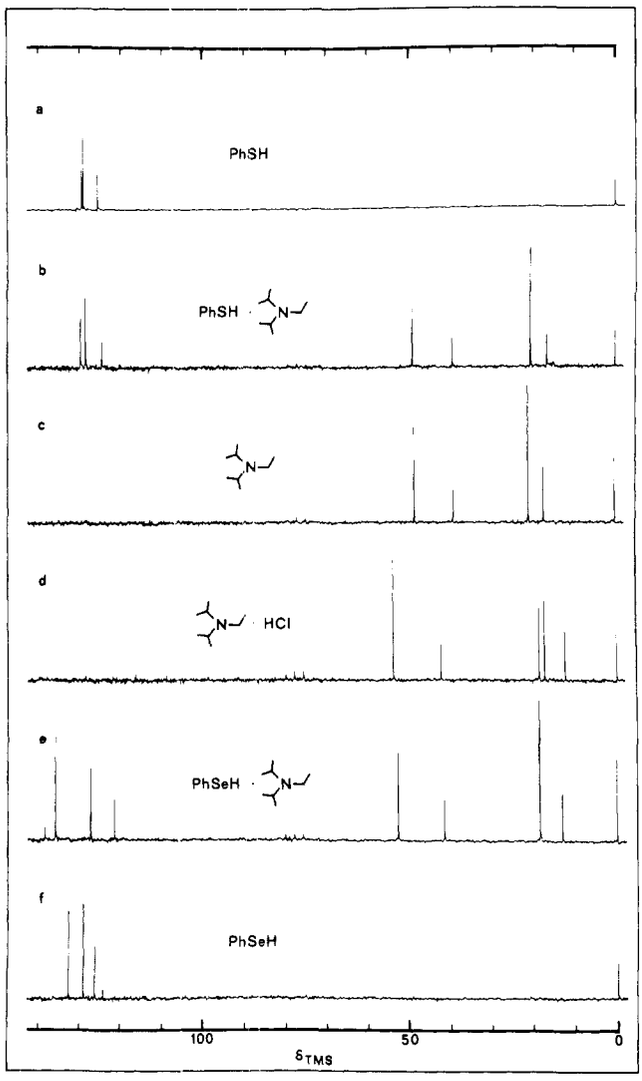
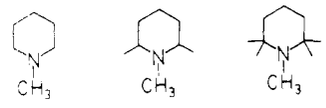


Figure 1. Carbon 13 NMR spectra in $CDCl_3$ solution.

lower nucleophilicity of PhS^- (see below).[7]

It is clear from the characteristics of this dealkylation that the nature of the amine (primary, secondary, or tertiary) should have little bearing on the success of the process. Most primary, secondary, and tertiary alkylamines react exothermically with PhSeH to form crystalline salts. Table II lists a number of examples of successful dealkylations we have carried out.

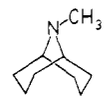
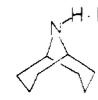
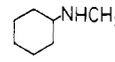
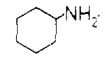
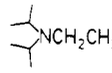
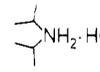
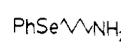
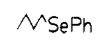
A surprising result was that primary amines, although they appeared to be protonated completely by PhSeH, underwent dealkylation only very slowly (last two entries in Table II). The origin of this effect is not clear but may be related to the fact that sterically encumbered amines are dealkylated markedly faster than unhindered ones. This is illustrated in the *N*-methylpiperidine examples below (percent dealkylation after reaction with 2 equiv of PhSeH at 150 °C in pyridine solution):[4]



60 min			55%
3 h	<10%	57%	100%
23 h	28%	80%	

(7) Direct comparison of PhS^- and $PhSe^-$ nucleophilicities has indicated roughly a factor of 5–10 more rapid reaction for $PhSe^-$ [R. G. Pearson, H. Sobel, and J. Songstad, *J. Am. Chem. Soc.*, **90**, 319 (1968); G. Guanti, C. Dell'Erba, and D. Spinelli, *Gazz. Chim. Ital*, **100**, 184 (1970)].

