Study of the Reductive Cleavage of Selenides with Nickel Boride. A Convenient Deselenization Procedure[1]

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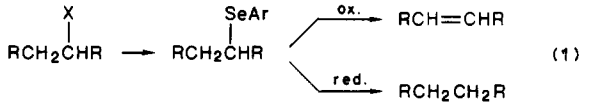
The reductive deselenization of a variety of organoselenium compounds can be performed rapidly, conveniently, and in high yield by using nickel boride. The latter reagent was generated in situ by adding sodium borohydride to nickel chloride hexahydrate and the substrate selenide in THF–methanol at 0 °C. Under these conditions, ca. 3–3.5 mol of borohydride was required to reduce all of the nickel salt to nickel boride and an excess of nickel boride was generally required to effect complete deselenization. Preformed nickel boride lost virtually all of its ability to cleave *n*-dodecyl phenyl selenide (**2**) after only 5 min, but continued to catalyze the decomposition of sodium borohydride. Deselenizing ability was not restored by the addition of hydrogen or further sodium borohydride to preformed nickel boride. Deuterium-labeling studies indicated that the hydrogen required for reductive deselenization originates from both the borohydride and the methanol solvent in a ratio of ca. 3:1. The use of sodium borodeuteride in methanol-*d* afforded 1-deuteriododecane of high isotopic purity, indicating that the procedure comprises a convenient method for preparing deuteriated products. The mechanism of nickel boride deselenization may involve transient nickel hydride or Ni(0) intermediates. The chemoselectivity of the reaction permits the cleavage of C–Se bonds in the presence of chlorides, nitriles, esters, sulfides, sulfones, ketones, and some olefins, but iodides and sulfinate esters undergo concomitant or preferential reduction. Electrochemical deselenization of **2** was also studied and resulted in anodic oxidation of the selenide to 1-dodecene instead of cathodic reduction to *n*-dodecane.

Organoselenium reagents are routinely employed in many types of synthetic transformations.[3] In a typical situation, an existing functional group is converted to an alkyl aryl selenide, followed by oxidative or reductive removal of the arylseleno moiety. Under oxidative conditions, selenoxide elimination[4] is generally observed, leading to an olefinic product, whereas reductive deselenization affords the corresponding alkane (eq 1).



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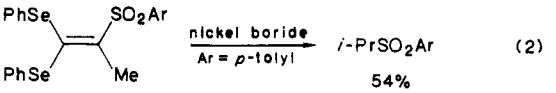
A variety of methods have been employed for the reductive cleavage of selenides, including the use of Raney nickel,[5] lithium triethylborohydride,[6] and lithium in ethylamine.[5f] However, these reagents serve effectively for a relatively constrained range of substrates, as they are also capable of reducing many other functionalities. Recently, free-radical deselenizations with tri-*n*-butyl-[7] or triphenyltin hydride[8] have proved particularly versatile, offering generally high yields and excellent selectivity in the presence of many other types of functionalities. Although this method has gained wide acceptance, it does suffer from some disadvantages. The tin hydride reagents are relatively expensive, their use normally requires elevated temperatures and reaction times of several hours, protection from the atmosphere is needed, and the tin selenide byproducts often require careful chromatographic separation from the desired products. Consequently, an alternative deselenization method to circumvent these drawbacks is desirable. Several years ago, in connection with other work, we had occasion to attempt the deselenization of ketene diselenoacetal **1** and observed that this could be achieved more efficiently with nickel boride than with tin hydrides[9] (eq 2). The reaction required only a few minutes and was conveniently carried out in an open Erlenmeyer flask, without the need for an inert atmosphere. Furthermore, since nickel boride can be easily generated in situ from inexpensive precursors (vide infra), a more detailed study of its behavior and utility in reductive deselenizations[10,11] in general, according to eq 3, appeared warranted.



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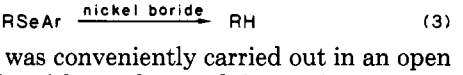

(3)

(1) We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

(2) Summer Research Assistant, 1987.

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Results and Discussion

The properties and synthetic applications of metal borides were recently reviewed by Ganem and Osby.[12] These species are conveniently obtained as fine black precipitates by the reduction of the corresponding metal salts with sodium borohydride in protic solvents.[13] Nickel boride obtained in this way has a Ni:B ratio of ~2:1 and contains adsorbed hydrogen consistent with the formula $(Ni_2B)_2H_3$.[14] It catalyzes the decomposition of sodium borohydride[13] and functions as a hydrogenation catalyst.[15] The activity of nickel boride varies widely with the conditions of its preparation, as well as with the type of precursor nickel salt.[15,16] The mechanisms of reductions effected by nickel boride are generally not well understood. Some initial experiments were therefore performed to optimize the conditions for nickel boride mediated deselenization and to gain insight into the nature of the process.

For this purpose, we chose *n*-dodecyl phenyl selenide (*n*-$C_{12}H_{25}SePh$, **2**) as a model substrate and reduced it under varying conditions. Selenide **2** was selected as it is easily prepared from 1-dodecanol by treating the corresponding tosylate with benzeneselenolate anion ($PhSe^-$), and because the formation of the reduction product dodecane can be easily monitored by GC analysis. We chose nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) as the Ni(II) salt as it has good solubility characteristics in the solvents employed (vide infra), and because it affords a high proportion of required boron-bound nickel on the surface of the resulting nickel boride.[17] We then proceeded to investigate the effects of solvents, the ratio of Ni(II) to $NaBH_4$, and the ratio of nickel boride to selenide **2**, as well as the effects of aging on the activity of the catalyst, and the source of the hydrogen (protic solvent or $NaBH_4$) which causes hydrogenolysis of the C–Se linkage.

Solvents and Reactant Ratios. Nickel boride for olefin hydrogenations is typically prepared in water (P-1 catalyst) or ethanol (P-2 catalyst).[15] For our purpose, a solvent was required that could dissolve $NiCl_2 \cdot 6H_2O$, $NaBH_4$ and also the relatively nonpolar selenides. We found that mixtures of tetrahydrofuran (THF) with methanol, ethanol, or 1-propanol gave comparable results in the deselenization of selenide **2**. The methanolic solutions proved to be the easiest to filter, and the ratio of THF:methanol could be changed from 16:1 to 1:6 without significantly affecting the outcome of the reaction. Consequently, various mixtures of these two solvents were employed in all subsequent deselenizations. An attempt to employ *N*,*N*-dimethylformamide as the solvent produced a nickel boride precipitate which proved more difficult to remove by filtration and afforded an inferior yield of dodecane from **2**. Since the reaction of $NaBH_4$ with Ni(II) salts is exothermic and results in the vigorous liberation of hydrogen gas, the reactions were generally performed at 0 °C.

Table I. Deselenization of Selenides 2 and 3 with Varying Quantities of Nickel Boride

moles of $NiCl_2 \cdot 6H_2O$ per mole of selenide[a]	% deselenization[b]	
	2	3
0.5	16	18
1.0	34	44
1.5	74	64
2.0	90	91
2.5	–	94
3.0	>98	–

[a] The molar ratio of $NaBH_4$ to $NiCl_2 \cdot 6H_2O$ was 3.1:1 in each case. [b] Determined by GC analysis with an internal standard.

