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Organic Tellurium and Selenium Chemistry. Reduction of Tellurides, Selenides, and Selenoacetals with Triphenyltin Hydride

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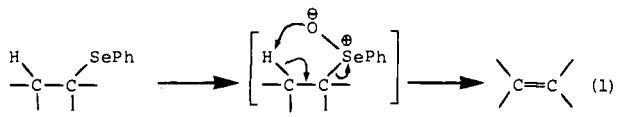
Abstract: Preparative and mechanistic details are described for the conversion of selenides into hydrocarbons [RSePh → RH] by heating with triphenyltin hydride at about 120 °C. The process has been extended to selenoacetals in a form that constitutes a reduction method for carbonyl compounds [RR′C=O → RR′C(SePh)$_2$ → RR′CH$_2$]. Selective reduction of selenoacetals in the presence of thioacetals is possible. Cold-labeled species can be prepared by using triphenyltin deuteride. Tellurides [RTePh] are available easily without problems arising from exposure to air provided that the work is done in a photographic darkroom equipped with a red safety light. These tellurides, as well as the corresponding dichlorides [RTe(Cl$_2$)Ph], are reduced under very mild conditions (25–80 °C) by triphenyltin hydride. The selenium- and tellurium-based chemistry has been used for the unusual process of reducing an epoxide in the presence of a ketone carbonyl.

Reduction of Selenium Compounds

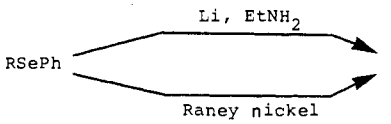
Introduction. The recognition that selenoxide fragmentation (eq 1) constitutes a powerful method for generating double



(1)

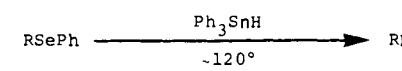
bonds,[1] particularly those conjugated with a carbonyl group, made it necessary to devise a variety of procedures for introducing selenium, usually as PhSe–, into organic molecules.[2] The more useful of these methods accomplish, at the same time, some additional elaboration of the molecular framework and two such processes are known: the formation of C–C bonds with selenium-stabilized carbanions[2a,3] and the process of *cyclofunctionalization*.[4,5]

The general utility of these reactions obviously increases as the range of functional group interconversions involving the unit C–SePh is extended. During our[6] work on cyclofunctionalization we needed to remove the benzeneseleno group from a number of compounds and replace it by hydrogen [>C–SePh → >C–H], this step being required for structure proof of the selenium-containing species. Two methods were explicitly available for reducing selenides: the carbon–selenium bond can be cleaved by lithium in ethylamine and by the use of Raney nickel[7] (eq 2). However, the dissolving metal re-



(2)

duction was not likely to be applicable to compounds having an aromatic ring, besides that attached to the selenium atom.[8] Raney nickel also was unsuitable for our purpose because there is evidence[7] that the reaction can proceed, in certain cases, via an olefin.[9] In many of our compounds the carbon atom adjacent to that carrying the benzeneseleno group is an asymmetric center and olefin formation might result in alteration of stereochemistry at that point. We looked, therefore, for an unambiguous method of reduction and found[10] that triphenyltin hydride is an excellent general reagent for this purpose (eq 3).



(3)

Reduction of Selenides. Our results are listed in Table I, which shows most of the compounds we have studied and gives also the nature and yield of each product, the conditions used, and the scale on which the work was done. Experiments 1–18

† Izaak Walton Killam Scholar; H. H. Parlee Memorial Predoctoral Fellow (1978–1979).
‡ National Research Council of Canada Postgraduate Scholar.

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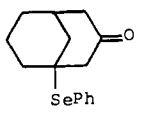
are all examples of eq 3. In each case the chromatographically pure phenyl selenide was heated with triphenyltin hydride, usually in refluxing toluene solution. We generally employed an excess of the tin reagent. The reductions were always carried out in a nitrogen atmosphere but no free-radical initiator was used. We find that triphenyltin hydride which has been freshly distilled[11] often leads to shorter reaction times. Experiments 10 and 12 (Table I) are probably examples of this effect. It is also an advantage to immerse the reaction mixture directly in an oil bath that has been *preheated* to 120 °C because in several cases we gained the impression that a slow warmup period caused loss of the tin hydride without a corresponding degree of chemical reduction of the selenide. It is also probably better practice to add the triphenyltin hydride in portions during the course of the reaction since the reagent undergoes thermal degradation. We have not, however, investigated this matter in a methodical fashion.