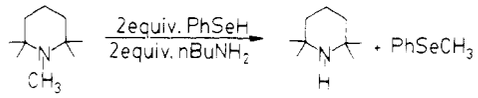
Table II. Dealkylation of Amines by Pyrolysis with Benzeneselenol

Amine	PhSeH (Equiv.)	Time (hr)	Product	Yield (%)
	1.6	48		89
	3	60 1		97 9
	2.5	96		85
	1.5	1[a]		98
	0.1	72		70[b]
	2.5	60 14 days		13 35
	2.5	60		20

[a] This reaction was run in pyridine solution since the ammonium selenolate salt did not melt at 150 °C and thus was stable at that temperature. [b] Yield based on PhSeH.

Two explanations appear reasonable: relief of steric strain in the S_N2 transition state (bulky leaving group) or a more subtle effect in which decreasing separation of ions in the ammonium selenolate ion pair of less hindered amines results in increased solvation and decreased nucleophilicity of the anion.[8] This effect, augmented by hydrogen bonding, should result in the lowest rates for primary amine dealkylations.

The demethylation of a mixture of 1,2,2,6,6-pentamethylpiperidine and *n*-butylamine proceeds at a similar rate as that of the tertiary amine alone. The fast rate of the hindered tertiary and slow rate of the unhindered primary amine cannot, therefore, be simply a consequence of a bulk property of the medium, since this is now the same for both, but must be the result of differences in the microenvironment of the reacting ion pair.



The other limitations of this dealkylation scheme are straightforward.

(1) The reaction will be very slow if the amine is not sufficiently basic to be significantly protonated by PhSeH. Thus neither *N*,*N*-dimethylaniline nor *N*,*N*-dimethylacetamide is demethylated at a useful rate at 150 °C.

(2) The alkyl groups must be susceptible to S_N2 displacement. Only pyrrolidine of all products in Table II undergoes a second dealkylation, and piperidine (but not pyrrolidine)[9] is essentially inert. Obviously, when a secondary or tertiary amine has two or more similar unhindered alkyl substituents, sequential dealkylations can occur. The reactivity difference between methyl and ethyl

(8) S. Alunni, E. Baciocchi, P. Perucci, and R. Ruzziconi, *J. Org. Chem.*, **43**, 2414 (1978).

(9) *N*,*N*-Dimethylpyrrolidinium iodide suffers substantial endocyclic dealkylation (82%) on treatment with $NaOCH_3$, whereas *N*,*N*-dimethylpiperidinium iodide gives only 3.6% of the endocyclic S_N2 product [G. Illuminati and C. Lillocci, *J. Org. Chem.*, **42**, 2201 (1977)].

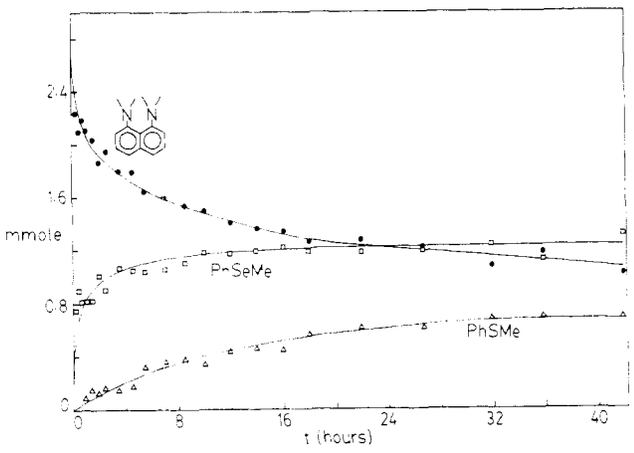
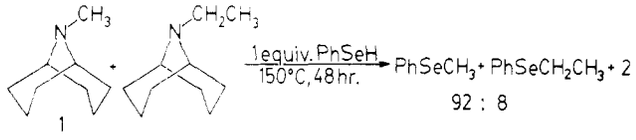