Brown and Ahuja[15c] reported that the activity of nickel boride catalyst in hydrogenation reactions in ethanol was similar when a molar ratio of Ni(II) salt:$NaBH_4$ of 1:1 or 1:2 was used, but was somewhat lower with a 2:1 ratio. Ganem and Osby[12] pointed out that the reduction of $NiCl_2$ with $NaBH_4$ follows eq 4,[18] where the stoichiometry re-

$$4NaBH_4 + 2NiCl_2 + 9H_2O \rightarrow Ni_2B + 3H_3BO_3 + 4NaCl + 12.5\ H_2 \quad (4)$$

quires 2 mol of $NaBH_4$/mol of Ni(II). Furthermore, since nickel boride catalyzes the decomposition of $NaBH_4$, more than 2 mol of the latter reagent is required for the complete reduction of the nickel salt if the decomposition proceeds at a rate competitive to that of the reduction. In order to determine more precisely the quantity of $NaBH_4$ required for the complete consumption of Ni(II), we added varying quantities of the borohydride to separate solutions containing the same amount of $NiCl_2 \cdot 6H_2O$. In each case, the reaction mixture was centrifuged to remove insoluble nickel boride. The supernatant liquid was examined both visually and spectroscopically for the characteristic green color of the Ni(II) salt. When 3 molar equiv of $NaBH_4$ or less was employed, the green color was clearly evident and the supernatant liquid produced more black precipitate upon further addition of $NaBH_4$. With 3.5 mol of $NaBH_4$, the color was imperceptible and addition of more borohydride produced only a faint darkening of the solution. These experiments indicate that it requires between 3.0 and 3.5 mol of $NaBH_4$ to fully reduce 1 mol of $NiCl_2 \cdot 6H_2O$ under these conditions. In most subsequent deselenization reactions, a ratio of Ni(II):$NaBH_4$ of ca. 1:3 was employed.

When *n*-dodecyl phenyl selenide (**2**) was treated with an equimolar amount of nickel boride (i.e., **2**:$NiCl_2 \cdot 6H_2O$:$NaBH_4$ = 1:1:3), only 34% of **2** was observed to react. Repetition of the experiment with increasing amounts of nickel boride revealed that over 2 mol of the reagent is required to complete the reaction. Cyclododecyl phenyl selenide (**3**), a secondary alkyl selenide, showed nearly identical behavior, as illustrated in Table I. These results suggest that the function of nickel boride is not merely catalytic in these processes,[19] in marked contrast to its role in, for instance, the catalytic hydrogenation of olefins.[15] The deselenization of **2** was improved only marginally to 43% when an equimolar amount of nickel boride and a large excess of $NaBH_4$ (i.e., **2**:$NiCl_2 \cdot 6H_2O$:$NaBH_4$ = 1:1:9) were employed. In each of these experiments, the nickel boride was generated in the presence of the selenide by

(12) For a recent review, see: Ganem, B.; Osby, J. O. *Chem. Rev.* **1986**, *86*, 763.
(13) Schlesinger, H. I.; Brown, H. C.; Finholt, A. E.; Gilbreath, J. R.; Hoekstra, H. R.; Hyde, E. K. *J. Am. Chem. Soc.* **1953**, *75*, 215.
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(16) Okamoto, Y.; Nitta, Y.; Imanaka, T.; Teranishi, S. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 2027.
(17) X-ray photoelectron spectroscopic studies have indicated that the activity of the nickel boride depends to a large extent on the proportion of boron-bound nickel on the catalyst surface (see ref 16), as opposed to nickel oxide and BO_2^-. By this criterion, $NiCl_2$ is a highly effective source of active nickel boride. For a more detailed discussion of the composition and properties of this catalyst, see ref 12.
(18) Presumably in alcohol solvents the stoichiometry would be the same, except that 9 mol of ROH would be consumed and 3 mol of the ester $B(OR)_3$ would be produced.
(19) We cannot definitively rule out the possibility that the arylseleno residue from the cleavage of the selenide rapidly poisons the surface of the catalyst, making a relatively large quantity of the latter necessary for complete reduction.

adding the $NaBH_4$ in portions to a solution containing the selenide and nickel salt.

Effect of Preformation of Nickel Boride. Somewhat surprisingly, we found that it was essential to add the substrate selenide to the Ni(II) solution *prior* to the addition of $NaBH_4$. When selenide **2** was introduced just 5 min after the addition of the borohydride was complete, deselenization failed to occur and no significant amount of dodecane was produced. Moreover, deselenization activity was not restored to preformed nickel boride by the passage of hydrogen gas through the suspension, or by adding a subsequent fresh portion of $NaBH_4$. In the latter instance, vigorous hydrogen evolution indicated that, although virtually devoid of deselenization activity, the preformed nickel boride retained its ability to catalyze the decomposition of the borohydride. Similarly, nickel boride that had been deposited on a solid support of alumina or silica gel again failed to reduce **2**.[20] This behavior contrasts with the reported reductions of other functional groups such as olefins,[15] nitro compounds,[21] α-halo ketones,[22] vicinal dibromides,[22] thiols,[23] and a dithioketal,[24] where preformed nickel boride worked effectively.

A possible explanation for the lack of deselenizing activity of preformed nickel boride could be the requirement for prior complexation of the selenide to Ni(II), followed by reduction and deselenization of the complex during the subsequent addition of $NaBH_4$. A similar argument was made by Nose and Kudo[25] to explain the nickel boride mediated reduction of heterocycles such as quinaldine, where the preformed reagent also failed to perform effectively. This explanation was refuted by Ganem and Osby,[12] who pointed out (inter alia) that the process reported by Nose and Kudo requires only a catalytic amount of Ni(II) that is rapidly reduced to nickel boride under the reaction conditions, and that substantial reduction of the heterocycle does occur when quinaldine is mixed with preformed, inactive nickel boride which is then treated with fresh $NaBH_4$. However, since such reactivation fails in the case of deselenization, and since catalytic quantities of Ni(II) result in incomplete reactions, these counterarguments do not necessarily apply to the present system. In order to resolve the question of whether or not complexation occurs between the selenide and Ni(II), we recorded the UV–visible spectrum of $NiCl_2 \cdot 6H_2O$ in THF–methanol before and after the addition of an equimolar amount of selenide **2**. There was no perceptible change in either the wavelengths or intensities of the absorptions of the nickel salt. This indicates that such complexation does not occur and is therefore not a prerequisite for deselenization.

An alternative explanation for the inactivity of preformed nickel boride is that rapid changes must occur on its surface soon after it is formed. It is possible that these simply involve surface contamination from byproducts, which suppress the reactivity of nickel boride toward selenides. However, its continued ability to catalyze the decomposition of $NaBH_4$, and to reduce certain other functional groups (vide supra), casts some suspicion on this hypothesis. A final possibility is the formation of a transient species during the reduction of Ni(II) with $NaBH_4$ that, either alone or in concert with nickel boride, is responsible for deselenization, but is not required for, say, olefin hydrogenations. The identity of this intermediate is highly speculative, but could include Ni(0) species[26] in conjunction with adsorbed, activated hydrogen, or nickel hydride.[27a]

Deuterium-Labeling Studies. Knowledge of the source of the hydrogen consumed in cleavage of the C–Se bond would provide further understanding of the mechanism. The hydrogen could originate exclusively from $NaBH_4$, from H_2 liberated by the nickel boride catalyzed reaction of methanol with $NaBH_4$, or less probably, exclusively from the solvent. In order to distinguish between these possibilities, we performed the deselenization of **2** with various combinations of $NaBD_4$, CH_3OD, and THF-d_8. In each case, the product dodecane was analyzed by GC–mass spectroscopy to determine the relative quantities of $C_{12}H_{25}D$ (M^+, 171) and $C_{12}H_{26}$ (M^+, 170).

When the reaction was performed in the usual manner with $NaBD_4$ in unlabeled solvents, the product consisted of 26% $C_{12}H_{26}$ and 74% $C_{12}H_{25}D$. On the other hand, the use of $NaBH_4$ and $NiCl_2 \cdot 6D_2O$ in CH_3OD and unlabeled THF gave a highly complementary product distribution of 77% $C_{12}H_{26}$ and 23% $C_{12}H_{25}D$. No detectable $C_{12}H_{25}D$ was formed when the sole source of deuterium was THF-d_8. These results indicate that both the borohydride and the protic solvent contribute hydrogen to the product alkane in a ratio of ca. 3:1, effectively excluding any mechanism that requires all of the hydrogen to originate from the borohydride. The involvement of H_2 (or HD) cannot be ruled out, although the above ratio of 3:1 is higher than would be expected if all of the hydrogen was produced in accord with eq 4, or from the methanolysis of the borohydride reagent. Since labeled THF did not furnish any significant hydrogen to the product, a radical mechanism proceeding by way of nickel boride induced homolytic cleavage of the C–Se bond, followed by hydrogen abstraction by the alkyl radical from the solvent, can also be eliminated. Similar radical mechanisms have been implicated in the reduction of alkyl halides with cobalt aluminide.[27b] Thus, whereas these experiments do not unequivocally identify the operative mechanism, they permit several alternative pathways to be ruled out.