The experimental procedure, involving, as it does, simple refluxing of a solution of substrate and reagent, is very easy to carry out. We have found that workup is, likewise, usually a straightforward process because the products can be separated from tin species by distillation or chromatography or by successive application of both techniques. Of the many examples we have studied only reduction of **37**[12] and **38**[4a] gave product



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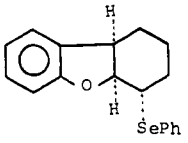
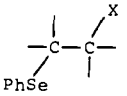


38

mixtures from which the desired materials could not easily, or efficiently, be separated by simple column or preparative layer chromatography.[13] In all other cases separation of the tin species was readily achieved and easily monitored by TLC or NMR.

The examples 1-18 show that the triphenyltin hydride method is widely general and is compatible with a range of functional groups.[14] Besides the presence of lactone, ether, phenol-ether, urethane, and alcoholic hydroxyl groups the reduction can be carried out in the presence of bivalent sulfur. For example, under our standard conditions, phenylthiodecane gave no decane as judged by VPC. Addition of phenylselenododecane to the reaction mixture caused rapid formation of dodecane.[15] No decane was detected.

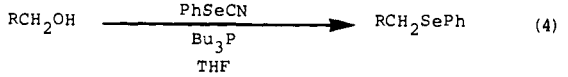
Many of our examples are of the structural type **39** where



39

X is a heteroatom. As described below, for certain specialized values of X (e.g., X = Cl) the reaction takes a different course.

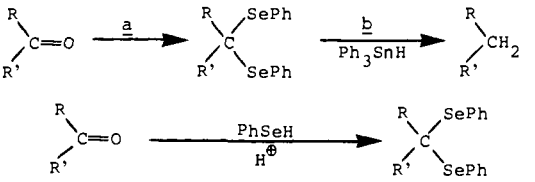
The reduction of dodecylselenobenzene requires comment because primary alcohols can be transformed efficiently into selenides by the mild reaction summarized in eq 4.[16] The tin



(4)

hydride reduction method can be used, therefore, for converting certain alcohols into hydrocarbons.[17]

Reduction of Selenoacetals. From the above work it seemed likely that selenoacetals might be reduced to hydrocarbons (eq 5, stage b) and, in the event, we have found this to be the case. Experiments 19-26 show some of the results. At the beginning of our research selenoacetals could be made by the conventional procedure (eq 6) but the selenoacetal compound class is now readily available from carbonyl compounds by use of boron-selenium reagents.[18] Therefore, the tin hydride reduction of selenoacetals is a mild alternative to the classical Wolff-Kishner process and we believe that it is a synthetically useful reaction. The general procedure is the same as that for monoselenides: the substrate and reagent are merely heated in refluxing toluene and, in particular, no radical initiator is used except for one case. In the absence of initiator the bis(methylseleno)acetal **22** underwent reduction (61% yield) in a process that was slow. In the presence of a trace of AIBN the reduction product is formed more quickly and at a lower temperature.



(5)

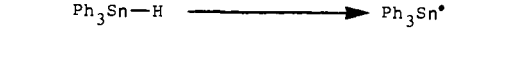
(6)

The estrone derivative **23** is a case where the reaction has been stopped at the halfway stage. Presumably, use of double the amount of reagent would effect complete reduction.

Since alkyl phenyl selenides can be reduced in the presence of bivalent sulfur (see above) we investigated the possibility of reducing selenoacetals in the presence of thioacetals. Table entries 24 and 25 prove that selective reduction is possible, the thio species being largely recoverable. The absence of a free-radical initiator in these selective reductions is a crucial feature: when experiment 25 was repeated in the presence of a trace of AIBN, the thioacetal was destroyed. An attempt to reduce the thioacetal by itself (experiment 26) in the presence of AIBN gave 5α-cholestane in poor yield.[19]

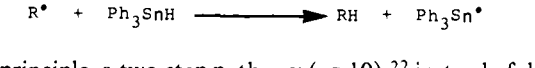
Deuteration. Lithium aluminum deuteride is commercially available and so the preparation of triphenyltin deuteride[20] is straightforward. As expected, this reagent can be used for deuteration of selenium compounds and experiments 27-29 show results of the method. The NMR spectra of the products confirm that clean incorporation of the heavy isotope has occurred and the procedure is, evidently, an easy one for making mono- and dideuterium species. The stereochemistry of the label in experiment 28 was not determined: the product is probably a mixture of α and β labeled isomers.