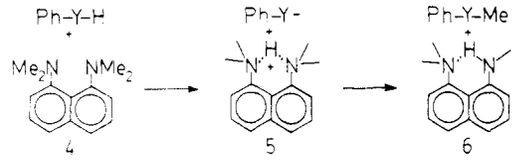
Figure 2. Competitive dealkylation of 1,8-bis(dimethylamino)naphthalene with $PhSe^-$ and PhS^- (in pyridine at 150 °C): (□) PhSeMe; (△) PhSMe; (●) 1,8-bis(dimethylamino)naphthalene.

groups is sufficient to allow reasonably selective demethylation, as shown by the experiment below:[4]



(3) The amine starting material and products must survive the elevated temperature and high nucleophilic conditions of the reaction. We have, for example, observed that several benzylamines, including benzylamine itself, benzylmethylamine, nicotine, and laudanosine, are not cleanly dealkylated under the conditions used. Failure of the laudanosine dealkylation to proceed cleanly is at least in part due to competitive demethylation of the aryl methyl ether groups (benzylselenol has been employed for the dealkylation of ethers[10]). We have also subjected 5-(*N*-methyl-*N*-butylamino)-2-pentanone and its ethylene ketal to our demethylation conditions. Although methyl phenyl selenide was formed in moderate yield, the ketone fragment was largely decomposed. Similarly, the isopropyl and ethyl ester of *N*-methylglycine suffered ester cleavage and *N*-demethylation when heated with benzeneselenol, but the glycine portion also underwent conversion to a mixture of materials which have not been characterized.

1,8-Bis(dimethylamino)naphthalene. The demethylation of 1,8-bis(dimethylamino)naphthalene (4) pro-



vided some interesting contrasts to the other amines in Table II. Mixing **4** and PhSeH in several different solvents frequently gave NMR spectra which indicated that initially (less than 30 min) no proton transfer had occurred, a reflection of the low *kinetic* basicity of this amine.[11] Proton transfer from PhSH to **4** was even slower, and solutions had to be heated to 65 °C to achieve conversion to **5**. The observation that even PhSH protonates **4** (a consequence of its extraordinary thermodynamic basicity) allowed a test of the relative nucleophilicities of $PhSe^-$ and PhS^- by an internal competition reaction. The results of one such experiment are illustrated in Figure 2.[4] The situation is clearly more complex than simple competition between the processes in eq 1 and eq 2. A third process,

$$5 + PhS^- \xrightarrow{k_S} 6 + PhSCH_3 \quad (1)$$

$$5 + PhSe^- \xrightarrow{k_{Se}} 6 + PhSeCH_3 \quad (2)$$

$$PhS^- + PhSeCH_3 \xrightarrow{k_x} PhSCH_3 + PhSe^- \quad (3)$$

the transfer of methyl between sulfur and selenium (eq 3), was also shown to be in effect by direct experiment.[4] Although computer simulation did not yield a viable minimization between the experimental and calculated data and thus give quantitative values for the rate constants of attack of $PhSe^-$ and PhS^- on 1,8-bis(dimethylamino)naphthalene, Figure 2 clearly shows that $PhSe^-$ is more nucleophilic in this system[8] by at least a factor of 5.

A possible explanation for the inability to fit the experimental data is the existence of yet another process, namely, the attack of selenide (or sulfide) anion on pyridine. This process, which has precedent in the Chichibabin reaction,[12] would act to further slow the appearance of phenyl methyl selenide. Observation of the aromatic protons of pyridine in a direct experiment with pyridine and benzeneselenol plus diisopropylamine (as the base) at 150 °C showed that some attack did in fact occur.

In Situ Generation of Benzeneselenol. Even though benzeneselenol is commercially available and easily prepared,[13] it would be desirable to bypass the necessity of working with this malodorous, toxic, and somewhat air-sensitive compound. It was reasoned that selenols could be generated in situ by reduction of diphenyl diselenide with a thiol such as PhSH (eq 4). The equilibrium

$$PhSeSePh + PhSh \rightleftharpoons PhSeH + PhSSePh \quad (4)$$

$$NR_3 + PhSeH \rightleftharpoons \overset{+}{H}NR_3 + PhSe^- \quad (5)$$

forming PhSeH may well be unfavorable, but this could be offset by the demonstrably favorable proton-transfer equilibrium (eq 5). This turned out not to be the case, since pyrolysis of mixtures of an amine, Ph_2Se_2, and several thiols (PhSH, $PhCH_2SH$, $HS(CH_2)_3SH$) led to no appreciable dealkylation of the amine. Only when dithiothreitol[14] was employed did dealkylation occur at a significant rate. Since dithiothreitol is more expensive than PhSeH, its use would appear to offer little advantage over the direct procedure.