Finally, we report that the reduction of selenide **2** with $NaBD_4$ and $NiCl_2 \cdot 6D_2O$ in THF–CH_3OD produced $C_{12}H_{25}D$ with an isotopic purity of >95%. This procedure therefore constitutes a convenient alternative to the use of Ph_3SnD[8b] in the synthesis of deuterium-labeled products by reductive deselenization.

Electrochemical Deselenization. The electrolysis of aqueous solutions with a nickel cathode is known to generate nickel hydride[28] along with adsorbed molecular hydrogen. It therefore seemed reasonable to expect that the conditions at the cathode surface might simulate, at least superficially, those occurring in the nickel boride experiments, where similar nickel hydride intermediates are among those postulated. In an attempt to test this hypothesis, we electrolyzed selenide **2** in THF–methanol–water (6:3:1) in the presence of 20 mM NaCl as the electrolyte in an undivided cell. The formation of 1-dodecene

(20) An effective alumina-supported desulfurization reagent was recently prepared from $FeCl_2$ and $NaBHEt_3$: Alper, H.; Ripley, S.; Prince, T. L. *J. Org. Chem.* **1983**, *48*, 250.
(21) Osby, J. O.; Ganem, B. *Tetrahedron Lett.* **1985**, *26*, 6413.
(22) Sarma, J. C.; Borbaruah, M.; Sharma, R. P. *Tetrahedron Lett.* **1985**, *26*, 4657.
(23) Clark, J.; Grantham, R. K.; Lydiate, J. *J. Chem. Soc. C* **1968**, 1122.
(24) Truce, W. E.; Roberts, F. E. *J. Org. Chem.* **1963**, *28*, 961.
(25) Nose, A.; Kudo, T. *Chem. Pharm. Bull.* **1984**, *32*, 2421.
(26) Sodium borohydride is reported to reduce aryl bromides to arenes in the presence of $Ni(Ph_3P)_3$. Lin, S.-T.; Roth, J. A. *J. Org. Chem.* **1979**, *44*, 309.
(27) (a) The formation of transient cobalt hydrides in certain cobalt boride reductions has been previously considered, although no direct evidence for their presence was reported. See: Osby, J. O.; Heinzman, S. W.; Ganem, B. *J. Am. Chem. Soc.* **1986**, *108*, 67. (b) Evidence included hydrogen atom abstraction from THF solvent. See ref 27a.
(28) Conway, B. E.; Angerstein-Kozlowska, H.; Sattar, M. A.; Tilak, B. V. *J. Electrochem. Soc.* **1983**, *130*, 1825.

rather than *n*-dodecane occurred, affording the alkene in 72% yield after 21 h. This indicates that the selenide reacts preferentially by anodic oxidation rather than cathodic reduction under these conditions. Whereas we are unaware of any existing examples of the anodic oxidation of alkyl aryl selenides to olefins per se, such processes have been suggested for selenide intermediates formed in the electrochemical oxyselenenylation–deselenenylation of olefins with diselenides.[29]

In order to avoid the electrochemical oxidation of the selenide, we electrolyzed it in the cathode compartment of a separated cell. Unfortunately, no reductive deselenization was again observed,[30] thereby preventing the corroboration of similar intermediates in electrochemical and nickel boride mediated deselenizations.

Synthetic Utility of Nickel Boride Deselenization. The preceding experiments suggested that the reductive cleavage of selenides could be conveniently accomplished with nickel boride. However, since nickel boride can effectively reduce many other functional groups as well,[12] it remained to be determined whether the method would provide the selectivity required in general synthetic applications. The results are summarized in Table II. Typically, the selenide and $NiCl_2{\cdot}6H_2O$ were dissolved in a magnetically stirred solution of THF–methanol at 0 °C in an open Erlenmeyer flask. The $NaBH_4$ was added cautiously in portions, resulting in the vigorous evolution of gas and the formation of a black precipitate. After 15 min, the solution was filtered through Celite and the filtrate was analyzed by GC or separated by flash chromatography to afford the deselenized product.

Table II indicates that this protocol permits the reductive cleavage of selenides in the presence of alkyl chlorides, nitriles, esters, sulfides, and sulfones (entries 3, 5, 6, 7, and 9 respectively) in high yield and with excellent selectivity. The ability to cleave selenides in the presence of sulfides is especially noteworthy since nickel boride has been previously employed in desulfurization reactions.[23,24,31] Another example of the efficient reduction of a selenide in the presence of a sulfide is shown in eq 5, where an

$$\underset{\textbf{24}\ (1\ \text{equiv})}{PhS(CH_2)_{11}CO_2Me} + \underset{\textbf{7}\ (1\ \text{equiv})}{PhSe(CH_2)_{11}CO_2Me} \xrightarrow[NaBH_4\ (6\ \text{equiv})]{NiCl_2{\cdot}6H_2O\ (2\ \text{equiv})} \textbf{24}\ (0.97\ \text{equiv}) + \underset{(1.02\ \text{equiv})}{n\text{-}C_{11}H_{23}CO_2Me} \quad (5)$$

equimolar mixture of sulfide **24** and selenide **7** was treated with 2 molar equiv of $NiCl_2{\cdot}6H_2O$ and 6 molar equiv of $NaBH_4$ to afford quantitative reduction of the selenide and 97% recovery of the unreacted sulfide. Entries 4 and 8 in Table II show that the iodide moiety of **5** (unlike chloride **4**) and the sulfinate ester function in **9** were reduced under these conditions and are therefore incompatible with this procedure.

Since nickel boride catalyzes the hydrogenation of olefins,[15] we wished to assess the relative ease of C–Se cleavage compared to C=C reduction. Entries 10–14 demonstrate that the relatively hindered olefin **13** survived deselenization largely intact, while less hindered systems such as **11**, **12**, and **14** afforded chiefly the corresponding alkanes. Allylic selenides **20** and **21** (entries 21 and 22) underwent deselenization without reduction of the C=C bond. Both α- and β-(phenylseleno)cyclododecanone (entries 17 and 18) produced the parent ketone in high yield, although a small amount of the α,β-unsaturated derivative was formed as a byproduct in the latter instance. The α-seleno ketone **22** underwent substantial overreduction to the alcohol under the normal conditions (entry 23), but this was largely suppressed when the amount of $NaBH_4$ was decreased (entry 24). It is possible that ketones which are easily reduced react directly with $NaBH_4$ at a competitive rate when the usual reactant ratios are employed in deselenization. Complications were observed when the selenide moiety was vicinal to a good leaving group. Thus, the chloride **18** produced only cyclododecane (entry 19) while the acetate **19** afforded a modest yield of the deselenized ester and a substantial amount of the parent cycloalkane (entry 20). The deselenization of the selenoacetal **23** proceeded smoothly with cleavage of both selenium residues (entry 25).

Conclusions. These results demonstrate that nickel boride mediated deselenization is an exceptionally rapid, convenient, and economical method for the reductive cleavage of selenides. While the precise mechanism of the reaction is still speculative, our evidence suggests that a transient Ni(0) or nickel hydride species on the nickel boride surface plays a key role in the process.