Mechanistic Considerations. The characteristic feature of reductions of alkyl halides by tin hydrides is the free-radical nature of the mechanism[21] and a chemically reasonable pathway for selenides is shown in eq 7-9, where the first stage occurs either thermally or by adventitious initiator.



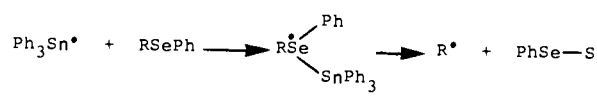
(7)

(8)

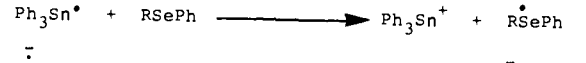


(9)

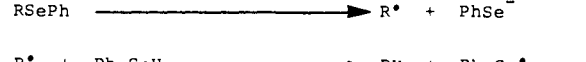
In principle, a two-step pathway (eq 10),[22] instead of direct displacement (eq 8), may be involved and a third possibility is the electron-transfer sequence of eq 11-13. Although the



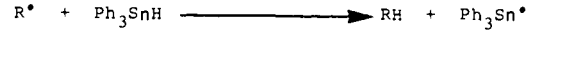
(10)



(11)



(12)



(13)

Table I[a]

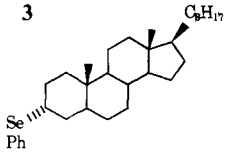
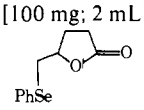
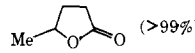
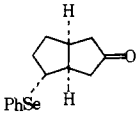
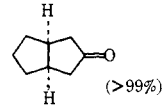
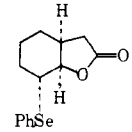
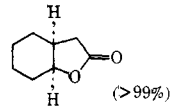
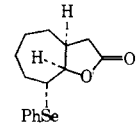
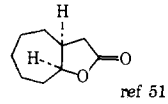
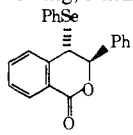
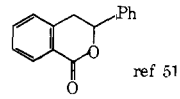
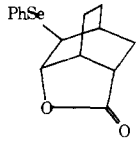
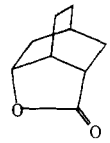
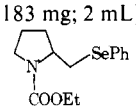
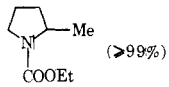
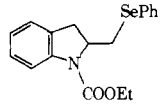
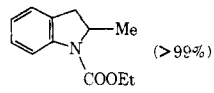
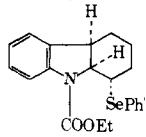
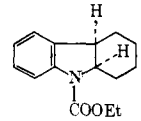
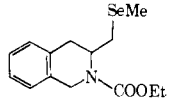
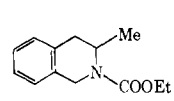
expt no.	starting material [wt used; vol of solvent[b]]	product (VPC purity)	% yield[c]	mmol Ph_3SnH/mmol substrate	time, h	temp, °C
1	**1** $C_{12}H_{25}SePh$ [975 mg; 9 mL]	dodecane (>99%)	73	2.5	2.5	120
2	**2** $PhCHCH_3$ | SePh [186 mg; —[d]]	PhEt (>96%)	73	1.8	2.5	120
3	**3**  [100 mg; 2 mL][e]	5α-cholestane	84	5.3	0.5	120
4	**4**  [256 mg; 3 mL]	 (>99%)	77	3.0	2.5	120
5	**5**  [282 mg; 3 mL]	 (>99%)	74	2.0	2.5	120
6	**6**  [375 mg; 10 mL]	 (>99%)	74	2.4	1.0	120
7	**7**  [202 mg; 3 mL]	 ref 51	82	1.5[f]	17	120
8	**8**  [189 mg; 3 mL]	 ref 51	80	1.5	0.75	120
9	**9**  [183 mg; 2 mL]	 ref 51	70	1.5	6	120
10	**10**  [315 mg; 8 mL]	 (>99%)	88	5[g]	19	120
11	**11**  [160 mg; 2 mL]	 (>99%)	80	4.1	4	120
12	**12**  [85 mg; 2 mL]		72	5.4[h]	23	120
13	**13**  [85 mg, —[i]]		63	3.8	12	130