Synthesis of Alkyl Selenides. The focal point of the above discussion has been the dealkylation of amines. The procedure can, however, also be considered as a unique method for the synthesis of alkyl phenyl selenides[15] as

(10) R. Ahmad, J. Saâ, and M. P. Cava, *J. Org. Chem.*, **42**, 1228 (1977).

(11) Amines of this type are known to undergo extraordinarily slow proton transfer [R. W. Alder, P. S. Bowman, W. R. S. Steele, and D. R. Winterman, *Chem. Commun.*, 723 (1968); R. W. Alder, N. C. Goode, N. Miller, F. Hibbert, K. Hunte, and H. J. Robbins, *J. Chem. Soc., Chem. Commun.*, 89 (1978)].

(12) (a) A. E. Chichibabin and O. A. Zeide, *J. Russ. Chem. Soc.*, **46**, 1216 (1914); *Chem. Abstr.*, **9**, 1901 (1915); (b) A. Rosowksy, and N. Papathanosopoulos, *J. Heterocycl. Chem.*, **9**, 1449 (1972).

(13) D. G. Foster, "Organic Syntheses", Collect. Vol. 3, Wiley, New York, N.Y., 1955, p 771; W. G. Salmond, M. A. Barta, A. M. Cain, and M. C. Sobala, *Tetrahedron Lett.*, 1683 (1977).

(14) Dithiothreitol will reduce some aliphatic diselenides [W. H. H. Gunther, *J. Org. Chem.*, **32**, 3931 (1967)] and was introduced for the reduction of disulfides by Cleland [W. W. Cleland, *Biochemistry*, **3**, 480 (1964)].

(15) Alkyl selenides are precursors to a number of other functional groups: H. J. Reich in "Oxidation of Organic Compounds, Part C", W. Trahanovsky, Ed., Academic Press, New York, N. Y., 1978, p 1; H. J. Reich, *Acc. Chem. Res.*, **12**, 22 (1979); D. L. J. Clive, *Tetrahedron*, **34**, 1285 (1978).

illustrated by the preparation of 4-amino-1-phenylselenobutane from pyrrolidine (Table II).

Experimental Section

Nuclear magnetic resonance spectra were measured on JEOL MH-100 or Brucker WH-270 (proton) and JEOL FX-60 (carbon) spectrometers.

Benzeneselenol was prepared by literature procedures[13] or by the procedure below, using $NaBH_4$ to reduce diphenyl diselenide.[16]

Caution! Selenium compounds are toxic and should be handled with care. When benzeneselenol is heated with alkylamines, gas (most probably hydrogen) is generated, so large-scale reactions (>10 mmol) should be carried out in a steel bomb, rather than in a sealed glass tube.

Preparation of Benzeneselenol. Solid $NaBH_4$ (2.6 g, 69 mmol) was added over a 15-min period to a suspension of diphenyl diselenide (9.36 g, 30 mmol) in 60 mL of absolute ethanol cooled to 0 °C under a stream of nitrogen. After completion of the addition, the mixture was allowed to warm to room temperature and stirred 30 min to give a clear solution. This was quenched with 200 mL of 5% HCl and extracted with 3 × 75 mL of 1:1 ether/pentane. The organic phase was dried over anhydrous sodium sulfate and the solvent evaporated. Distillation [60–63 °C (30 mm)] gave 8.15 g (86% yield) of a colorless foul-smelling oil which could be stored indefinitely as a solid below −10 °C under nitrogen (approximate melting point −5 to −10 °C): NMR ($CDCl_3$) δ 1.52 (s, 1 H), 7.2–7.4 (m, 3 H), 7.4–7.7 (m, 2 H).