Experimental Section

Melting points were determined on an A. H. Thomas hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 467 or Nicolet 5DX spectrometer, and UV–visible spectra were obtained with a Varian Carey 219 instrument. ^1H NMR spectra were obtained on an Hitachi Perkin-Elmer R24B, Varian XL200, or a Bruker AM400 spectrometer at 60, 200, and 400 MHz, respectively, with $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. Low- and high-resolution mass spectra were recorded on either a Kratos MS80 or a VG 7070E spectrometer, and GC–mass spectra were obtained on a VG 7070F instrument employing a 30-m Megabore DB-1 column (J and W Scientific Co.). We thank Drs. R. Yamdagni and W. S. Lin (University of Calgary) for assistance in recording NMR and mass spectra and P. A. D'Agostino of the Defence Research Establishment, Suffield, Alberta for several high-resolution mass spectra. Elemental analyses were determined by Dr. W. S. Lin at the University of Calgary.

Preparative TLC was performed on Analtech 20 × 20 cm glass plates coated with 1 mm of silica gel GF. GC analyses were performed on a Varian 3700 chromatograph equipped with a Varian CDS111C integrator or on a Hewlett-Packard 5890 chromatograph fitted with a HP 3390A integrator. Both instruments used flame-ionization detectors and a 15-m Megabore DB-17 column (J and W Scientific Co.) or a 2 m × 0.3 cm stainless steel column packed with 3% OV-17 on Chromosorb W-HP. All quantitative analyses were carried out with *n*-decane, *n*-undecane, or *n*-dodecane as the internal standard.

Nickel chloride hexahydrate and sodium borohydride were purchased from the Fisher Scientific Co., while $NaBD_4$ (98 atom % D) and deuteriated solvents (99.5 atom % D) were obtained from the Aldrich Chemical Co. All other reagents were commercially available unless indicated otherwise.

Preparation of Substrates for Reduction. Selenides **2**[32] and **3**[33] were prepared by variations of literature procedures, via the reactions of *n*-dodecyl and cyclododecyl tosylates, respectively, with NaSePh. Selenides **13**,[9] **14**,[34] **19**,[35] **20**,[36] **21**,[36] and **22**[4c] were

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(30) Under these conditions the selenide remained largely unreacted and no significant amount of *n*-dodecane could be detected even after prolonged reaction times.

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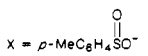
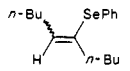
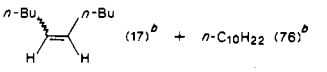
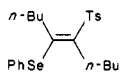
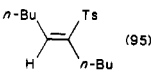
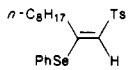
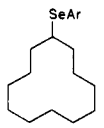
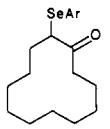
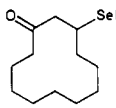
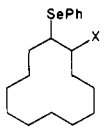
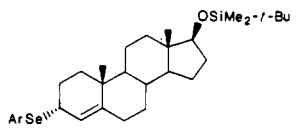
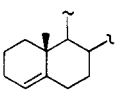
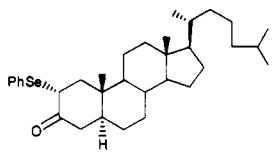
Table II. Deselenization with Nickel Boride

entry	selenide	no.	selenide:$NiCl_2{\cdot}6H_2O$:$NaBH_4$ molar ratio	THF:MeOH ratio	products (% yield)[a]
1	n-$C_{12}H_{25}SePh$	**2**	1:3:9.3	1:3	n-$C_{12}H_{26}$ (>98)[b]
2			1:2:6.2[c]	1:3	n-$C_{12}H_{25}D$ (>95)[b]
	$X(CH_2)_{11}SePh$				
3	X = Cl	**4**	1:2:6.2	1:3	n-$C_{11}H_{23}Cl$ (82)[b]
4	X = I	**5**	1:2:6.2	1:3	n-$C_{11}H_{24}$ (76)[b]
5	X = CN	**6**	1:2.2:6.8	1:3	n-$C_{11}H_{23}CN$ (88)[b]
6	X = MeO_2C	**7**	1:2.3:6.9	1:1	n-$C_{11}H_{23}CO_2Me$ (90)
7	X = PhS	**8**	1:2.2:6.8	1:3	n-$C_{11}H_{23}SPh$ (76)
8	 X = p-$MeC_6H_4SO^-$	**9**	1:1:3.2	1:3	$HO(CH_2)_{11}SePh$ (32) + **9** (28)
9	X = Ts	**10**[d]	1:2:6.2	1:3	n-$C_{11}H_{23}Ts$ (92)
10	$PhSe(CH_2)_9CH{=}CH_2$	**11**	1:1:3.1	1:3	n-$C_{11}H_{24}$ (30)[b] + **11** (47)[b]
11			1:2:6.2	1:3	n-$C_{11}H_{24}$ (78)[b]
12		**12**	1:3:9.3	1:3	 (17)[b] + n-$C_{10}H_{22}$ (76)[b]
13		**13**[d]	1:4:12	1:1	 (95)
14		**14**[d]	1:2:6	1:1	n-$C_{10}H_{21}Ts$ (80)
					
15	Ar = Ph	**3**	1:2.5:7.8	1:6	cyclododecane (94)[b]
16	Ar = p-$NO_2C_6H_4$	**15**	1:6:18	1:1	cyclododecane (71)
17		**16**	1:1.6:4.8	1:1	cyclododecanone (93)
18		**17**	1:2:6.2	1:2.4	cyclododecanone (85)[b] + 2-cyclododecenone (7)[b]
					
19	X = Cl	**18**	1:2:6	1:1	cyclododecane (100)
20	X = OAc	**19**	1:2:6	1:1	cyclododecyl acetate (50)[e] + cyclododecane (29)[e]
					
21	Ar = o-$NO_2C_6H_4$	**20**	1:2.6:7.8	1:1	 (83)
22	Ar = p-$NO_2C_6H_4$	**21**	1:3.6:10.8	3:1	(91)
23		**22**	1:2:6.2	8:7	3-cholestanone (68)[b] + 3-cholestanol (32)[b]
24			1:2:4	2.7:1	3-cholestanone (82) + 3-cholestanol (13)
25	$(PhSe)_2CH(CH_2)_{10}CH_3$	**23**	1:8:25	1:2.3	n-$C_{12}H_{26}$ (62)[b]

[a] Isolated yield unless otherwise indicated. [b] GC yield determined with an internal standard. [c] $NaBD_4$, $NiCl_2{\cdot}6D_2O$, and CH_3OD were employed. [d] Ts = p-$CH_3C_6H_4SO_2$. [e] The mixture of products was isolated, and their relative proportions were determined by GC.

prepared by previously reported methods.

11-(Phenylseleno)-1-undecanol and Its Tosylate. Diphenyl diselenide (3.12 g, 10 mmol) was added in portions to a solution of $NaBH_4$ (1.51 g, 20 mmol) and NaOH (13.25 mL of a 1.51 M aqueous solution, 20 mmol) in 80 mL of ethanol. The solution was refluxed until a clear, colorless solution was obtained. 11-Bromo-1-undecanol (5.02 g, 20 mmol) was added, and the solution was refluxed for 22 h. Most of the ethanol was then removed by distillation, H_2O (40 mL) was added, and the product was extracted three times with ether, washed with aqueous NaCl, dried ($MgSO_4$), and evaporated to dryness. Recrystallization from hexane afforded 5.1 g of the title alcohol as a white solid, mp

56–56.5 °C. The concentrated mother liquor afforded an additional 1.0 g of the product: total yield, 93%; IR (KBr) 3453, 1578, 1478, 1465, 1437, 1062, 729, 689 cm^{-1}; ^1H NMR (60 MHz) δ 7.6–7.1 (m, 5 H), 3.60 (t, J = 6 Hz, 2 H), 2.88 (t, J = 7 Hz, 2 H), 1.9–1.2 (complex, 18 H); mass spectrum, m/e (relative intensity) 328 (M^+, ^{80}Se, 14), 158 (46), 55 (100); exact mass calcd for $C_{17}H_{28}OSe$ 328.13054, found 328.1306.

The above product (4.91 g, 15 mmol) was treated with *p*-toluenesulfonyl chloride (3.15 g, 16.5 mmol) in dry pyridine (20 mL) for 15 h at room temperature, to afford 4.20 g (58%) of the corresponding tosylate, mp 55–56 °C (from hexane). Anal. Calcd for $C_{24}H_{34}O_3SSe$: C, 59.86; H, 7.12. Found: C, 60.07; H, 6.88.