Table I (*Continued*)

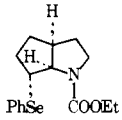
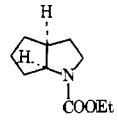
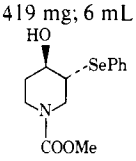
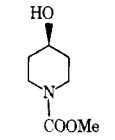
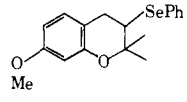
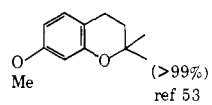
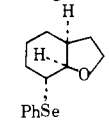
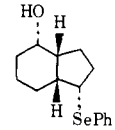
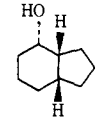
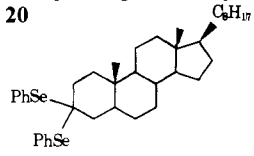
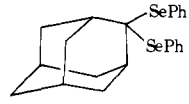
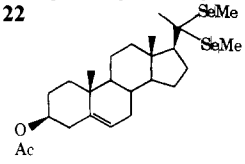
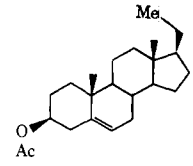
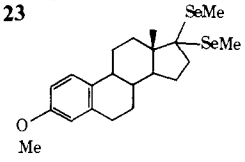
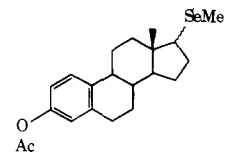
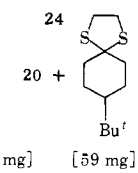
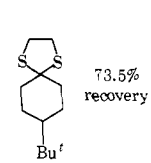
expt no.	starting material [wt used; vol of solvent[b]]	product (VPC purity)	% yield[c]	mmol Ph_3SnH/mmol substrate	time, h	temp, °C
14	**14**  [419 mg; 6 mL]		97	2.7	4	120
15	**15**  [817 mg; 8 mL]		60	4.0	3.3	120
16	**16**  [378 mg; 3 mL]	 (>99%) ref 53	86	2.1	0.75	120
17	**17**  [420 mg; —[d]]	 (>99%)	62	2.1	1	120
18	**18**  [295 mg; 5 mL]	 (>98%) ref 54	89	1.5	3	120
19	**19** $C_{10}H_{21}CH(SePh)_2$ [305 mg; 0.25 mL]	undecane	84 (VPC) 90 (VPC)	2.7[j]	3 15	120 120
20	**20**  [341 mg; 5 mL]	5α-cholestane	87	3.0	1	120
21	**21**  [300 mg; 4 mL[e]]	adamantane (>99)	91	3.7	0.75	120
22	**22**  [30 mg; 1.5 mL] [170 mg; 2 mL]		61 73	6.2[j] 2.2[k]	8 0.5	120 100
23	**23**  [270 mg; 4 mL]		64	1.9	2.5	120
24	 [83 mg] [59 mg] [1 mL]	5α-cholestane  73.5% recovery	77.5	3.9[l]	3	120

Table I (*Continued*)