Demethylation of *N*-Methylgranatanine (*N*-Methyl-9-azabicyclo[3.3.1]nonane,[17] 1). *N*-Methyl-9-azabicyclo[3.3.1]-nonane (1; 1.34 g, 9.6 mmol) and PhSeH (1.69 mL, 16 mmol) were mixed, sealed in a thick-walled tube under nitrogen, and heated at 150 °C for 48 h. After being cooled, the tube was opened and the contents were poured into 100 mL of freshly distilled ether. Under anhydrous conditions, hydrogen chloride was bubbled through the solution, forming a thick white precipitate. Dry nitrogen was then bubbled through this mixture for 10 min to remove excess HCl. The precipitate was collected by suction filtration, washed with dry ether, and dried under high vacuum to give 1.37 g (89% yield) of granatanine hydrochloride (2·HCl), an off-white powder: ^1H NMR ($CDCl_3$) δ 1.6–2.6 (m, 12 H), 3.64 (m, 2 H), 9.16 (s, 2 H); ^{13}C NMR 46.59, 27.31, 18.87 ppm.

Anal. Calcd for $C_8H_{16}ClN$: C, 59.43; H, 9.98. Found: C, 59.32; H, 10.07.

Demethylation of *N*-Methylcyclohexylamine. *N*-Methylcyclohexylamine (0.326 mL, 2.5 mmol) and PhSeH (0.792 mL, 7.5 mmol) were sealed in a thick-walled tube and heated at 150 °C for 100 h. Workup was as in the *N*-methylgranatanine example to give 0.33 g (97% yield) of cyclohexylamine hydrochloride; mp 203–205 °C.

Deethylation of Diisopropylethylamine. Diisopropylethylamine (0.87 mL, 5 mmol) and PhSeH (1.32 mL, 12.5 mmol) were sealed in a thick-walled tube and heated at 150 °C for 96 h. Workup was as in the *N*-methylgranatanine example to give 0.57 g (85% yield) of diisopropylamine hydrochloride; mp 211.5–213 °C.

This reaction was also run by using 40 mmol of diisopropylethylamine (7.00 mL) and 95 mmol of PhSeH (10.00 mL) and heating in a sealed tube at 150 °C for 72 h. The contents of the tube were taken up in dilute HCl and extracted with ether. The organic phase was washed with saturated NaCl, dried over anhydrous Na_2SO_4, and concentrated to give 6.33 g (86% yield) of $PhSeCH_2CH_3$ after distillation [39–40 °C (0.035 mm)]. The aqueous phase was basified with solid NaOH to pH 12 and extracted with ether, and the ether was dried by refluxing over solid NaOH overnight. After filtration, the amine was precipitated with dry HCl as done previously to give 4.32 g (80%) of diisopropylamine hydrochloride. The aqueous workup can be omitted and the amine hydrochloride precipitated directly as for the small-scale run above.

Demethylation of 1,8-Bis(*N*,*N*-dimethylamino)naphthalene (4). Amine 4 (107 mg, 0.5 mmol) and PhSeH (0.106 mL, 1.0 mmol) were dissolved in 0.3 mL of pyridine and sealed in a thick-walled tube. Pyridine was required to dissolve the high-melting salt formed between the amine and benzeneselenol alone. The sample was heated at 150 °C for 75 min. After cooling, the mixture was dissolved in dilute HCl and washed with 1:1 ether/pentane. The aqueous phase was basified to pH 12 with solid NaOH and reextracted with 1:1 ether/pentane. The organic phase was washed with brine and dried through a cone of anhydrous sodium sulfate, and the solvent was evaporated. The dark yellow oil was purified by preparative TLC on silica gel, using 50% ether/pentane as eluent. The major band at R_f 0.7 gave 98 mg (98% yield) of pure 1-(*N*,*N*-dimethylamino)-8-(*N*-methylamino)naphthalene which was spectrally identical with an authentic sample:[18] NMR ($CDCl_3$) δ 8.0–9.3 (br, 1 H, NH), 7.0–7.6 (m, 5 H), 6.44 (br, d, J = 8 Hz, 1 H), 2.93 (s, 3 H), 2.70 (s, 6 H).