1-Chloro-11-(phenylseleno)undecane (4). 11-(Phenylseleno)-1-undecanol (655 mg, 2.0 mmol) and tri-*n*-butylphosphine (0.75 mL, 3.0 mmol) were refluxed in 5 mL of carbon tetrachloride for 24 h. The solution was evaporated in vacuo, and the residue was flash chromatographed over silica gel. Elution with hexane afforded 406 mg (59%) of the chloride **4** as a homogeneous oil (GC): IR (film) 1579, 1477, 1437, 1073, 1023, 734, 691 cm^{-1}; ^1H NMR (60 MHz) δ 7.6–7.1 (m, 5 H) 3.47 (t, J = 7 Hz, 2 H), 2.87 (t, J = 7 Hz, 2 H), 2.0–1.2 (complex, 18 H); mass spectrum, m/e (relative intensity) 346 (M^+, ^{80}Se, ^{35}Cl, 60), 310 (31), 158 (80), 157 (56), 156 (89), 155 (67), 55 (100); exact mass calcd for $C_{17}H_{27}ClSe$ 346.09664, found 346.0959.

1-Iodo-11-(phenylseleno)undecane (5). The tosylate of 11-(phenylseleno)-1-undecanol (0.72 g, 1.5 mmol) and KI (2.50 g, 15.0 mmol) were refluxed in 20 mL of acetone for 17 h. The acetone was removed in vacuo, and the residue was triturated with water, extracted three times with ether, washed with aqueous NaCl, dried ($MgSO_4$), and evaporated to dryness. Flash chromatography over silica gel (elution with hexane) afforded 0.63 g (96%) of the iodide **5** as a pale yellow oil: IR (film) 1579, 1477, 1437, 1073, 1023, 734, 690 cm^{-1}; ^1H NMR (60 MHz) δ 7.6–7.0, (m, 5 H), 3.13 (t, J = 7 Hz, 2 H), 2.87 (t, J = 8 Hz, 2 H), 2.0–1.1 (complex, 18 H); mass spectrum, m/e (relative intensity) 438 (M^+, ^{80}Se, 18), 158 (53), 55 (96), 41 (100); exact mass calcd for $C_{17}H_{27}ISe$ 438.03226, found 438.0320.

12-(Phenylseleno)dodecanenitrile (6). The tosylate of 11-(phenylseleno)-1-undecanol (577 mg, 1.20 mmol), NaI (900 mg, 6.00 mmol), and NaCN (588 mg, 12.00 mmol) were refluxed in 20 mL of acetone for 20 h. Workup and flash chromatography as in the preparation of iodide **5** produced 158 mg (30%) of the iodide **5** (elution with hexane) and 260 mg (64%) of the nitrile **6** (elution with dichloromethane) as a homogeneous (GC) pale yellow oil: IR (film) 2246, 1579, 1478, 1437, 1073, 1023, 735, 691 cm^{-1}; ^1H NMR (60 MHz) δ 7.5–7.0 (m, 5 H), 2.78 (t, J = 7 Hz, 2 H), 2.28 (t, J = 6 Hz, 2 H), 1.9–1.1 (complex, 18 H); mass spectrum, m/e (relative intensity) 337 (M^+, ^{80}Se, 23), 158 (70), 157 (29), 156 (38), 155 (25), 55 (84), 41 (100); exact mass calcd for $C_{18}H_{27}NSe$ 337.13086, found 337.1292.

Methyl 12-(Phenylseleno)dodecanoate (7). The ester **7** was prepared from dodecanolide by methanolysis with sodium methoxide, tosylation with *p*-toluenesulfonyl chloride in pyridine, and treatment of the tosylate with NaSePh generated in situ from diphenyl diselenide and $NaBH_4$. The product **7** had spectra in accord with those reported in the literature.[37]

1-(Phenylseleno)-11-(phenylthio)undecane (8). Benzenethiol (57 μL, 0.55 mmol) was added to 3 mL of freshly prepared 0.33 M NaOMe in methanol. After 30 min, the tosylate of 11-(phenylseleno)-1-undecanol (241 mg, 0.50 mmol) was added with 1 mL of THF to assist in its dissolution. The mixture was stirred at room temperature for 20 h and was then diluted with water, extracted several times with ether, washed with aqueous NaCl, and dried ($MgSO_4$). Evaporation of the solvent afforded 195 mg (93%) of the title compound as a pale yellow oil of >97% purity (GC): IR (film) 1580, 1478, 1438, 1073, 1023, 736, 690 cm^{-1}; ^1H NMR (60 MHz) δ 7.6–7.0 (m, 10 H), 2.90 (2 overlapping t, 4 H), 2.0–1.1 (complex, 18 H); mass spectrum, m/e (relative intensity) 420 (M^+, ^{80}Se, 14), 158 (44), 69 (67), 55 (100); exact mass calcd for $C_{23}H_{32}SSe$ 420.13899, found 420.1339.

11-(Phenylseleno)undecyl *p*-Toluenesulfinate (9) and 11-(Phenylseleno)undecyl *p*-Tolyl Sulfone (10). The tosylate of 11-(phenylseleno)-1-undecanol (963 mg, 2.00 mmol) and sodium *p*-toluenesulfinate (642 mg, 3.00 mmol) were stirred in 6 mL of dry DMF for 24 h. The solution was diluted with water, extracted several times with ether, washed with aqueous NaCl, and dried ($MgSO_4$). The residue was separated by preparative TLC (20% ethyl acetate–hexane) to furnish 304 mg (33%) of sulfinate ester **9**: R_f 0.56; mp 47 °C (from chloroform–hexane); IR (KBr) 1596, 1578, 1479, 1468, 1436, 1127, 1108, 934, 816, 743, 738 cm^{-1}; ^1H NMR (400 MHz) δ 7.59 (d, J = 8 Hz, 2 H), 7.48 (m, 2 H), 7.33 (d, J = 8 Hz, 2 H), 7.3–7.2 (m, 3 H), 4.01 (dt, J = 9.8, 6.7 Hz, 1 H), 3.60 (dt, J = 9.8, 6.6 Hz, 1 H), 2.90 (t, J = 7.5 Hz, 2 H), 2.42 (s, 3 H), 1.7–1.2 (complex, 18 H); mass spectrum, m/e (relative intensity) 466 (M^+, ^{80}Se, 17), 328 (46), 158 (66), 157 (78), 156 (52), 155 (38), 139 (62), 91 (69), 55 (100). Anal. Calcd for $C_{24}H_{34}O_2SSe$: C, 61.92; H, 7.36. Found: C, 61.65; H, 7.21.

A more polar band provided 185 mg (20%) of sulfone **10**: R_f 0.43; mp 58–58.5 °C (from chloroform–hexane); IR (KBr) 1595, 1579, 1478, 1438, 1317, 1301, 1288, 1146, 1088, 737 cm^{-1}; ^1H NMR (60 MHz) δ 7.75 (d, J = 8 Hz, 2 H), 7.5–7.0 (m, 7 H), 3.2–2.6 (m, 4 H), 2.43 (s, 3 H), 2.0–1.1 (complex, 18 H); mass spectrum, m/e (relative intensity) 466 (M^+, ^{80}Se, 16), 158 (29), 157 (85), 91 (50), 69 (52), 55 (100). Anal. Calcd for $C_{24}H_{34}O_2SSe$: C, 61.92; H, 7.36. Found: C, 62.15; H, 7.15.