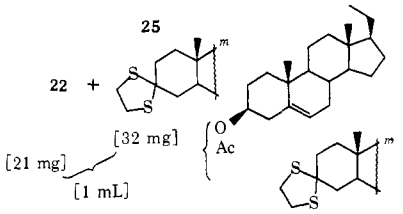
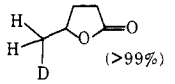
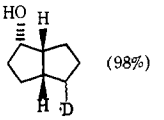
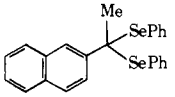
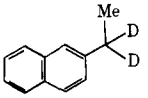
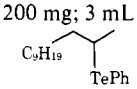
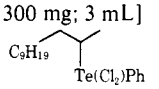
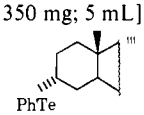
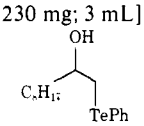
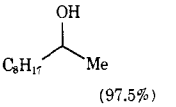
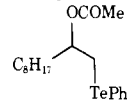
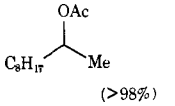
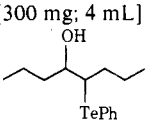
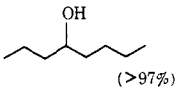
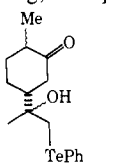
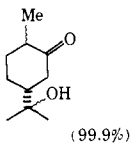
expt no.		starting material [wt used; vol of solvent[b]]	product (VPC purity)	% yield[c]	mmol Ph_3SnH/mmol substrate	time, h	temp, °C
25		 [21 mg] [32 mg] [1 mL]		60.7 83.2	8.5[n]	9.5	120
26	**25**						
		[83 mg; 1 mL]	5α-cholestane	28.9	3.7[o]	2.5	120
		[115 mg; 1 mL]	5α-cholestane	25.9	5.5[o]	1.5	120
27	**4**		 (>99%)	64	3.4 Ph_3SnD	2.5	120
		[344 mg; 1.5 mL]					
28				98	3.3[n] Ph_3SnD	6	120
	18		 (98%)				
		[1.2 mg; 7 mL]					
29	**26**			95.6 (VPC) 88.9 (VPC)	6.0 Ph_3SnD	17 1	120
		[54 mg; 0.2 mL]					
30	**27**	$C_{12}H_{25}TePh$ [160 mg; 1 mL]	dodecane (>96%)	87	2.4	5	room temp
31	**28**	$C_{12}H_{25}Te(Cl_2)Ph$					
		[256 mg; 3 mL]	dodecane (97.6%)	70	3.5	2	room temp
		[200 mg; 3 mL]	dodecane (>99%)	77	3.3	0.5	80
32	**29**		dodecane (>99%)	77	2.8	0.75	80
		[300 mg; 3 mL]					
33	**30**		dodecane (97.5%)	92	4	1.25	room temp
		[220 mg; 3 mL]					
34	**31**	$C_{12}H_{25}TeMe$ [350 mg; 5 mL]	dodecane (>98%)	84	2.2	3.5	room temp
35	**32**		5α-cholestane	89	2.5	2	80
		[230 mg; 3 mL]					
36	**33**		 (97.5%)	88	2.2	1.5	80
		[430 mg; 6 mL]					
37	**34**		 (>98%)	71	2.0	40 min	80
		[300 mg; 4 mL]					
38	**35**		 (>97%)	95	2.1	50 min	80
		[240 mg; 3 mL]					
39	**36**		 (99.9%)	70	2.1	5	80
		[355 mg; 3 mL]					

Table I (*Continued*)

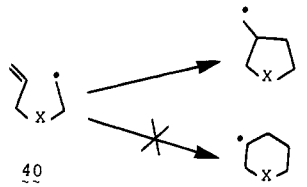
expt no.	starting material [wt used; vol of solvent[b]]	product (VPC purity)	% yield[c]	mmol Ph_3SnH/mmol substrate	time, h	temp, °C
40	**29** $+C_{18}H_{17}SePh$ **37** [374 mg] [270 mg] [4 mL]	dodecane	90 (VPC)	2.3[q]	35 min	80
		octane	~0 (VPC)			

[a] The table shows the number of mmol of Ph_3SnH used/mmol of substrate. Each mmol of Te–Cl, Te–$C_{aliphatic}$, and Se–$C_{aliphatic}$ requires 1 mmol of Ph_3SnH. Reactions were monitored by TLC unless otherwise indicated. For reactions carried out in refluxing solvents, oil-bath temperatures were set at 120–125 °C for toluene and 80–85 °C for benzene. For liquid products VPC purity is usually indicated in the "product" column. Purities in parentheses are for distilled materials. [b] Unless otherwise stated toluene was used for selenium compounds and benzene for tellurium compounds. [c] Refers to isolated material except where noted and of purity indicated in the "product" column. Yields for entries 12–25 refer to distilled material. [d] No solvent was used. [e] Benzene was used as solvent with oil bath set at 120 °C. [f] Added in three equal portions at 30-min intervals. [g] 1, 1, 1.8, and 1.2 mmol of Ph_3SnH added at times 0, 2, 13, and 18 h, respectively. [h] Added in portions during first 14 h. [i] No solvent used. Oil bath set at 130 °C. [j] Added portions during first 2 h. [k] A trace of AIBN was added to the reaction mixture. This reduction was done at 100 °C. [l] Added in two equal portions at times 0 and 2 h. [m] Cholestane skeleton. [n] Added in portions during first 7 h. In the presence of a trace of AIBN, the thioacetal is destroyed in this experiment. [o] A trace of AIBN was added to the reaction mixture. [p] Added in portions at times 0 and 3 h. [q] Calculated for telluride.

reduction of halides is not thoroughly understood, the broad outline is known.[21] We have found evidence for carbon radicals in our own experiments but have not examined the physical organic chemical problem of distinguishing between the detailed pathways just described.