Preparation of 1-(Phenylseleno)-4-aminobutane. Pyrrolidine (1.64 mL, 20 mmol) and PhSeH (0.21 mL, 2 mmol) were sealed in a thick-walled tube and heated at 150 °C for 3 days. After cooling, the reaction mixture was poured into dilute NaOH and extracted with 1:1 ether/pentane. The organic phase was washed with brine and dried through a cone of anhydrous sodium sulfate, and the solvent was evaporated to give a pale yellow oil. This was dissolved in anhydrous ether and the salt precipitated with dry HCl gas. Excess HCl was removed by bubbling nitrogen through the mixture. Vacuum filtration gave 371 mg (70% yield based on PhSeH) of a white powder, 1-(phenylseleno)-4-aminobutane hydrochloride: mp 152–152.5 °C; NMR (270 MHz, $CDCl_3$) δ 1.8 (m, 2 H), 1.9 (m, 2 H), 2.88 (t, J = 7.0 Hz, 2 H), 3.0 (m, 2 H), 7.2 (m, 3 H), 7.4 (m, 2 H).

Anal. Calcd for $C_{10}H_{17}ClNSe$: C, 45.38; H, 6.09. Found: C, 45.34; H, 6.30.

A similar experiment with 0.328 mL (4 mmol) of pyrrolidine and 0.42 mL (4 mmol) of PhSeH gave 86% of 1-(phenylseleno)-4-aminobutane hydrochloride and 14% of 1,4-bis(phenylseleno)butane, the product of bis dealkylation: mp 59.5–60.5 °C; NMR (270 MHz, $CDCl_3$) δ 1.78 (m, 4 H), 2.86 (m, 4 H), 7.2 (m, 3 H), 7.5 (m, 2 H).

Anal. Calcd for $C_{16}H_{18}Se_2$: C, 52.19; H, 4.93. Found: C, 52.40; H, 5.09.

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Registry No. *N*-Methylpiperidine, 626-67-5; 1,2,6-trimethylpiperidine, 669-81-8; 1,2,2,6,6-pentamethylpiperidine, 79-55-0; *N*-methylgranatanine, 491-25-8; *N*-methylcyclohexylamine, 100-60-7; diisopropylethylamine, 20634-92-8; 1,8-bis(*N*,*N*-dimethylamino)-naphthalene, 20734-58-1; pyrrolidine, 123-75-1; 1-butanamine, 109-73-9; 3-amino-1-propanol, 156-87-6; granatanine hydrochloride, 6760-43-6; cyclohexylamine hydrochloride, 4998-76-9; diisopropylamine hydrochloride, 5326-84-1; 1-(*N*,*N*-dimethylamino)-8-(*N*-methylamino)naphthalene, 20734-57-0; 1-(phenylseleno)-4-aminobutane hydrochloride, 70813-84-2; (butylseleno)benzene, 28622-61-9; 1-(benzeneseleno)-3-propanol, 70813-85-3; benzeneselenol, 645-96-5; diphenyl diselenide, 1666-13-3; (ethylseleno)benzene, 17774-38-8; 1,4-bis(phenylseleno)butane, 70813-86-4; *N*-ethylgranatanine, 64776-29-0; (methylseleno)benzene, 4346-64-9; benzenethiol, 108-98-5; DBU, 41015-70-7.

Supplementary Material Available: Experimental details for the kinetic experiments and Figures 1 and 2 (4 pages). Ordering information is given on any current masthead page.

(16) For a convenient preparation of diphenyl diselenide see: H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, **97**, 5434 (1975); H. J. Reich, M. L. Cohen, and P. D. Clark, *Org. Synth.*, in press.

(17) J. R. Wiseman and H. O. Krabbenhoft, *J. Org. Chem.*, **40**, 3222 (1975).

(18) We thank Professor R. W. Alder for a sample of this amine.