11-(Phenylseleno)-1-undecene (11). Diphenyl diselenide (1.44 g, 4.62 mmol) was added to a solution of $NaBH_4$ (0.35 g, 9.25 mmol) in 20 mL of ethanol and 6.12 mL of 1.51 M aqueous NaOH. The solution was refluxed until it became clear and colorless. The tosylate of 10-undecen-1-ol (3.00 g, 9.25 mmol), prepared from the alcohol and *p*-toluenesulfonyl chloride in pyridine followed by the usual workup, was then added, and the mixture was stirred for 18 h. The mixture was then poured into water, extracted three times with ether, washed with aqueous NaCl, and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure afforded 2.76 g (97%) of the selenide **11** as a pale yellow oil of 97% purity (GC): IR (film) 1640, 1579, 1477, 1438, 1023, 909, 734, 690 cm^{-1}; ^1H NMR (60 MHz) 7.6–7.1 (m, 5 H), 6.2–4.7 (m, 3 H), 2.90 (t, J = 7 Hz, 2 H), 2.3–1.1 (complex, 16 H); mass spectrum, m/e (relative intensity) 310 (M^+, ^{80}Se, 13), 158 (51), 157 (15), 156 (23), 69 (62), 55 (100); exact mass calcd for $C_{17}H_{26}Se$ 310.11997, found 310.1202.

5-(Phenylseleno)-5-decene (12). The title compound[38a] was prepared by the addition of PhSeBr to *trans*-5-decene, followed by dehydrobromination with potassium *tert*-butoxide in THF at 0 °C, according to a literature procedure[38b–e] described for the preparation of other vinyl selenides.

Cyclododecyl *p*-Nitrophenyl Selenide (15).[39] Cyclododecanol (0.92 g, 5.0 mmol) and *p*-nitrophenyl selenocyanate (1.25 g, 5.5 mmol) were dissolved in 40 mL of dry THF. Tri-*n*-butylphosphine (1.50 mL, 6.0 mmol) was added, and the solution was stirred for 1 h. It was then concentrated in a stream of N_2 and flash chromatographed over silica gel (elution with 30% benzene–hexane) to afford 0.88 g (48%) of the title compound: mp 75–76 °C (from ether–methanol); IR (Nujol) 1597, 1575, 1512, 1065, 854, 843, 735 cm^{-1}; ^1H NMR (60 MHz) δ 7.83 (d, J = 8 Hz, 2 H), 7.25 (d, J = 8 Hz, 2 H), 3.42 (m, 1 H), 1.9–1.2 (complex, 22 H); mass spectrum, m/e (relative intensity) 369 (M^+, ^{80}Se, 5), 203 (16), 111 (40), 97 (75), 83 (79), 69 (82), 55 (100). Anal. Calcd for $C_{18}H_{27}NO_2Se$: C, 58.69; H, 7.39; N, 3.80. Found: C, 58.61; H, 7.36; N, 3.49.

2-(Phenylseleno)- and 3-(Phenylseleno)cyclododecanone (16 and 17). The title compound **16** and its selenoxide elimination product, 2-cyclododecenone, were prepared by the method of Sharpless et al.[4c]

Sodium borohydride (341 mg, 9.0 mmol) was added in small portions to a mixture of diphenyl diselenide (1.40 g, 4.50 mmol) in 30 mL of ethanol at 0 °C under nitrogen. (**Caution**: vigorous reaction!) The solution was stirred at 0 °C until it was colorless and clear and then was acidified with aqueous HCl to pH <3. 2-Cyclododecenone (1.08 g, 6.00 mmol) in 30 mL of ethanol–THF (2:1) was added over 5 min, and the mixture was stirred at room

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(38) (a) Comasseto, J. V.; Ferreira, J. T. B.; Petragnani, N. *J. Organomet. Chem.* **1981**, *216*, 287. (b) Raucher, S. *J. Org. Chem.* **1977**, *42*, 2950. (c) Raucher, S.; Hansen, M. R.; Colter, M. A. *J. Org. Chem.* **1978**, *43*, 4885. (d) Kataev, E. G.; Mannafov, T. G.; Remizov, A. B.; Komarovskaya, O. A. *Zh. Org. Khim.* **1975**, *11*, 2322.

(39) For the similar preparation of other selenides from alcohols, see: Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485.

temperature for 5 h. After partial evaporation of the solvent, 60 mL of water was added and the mixture was extracted several times with ether, washed with aqueous NaCl, dried ($MgSO_4$), and evaporated in vacuo. The residue was flash chromatographed over silica gel (elution with 40% dichloromethane–hexane) to afford 1.76 g (87%) of product **17** as white needles: mp 81 °C (from hexane); IR (KBr) 1698, 1578, 1467, 1436, 1374, 1272, 1206, 1130, 1022, 738, 692 cm^{-1}; ^1H NMR (400 MHz) δ 7.55 (m, 2 H), 7.28 (m, 3 H), 3.86 (m, 1 H), 2.99 (dd, J = 15.8, 11.7 Hz, 1 H), 2.65 (dd, J = 15.8, 3.4 Hz, 1 H), 2.39 (m, 2 H), 1.9–1.2 (complex, 16 H); mass spectrum, m/e (relative intensity) 338 (M^+, ^{80}Se, 35), 181 (47), 158 (54), 157 (45), 156 (47), 155 (42), 154 (41), 81 (88), 68 (76), 55 (100). Anal. Calcd for $C_{18}H_{26}OSe$: C, 64.02; H, 7.77. Found: C, 64.25; H, 7.77.

1-Chloro-2-(phenylseleno)cyclododecane (18). The title compound was prepared in situ by the addition of benzeneselenenyl chloride (192 mg, 1.00 mmol) to cyclododecene[40] (166 mg, 1.00 mmol, *E,Z* mixture) in 5 mL of THF. For deselenization, it was diluted with 5 mL of methanol and treated sequentially with $NiCl_2{\cdot}6H_2O$ and $NaBH_4$, as indicated in Table II.

1,1-Bis(phenylseleno)dodecane (23). Bis(phenylseleno)methane was prepared by the reaction of diphenyl diselenide with diazomethane in the presence of copper powder.[41] The selenoacetal (0.978 g, 3.00 mmol) in 2 mL of dry THF was added to a freshly prepared solution of LDA (3.00 mmol) in 2 mL of THF at −78 °C under argon. After 15 min, 1-iodoundecane (0.888 g, 3.15 mmol) in 2 mL of THF was added and the solution was stirred for 15 min at −78 °C and then for 1.5 h at room temperature. The reaction was quenched with aqueous NH_4Cl, and the product was extracted three times with ether, washed with aqueous NaCl, dried ($MgSO_4$), and evaporated in vacuo to furnish 1.45 g (100%) of the desired product **23**[42] as a homogeneous (TLC, NMR) oil: IR (film) 1578, 1476, 1437, 1022, 738, 690 cm^{-1}; ^1H NMR (400 MHz) δ 7.57 (m, 4 H), 7.28 (m, 6 H), 4.48 (t, J = 6.5 Hz, 1 H), 1.93 (m, 2 H), 1.3–1.2 (complex, 18 H), 0.88 (t, J = 7 Hz, 3 H); mass spectrum, m/e (relative intensity) 482 (M^+, ^{80}Se, 10), 325 (80), 183 (60), 157 (65), 69 (94), 55 (100); exact mass calcd for $C_{24}H_{34}Se_2$ 482.09909, found 482.0989.

Methyl 12-(Phenylthio)dodecanoate (24). The title compound was prepared in a manner analogous to that of the selenium derivative **7**, except that benzenethiol was employed as the nucleophile. The product had the following: mp 35–36 °C (from methanol); IR (Nujol) 1729, 1171, 738, 690 cm^{-1}; ^1H NMR (60 MHz) δ 7.0 (m, 5 H), 3.44 (s, 3 H), 2.70 (t, J = 7 Hz, 2 H), 2.10 (t, J = 7 Hz, 2 H), 1.7–1.1 (complex, 18 H); mass spectrum, m/e (relative intensity) 322 (M^+, 52), 291 (5), 110 (94), 64 (97), 44 (100). Anal. Calcd for $C_{19}H_{30}O_2S$: C, 70.76; H, 9.38; S, 9.94. Found: C, 70.95; H, 9.53; S, 9.71.