As simple probes for free radical chain reactions we examined in a qualitative way the rate of reduction of dodecylselenobenzene in the presence and absence of small amounts (5 mol %) of AIBN. It was clear from VPC examination of the reaction mixtures that, for small extents of conversion, the rate is higher in the presence of an initiator. Other experiments, intended to quench the reaction by addition of inhibitors such as hydroquinone or galvinoxyl, were less decisive because essentially stoichiometric amounts appeared to be necessary for strong inhibition.

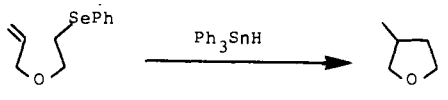
A more informative test was based on the characteristic that olefinic radicals such as **40** (X = CH_2 or O) undergo 5-exo rather than 6-endo closure[23,24] (eq 14). When we applied the



(14)

40

triphenyltin hydride reaction to **41,** we obtained 3-methyltetrahydrofuran (eq 15). From this observation, and the effects

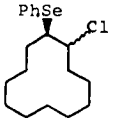


(15)

41

of AIBN, we consider that carbon radicals are involved.

The tributyltin hydride reduction of vicinal dihalides usually leads to olefins[25] and the vicinally functionalized selenide **42**[26]



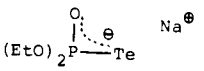
42

likewise gives cyclododecene[27] on treatment with triphenyltin hydride.

The fate of the triphenyltin group in our reactions was also examined. Treatment of octylselenobenzene with triphenyltin hydride (1.99 mmol/mmol selenide) in refluxing toluene gave triphenyltin phenylselenide in 48% yield (after recrystallization to mp 86–87 °C).[28] Little bis(triphenyltin) selenide[30] was detected (by TLC).

Reduction of Tellurides

Introduction. The fact that sulfides are essentially inert to triphenyltin hydride under the conditions we use, but that selenides are reduced smoothly at the reflux temperature of toluene, suggested that tellurides might, *in general,* react under truly mild conditions, possibly even at room temperature.[31] However, the impression to be gained from the literature[2d,32] is that tellurides are difficult to handle. They are air sensitive and the oxidation products have not been properly defined. In fact, the whole subject of organic tellurium chemistry, though large and quite active, has provided little in the way of reagents or methodology for processes that are difficult by classical means. To our knowledge, the only example to date is the salt **43,**[33] which is a reagent for deoxygenating terminal epoxides. Compared with organic selenium chemistry, the tellurium area is quite undeveloped, but the subject *can* provide useful reagents and methodology as shown by the properties of **43** and the work described below.



43

We have used an effective experimental protocol for making and handling tellurides and have found that they are reduced by triphenyltin hydride. The reaction is a general one and it occurs in a clearly defined manner under thermally mild conditions.

Preparation of Tellurides. We have observed that tellurides, for example, those shown in Table I (compounds **27–36**), can be prepared quite easily without need for protection from air during purification, provided that they are made in a photographic darkroom containing no light source other than a red safety lamp. There were statements in the literature that tellurides are light sensitive[34a] and the use of red light was found essential in work with dibenzyl ditelluride.[34b] The advantage of working under red safety lights is not a casual observation: our experience makes us believe that it is a practice which will prove essential for much further work in organic tellurium chemistry.[35]

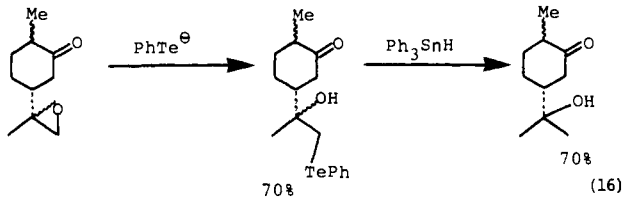
The tellurides we have used were prepared by displacement of halide or by epoxide opening using species that can be rep-

resented[36] as $PhTe^-$ or $MeTe^-$. Both telluride anions are easily generated (under nitrogen) by adding sodium borohydride (2 mol) to an ethanol solution of the ditelluride (1 mol). This step[37] is entirely analogous to the corresponding selenium chemistry[1b] except for the very stringent precautions taken to protect the tellurides from light.

The structures of the tellurides are evident from their spectroscopic properties and from further transformations, but it was only in the case of the telluride dichlorides, **28** and **30,** and the alcohol **33** and its acetate **34** that satisfactory (±0.3%) combustion analytical data could be obtained (in a conventionally illuminated laboratory). Telluride dichlorides have traditionally been used to characterize tellurides; the chloro species are not light sensitive (in the sense that special precautions are needed).

Reduction of Tellurides. The experiments listed in Table I (entries 30-40) show that tellurides are reduced easily by triphenyltin hydride. The reaction occurs under mild conditions, a temperature between 25 and 80 °C in benzene solution being generally suitable.[38] As with selenides, no initiator is added and, in two cases where a direct comparison was made (entries 30 and 31, 32 and 33), the telluride dichloride was reduced much more readily than the parent telluride. The reason for this is not clear as the reaction does proceed via the telluride itself, a fact that was established by monitoring the reaction by NMR.

Several experiments in which tellurides were generated (by epoxide opening) in the presence of cyclohexanone and were then reduced, again in the presence of the ketone, suggested—on the basis of VPC measurements—that the tellurium-based methodology is highly chemoselective as well as being mild. We have demonstrated this by the transformations shown in eq 16[39] (see also entry 39 of Table I). The overall



(16)

sequence constitutes reduction of an epoxide in the presence of a carbonyl group. Such a two-step transformation is not straightforward by conventional methods and the reaction is, therefore, the second example[33] in organic tellurium chemistry of a process for which classical methodology is lacking.

Conclusion

It is clear that selenides, tellurides, and selenoacetals are, in general, reduced smoothly by triphenyltin hydride. An initiator is not normally required[40] but, when used, the chemoselectivity of the method may diminish. It is likely that cases will arise where the more vigorous thermal requirements of selenide reduction, or the presence of an initiator, are undesirable; in these situations the tellurium route offers an alternative.

Experimental Section

Except where stated to the contrary the following particulars apply. Experiments were done under a slight static pressure of nitrogen, purified by passage through a column (3.5 × 42 cm) of R-311 catalyst[41] and then through a similar column of Drierite. Solvents were distilled before use for chromatography. Dry pyridine was distilled from CaH_2; dry THF and ether were distilled from sodium. Toluene for tin hydride reductions was usually distilled. During product isolation, solutions were dried (where necessary) over Na_2SO_4 and evaporated under water-pump vacuum at room temperature. Where nonvolatile products were isolated simply by evaporation of their solutions the residues were kept under oil pump vacuum and checked for constancy of weight; in the case of volatile products a water pump was used and removal of solvent was monitored by VPC. Isolated bulk products were submitted directly for combustion analysis without need for additional purification. Plates for PLC were 60 × 20 × 0.1 cm and were heated at 110 °C for 1 h before use. Alumina for TLC was Merck Type GF-254 (Type 60/E), and silica gel for TLC and PLC was Merck Type 60-PF-254. Alumina for column chromatography was Camag neutral aluminum oxide of Brockmann activity 3. Mass spectra were run at an ionizing voltage of 70 eV. Boiling points quoted for products distilled in a Kugelrohr apparatus refer to the oven temperature. Specific details for handling tellurium compounds are given below.

The following compounds were prepared by the methods cited: **1**,[42] **4–9**[4b,c] (the stereochemical assignment to **8** is tentative), **10–13**,[4e] **16**,[4a] **17**,[4d] **18**,[4b] **19**,[18a,b,c] **20**,[10a,18a,c] **21**,[10a,18a,c] **22**,[18c] **23**,[18c] **24**,[18b] **25**,[43] **26**,[18b] and **37**.[44]

Compound **14** was made by the general procedure used for **10–13.** Experimental details will be published in the full paper on cyclofunctionalization of urethanes.

Dimethyl ditelluride was prepared (73% yield) by the literature method[45] and had NMR (CCl_4) δ 2.68 (s).

Diphenyl ditelluride[46] had NMR ($CDCl_3$) δ 7.22 (m, 6 H), 7.85 (m, 4 H).