Nickel Boride Deselenizations. Nickel boride deselenizations were performed as in the typical procedure given below, with minor variations indicated in Table II. Details of the isolation and identification of the products are given below for each entry in Table II, along with any major deviations from the typical procedure.

Typical Procedure: Deselenization of 2 (Entry 1). *n*-Dodecyl phenyl selenide (**2**) (163 mg, 0.50 mmol) and $NiCl_2{\cdot}6H_2O$ (357 mg, 1.50 mmol) were dissolved in 5 mL of THF–methanol (1:3) at 0 °C in an Erlenmeyer flask. Sodium borohydride (176 mg, 4.65 mmol) was added to the stirred solution in small portions (**CAUTION**: vigorous reaction with gas evolution), and a fine black precipitate formed immediately. After being stirred at 0 °C for an additional 15 min, the mixture was filtered through Celite and washed with methanol and THF. *n*-Undecane (60 μL, 44 mg) was added to the filtrate to serve as the internal standard, and GC analysis indicated the yield of *n*-dodecane to be >98%. The identity of the product was confirmed by a comparison of its GC–mass spectrum with that of an authentic sample.

In a separate experiment, the $NiCl_2{\cdot}6H_2O$ and $NaBH_4$ were permitted to react as described above. After 5 min, selenide **2** was added, and after the mixture was stirred for 15 min, GC analysis revealed only the presence of the unreacted selenide and no detectable formation of *n*-dodecane. The addition of a second portion of equal size of $NaBH_4$ to this mixture resulted in the usual vigorous evolution of hydrogen. Subsequent GC analysis indicated the presence of **2** and only traces (<5%) of *n*-dodecane.

In a third experiment, the selenide was added to preformed nickel boride after 5 min as described above. Hydrogen gas was then passed through the reaction mixture for several hours. GC analysis revealed only the presence of unreacted selenide.

Deselenization of 2 with Deuteriated Reagents (Entry 2). The reaction was performed as in entry 1, except that $NiCl_2{\cdot}6D_2O$ (prepared from anhydrous $NiCl_2$[43] and D_2O), CH_3OD, and $NaBD_4$ were employed. GC–mass spectral analysis of the product indicated it to be >95% *n*-$C_{12}H_{25}D$. When the reaction was repeated with $NaBD_4$ in unlabeled solvents, and with $NaBH_4$ and $NiCl_2{\cdot}6D_2O$ in CH_3OD and unlabeled THF, the ratios of *n*-$C_{12}H_{25}D$ to *n*-$C_{12}H_{26}$ were 74:26 and 23:77, respectively. In each case a correction was made for the contribution of the M + 1 peak of *n*-$C_{12}H_{26}$ to the M^+ peak of *n*-$C_{12}H_{25}D$.

Deselenization of Selenides 4–6 (Entries 3–5). The products were identified by comparison of their GC–mass spectra with those of authentic samples of 1-chloroundecane,[44] *n*-undecane, and dodecanenitrile,[45] respectively. Attempts to reduce **5** with smaller amounts of nickel boride resulted in mixtures containing poor yields of 1-iodoundecane and substantial amounts of *n*-undecane.

Deselenization of Ester 7 (Entry 6). The product was isolated by flash chromatography over silica gel (elution with dichloromethane) to afford an oil identified as methyl 1-dodecanoate by its IR, ^1H NMR, and mass spectra.

Deselenization of Sulfide 8 (Entry 7). The product, phenyl *n*-undecyl sulfide, was isolated by preparative TLC (5% ethyl acetate–hexane): R_f 0.65; mp 29–30 °C (from hexane) (lit.[46] mp 31–33 °C); identical with an authentic sample (TLC, ^1H NMR).

Deselenization of Sulfinate Ester 9 (Entry 8). The reaction mixture was separated by preparative TLC (20% ethyl acetate–hexane) to afford 11-(phenylseleno)-1-undecanol: R_f 0.29; identical (mp, ^1H NMR, mass spectrum) with an authentic sample (vide supra). A more mobile band afforded unreacted starting material **9**: R_f 0.57; identical with an authentic sample (TLC, IR, ^1H NMR).

Deselenization of Sulfone 10 (Entry 9). The reaction mixture was filtered through Celite, evaporated in vacuo, and triturated with dichloromethane. The solution was again filtered through Celite to remove a small amount of insoluble material, and the filtrate was evaporated to dryness to afford *p*-tolyl undecyl sulfone as a homogeneous (TLC) white solid: mp 65–69 °C (lit.[47] mp 70–71 °C); identical with an authentic sample (TLC, IR, ^1H NMR).

Deselenization of Olefin 11 (Entries 10 and 11). The products were identified by comparison of their GC–mass spectra with those of authentic samples. GC analysis indicated that no substantial 1-undecene was formed under the conditions given in Table II.

Deselenization of Olefin 12 (Entry 12). The products were identified by comparison of their GC–mass spectra with those of authentic samples.

Deselenization of Vinyl Sulfone 13 (Entry 13). The product was isolated by flash chromatography over silica gel (elution with chloroform) to afford a mixture of *E,Z* isomers of 5-(*p*-tolylsulfonyl)-5-decene,[48] identified by its IR, ^1H NMR, and mass spectra. The *E*:*Z* ratio was determined to be 73:27 by NMR integration of the triplets from the vinylic hydrogens at δ 6.86 and 5.96, respectively.

Deselenization of Vinyl Sulfone 14 (Entry 14). The

(40) For a review of the additions of selenenyl halides to olefins, see: Schmid, G. H.; Garratt, D. G. In *The Chemistry of Double-Bonded Functional Groups*; Patai, S., Ed.; Wiley: Chichester, 1977; Suppl. A, Part 2, Chapter 9.

(41) (a) Back, T. G.; Kerr, R. G. *Tetrahedron* **1985**, *41*, 4759. (b) Petragnani, N.; Schill, G. *Chem. Ber.* **1970**, *103*, 2271.

(42) For some previous examples of alkylations of anions derived from selenoacetals and LDA, see: Van Ende, D.; Cravador, A.; Krief, A. *J. Organomet. Chem.* **1979**, *177*, 1.

(43) *Handbook of Preparative Inorganic Chemistry*; Brauer, G., Ed.; Academic: New York, 1965; Vol. 2, pp 1515 and 1544.

(44) Prepared by the general procedure of Hooz and Gilani: Hooz, J.; Gilani, S. S. H. *Can. J. Chem.* **1968**, *46*, 86.

(45) Prepared by the reaction of KCN with undecyl tosylate.

(46) Lang, D.; Long, L., Jr. U.S. Patent 3 344 173, Sept 26, 1967; *Chem. Abstr.* **1968**, *68*, 21696a.

(47) Murata, Y.; Inomata, K.; Kinoshita, H.; Kotake, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2539.

(48) Back, T. G.; Collins, S. *J. Org. Chem.* **1981**, *46*, 3249.

product, *n*-decyl *p*-tolyl sulfone, was isolated by flash chromatography over silica gel (elution with chloroform): mp 50–52 °C (from hexane); IR (Nujol) 1595, 1319, 1148, 767, 671 cm^{-1}; ^1H NMR (200 MHz) δ 7.78 (d, J = 8.3 Hz, 2 H), 7.36 (d, J = 8.3 Hz, 2 H), 3.06 (crude t, J = 8 Hz, 2 H), 2.46 (s, 3 H), 1.7 (m, 2 H), 1.2 (complex, 14 H), 0.87 (t, J = 6.5 Hz, 3 H); mass spectrum, m/e (relative intensity) 296 (M^+, 13), 91 (93), 43 (100). Anal. Calcd for $C_{17}H_{28}O_2S$: C, 68.87; H, 9.52; S, 10.82. Found: C, 68.85; H, 9.82; S, 10.55.

Deselenization of Selenides 3 and 15 (Entries 15 and 16). In entry 15, the yield of the product cyclododecane was determined by GC analysis of the reaction mixture. In entry 16, the cyclododecane was isolated by flash chromatography over silica gel (elution with benzene) and was identical (mp, ^1H NMR) with an authentic sample.

Deselenization of Ketone 16 (Entry 17). The product cyclododecanone was isolated by flash chromatography over silica gel (elution with chloroform) and identified by comparison (mp, IR, ^1H NMR) with an authentic sample.

Deselenization of Ketone 17 (Entry 18). The products were identified by comparison of their GC–mass spectra with those of authentic samples. When larger quantities of nickel boride were employed, the formation of cyclododecanol was also observed.

Deselenization of Chloride 18 (Entry 19). The product cyclododecane was isolated by flash chromatography over silica gel (elution with dichloromethane) and was identical with an authentic sample (mp, GC, ^1H NMR).

Deselenization of Acetate 19 (Entry 20). The unseparated products, cyclododecane and cyclododecyl acetate, were isolated by flash chromatography over silica gel (elution with benzene), and their relative proportions were determined by GC analysis and ^1H NMR integration. The IR and ^1H NMR spectra of the mixture of products were identical with the superimposed spectra of the individual authentic components.

Deselenization of Steroidal Selenide 20 (Entry 21). The product, 4-androsten-17β-ol *tert*-butyldimethylsilyl ether, was isolated by flash chromatography over silica gel (elution with chloroform): GC purity >99%; mp 105–107 °C (from dichloromethane–methanol); IR (chloroform) 1655 (weak), 1473, 1260, 1142, 1086, 915, 893, 876, 837 cm^{-1}; ^1H NMR (200 MHz) δ 5.28 (m, 1 H), 3.53 (t, J = 8.1 Hz, 1 H), 2.2–0.7 (complex, 36 H), s at δ 1.02, 0.86, and 0.71; mass spectrum, m/e (relative intensity) 388 (M^+, <1) 331 (13), 255 (26), 98 (70), 81 (97), 55 (100). Anal. Calcd for $C_{25}H_{44}OSi$: C, 77.25; H, 11.41. Found: C, 76.81; H, 11.84.

The product was converted to the known 4-androsten-17β-ol by treatment with tetrabutylammonium fluoride in THF for 2 days; mp 144–148 °C (from hexane) (lit.[49] mp 147–149 °C).

Deselenization of Steroidal Selenide 21 (Entry 22). The product was isolated as in entry 21 and had properties (mp, GC, IR) identical with those of the preceding product.

Deselenization of Steroidal Selenide 22 (Entries 23 and 24). The products were either identified by GC (entry 23) or isolated by flash chromatography over silica gel (entry 24). Elution with 10% ethyl acetate–hexane afforded 3-cholestanone, and further elution with 15% ethyl acetate–hexane provided 3β-cholestanol. The products were identified by their IR and ^1H NMR spectra.

Deselenization of Diselenoacetal 23 (Entry 25). The product, *n*-dodecane, was identified by comparison of its GC–mass spectrum with that of an authentic sample.

(49) Heusler, K.; Kalvoda, J.; Wieland, P.; Anner, G.; Wettstein, A. *Helv. Chim. Acta* **1962**, *45*, 2575.

Selective Deselenization of Selenide 7 in the Presence of Sulfide 24. The reaction was performed in the usual manner, with a reactant ratio of **7**:**24**:$NiCl_2 \cdot 6H_2O$:$NaBH_4$ of 1:1:2:6. An unseparated mixture of methyl *n*-dodecanoate and sulfide **24** was obtained by preparative TLC (benzene). The identity of the products was confirmed by GC–mass spectrometry and by the ^1H NMR spectrum of the mixture. GC analysis indicated that no selenide **7** or other byproducts were present. The mixture was evacuated to 0.05 Torr for 2 days to remove methyl *n*-dodecanoate, leaving a crystalline residue of homogeneous (GC) **24** recovered in 97% yield, mp 32–34 °C. The yield of methyl *n*-dodecanoate was determined to be 102% (based on its exclusive formation from selenide **7**) by difference.

Electrochemical Deselenization of Selenide 2. The electrochemical reduction of selenide **2** was carried out by using standard three-electrode circuitry controlled by an EG&G PARC 173 potentiostat, a 175 function generator, and an HP 7045B X/Y recorder. The working electrode (WE) was used as the cathode and consisted of a high-purity Ni plate (area ca. 1.2 cm^2) press-contacted to a Ag wire in a Teflon holder. The reference electrode (RE) was a saturated sodium chloride electrode (SSCE) in a ca. 0.1 M NaCl solution, while the counter electrode (CE) was a high-area, high-purity Pt gauze. The WE and CE were placed in the main compartment of the electrochemical cell, while the RE was connected to the WE compartment via a standard Luggin capillary. Twenty milliliters of 10 mM selenide **2** in THF–methanol–water (6:3:1) was placed into the cell, and the solution was stirred magnetically prior to and throughout the electrolysis. The potential of the WE was set at −2.7 V vs the SSCE, at which value visible hydrogen evolution occurred. Samples of the solution were withdrawn periodically for GC analysis, using *n*-undecane as an internal standard. The yield of 1-dodecene was 72% after 21 h. The identity of the alkene was confirmed by GC–mass spectral analysis.

When the experiment was repeated with the selenide in the cathode compartment of a divided cell, no significant deselenization was observed. The unreacted selenide (ca. 95%) was still present after 24 h (GC, TLC).

Registry No. **2**, 42066-69-3; **3**, 42066-65-9; **4**, 114996-81-5; **5**, 114996-82-6; **6**, 114996-83-7; **7**, 74785-93-6; **8**, 114996-84-8; **9**, 114996-85-9; **10**, 114996-86-0; **11**, 114996-87-1; **12**, 114996-88-2; **13**, 94473-26-4; **14**, 94473-27-5; **15**, 114996-89-3; **16**, 42858-37-7; **17**, 114996-90-6; **18**, 71518-95-1; **19**, 94473-31-1; **20**, 91384-94-0; **21**, 91384-95-1; **22**, 115073-73-9; **23**, 114996-91-7; **24**, 94473-28-6; $C_{12}H_{26}$, 112-40-3; $C_{12}H_{25}D$, 113122-31-9; $C_{11}H_{23}Cl$, 2473-03-2; $C_{11}H_{24}$, 1120-21-4; $C_{11}H_{23}CN$, 2437-25-4; $C_{11}H_{23}CO_2Me$, 111-82-0; $C_{11}H_{23}SPh$, 17763-59-6; $C_{11}H_{23}Ts$, 87657-55-4; PhSeBr, 34837-55-3; $C_{10}H_{21}Ts$, 66606-03-9; BuCH=CHBu, 19689-19-1; $C_{10}H_{22}$, 124-18-5; (*E*)-BuCH=C(Ts)Bu, 77825-85-5; (*Z*)-BuCH=C(Ts)Bu, 77825-84-4; cyclododecane, 294-62-2; cyclododecanone, 830-13-7; 2-cyclododecenone, 42858-38-8; cyclododecyl acetate, 6221-92-7; 3-chloestanone, 566-88-1; 3-chloestanol, 16720-60-8; diphenyl diselenide, 1666-13-3; 11-bromo-1-undecanol, 1611-56-9; 11-(phenylseleno)-1-undecanol, 114996-92-8; 11-(phenylseleno)-1-undecanol tosylate, 114996-93-9; dodecanolide, 947-05-7; benzenethiol, 108-98-5; sodium *p*-toluenesulfinate, 824-79-3; 10-undecen-1-ol, 112-43-6; 10-undecen-1-ol tosylate, 51148-67-5; *trans*-5-decene, 7433-56-9; benzeneselenyl chloride, 5707-04-0; (*E*)-cyclododecene, 1486-75-5; (*Z*)-cyclododecene, 1129-89-1; bis(phenylseleno)methane, 20343-90-2; 1-iodoundecane, 4282-44-4; cyclododecanol, 1502-05-2; *p*-nitrophenyl selenocyanate, 19188-18-2; 1-dodecene, 112-41-4; 4-androsten-17β-ol, 115073-74-0; 4-androsten-17β-ol *tert*-butyldimethylsilyl ether, 94473-32-2.