[1-(Phenylseleno)ethyl]benzene (2).[47] Tri-*n*-butylphosphine (950 mg, 4.7 mmol) was injected dropwise into a magnetically stirred solution of *sec*-phenethyl alcohol (465 mg, 3.81 mmol) and phenyl selenocyanate (865 mg, 4.75 mmol) in dry THF (10 mL). After an overnight period, evaporation of the solvent and chromatography of the residual oil over silica gel (2 × 70 cm) with 3:7 chloroform–hexane gave 615 mg (61%) of **2**: NMR ($CDCl_3$) δ 1.72 (d, J = 7.4 Hz, 3 H), 4.42 (q, J = 7.4 Hz, 1 H), 6.9—7.65 (m, 10 H).

***N*-Carbomethoxy-4-hydroxy-3-(phenylseleno)piperidine (15).** The first stage of this experiment was not done under a nitrogen atmosphere. Methyl chloroformate (8.69 g, 92 mmol) was added to a magnetically stirred solution of 1,2,3,6-tetrahydropyridine (3.85 g, 46 mmol) in H_2O (20 mL). Sodium hydroxide (3.68 g, 92 mmol) was added in portions and, after the end of the addition, vigorous stirring was continued for 15 min. The mixture was then extracted with ether and the organic extract was dried and evaporated. Distillation of the residue gave 4.36 g (66%) of *N*-carbomethoxy-1,2,5,6-tetrahydropyridine: bp 99–100.5 °C (20 mm); NMR ($CDCl_3$) δ 2.0–2.3 (m, 2 H), 3.52 (t, J = 5.8 Hz, 2 H), 3.7 (s, 3 H), 3.9 (m, 2 H), 5.5–5.95 (m, 2 H); exact mass 141.0786 (calcd for $C_7H_{11}NO_2$, 141.0790). Anal. Calcd for $C_7H_{11}NO_2$: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.38; H, 8.03; N, 9.97.

A portion (1.139 g, 8.07 mmol) of the above urethane was dissolved in dry ether (5 mL) containing silver trifluoroacetate (2.226 g, 10.1 mmol). The solution was cooled to −15 °C and PhSeCl (1.766 g, 9.22 mmol) in ether (13 mL) was injected, with magnetic stirring, over 20 min. The cold bath (−15 °C) was left in place for a further 15 min and was then removed. The mixture was stirred overnight with protection from light. It was then filtered and insoluble material was washed with ether. The combined filtrates were washed with saturated aqueous $NaHCO_3$, dried, and evaporated. The residue was stirred overnight at room temperature with a mixture of $NaHCO_3$ (3 g), methanol (35 mL), and water (8 mL). The methanol was then evaporated to afford material that was extracted with CH_2Cl_2 (3 × 20 mL). The combined extract was dried and evaporated. Chromatography of the residue over silica gel (3 × 64 cm) with 1:1 ethyl acetate–hexane gave 1.994 g (78%) of **15** as a viscous, homogeneous (TLC, silica or alumina, 1:1 ethyl acetate–hexane) oil: NMR ($CDCl_3$, 400 MHz) δ 1.44–1.66 (m, 1 H), 2.00–2.18 (m, 1 H), 2.66–3.04 (m, 4 H), 3.37–3.55 (m, 1 H), 3.68 (s, 3 H), 3.9–4.24 (m, 1 H), 4.24–4.64 (m, 1 H), 7.22–7.43 (m, 3 H), 7.54–7.68 (m, 2 H); exact mass 315.0374 (calcd for $C_{13}H_{17}NO_3Se$, 315.0373). Anal. Calcd for $C_{13}H_{17}NO_3Se$: C, 49.69; H, 5.45; N, 4.46; O, 15.27. Found: C, 49.92; H, 5.49; N, 4.51: O, 14.9. Final proof of structure for **15** comes from the identification of the triphenyltin hydride reduction product as a 4-hydroxy- (as opposed to 3-hydroxy-) tetrahydropyridine.[48]

3α-Phenylseleno-5α-cholestane (3). Tri-*n*-butylphosphine (658.3 mg, 3.25 mmol) was injected dropwise over 10 min into a magnetically stirred solution of 3β-cholestanol (1.0395 g, 2.67 mmol) and phenyl selenocyanate (603.5 mg, 3.31 mmol) in dry THF (8 mL). After an overnight period at room temperature substantial quantities of cholestanol remained (TLC). More phenyl selenocyanate (294.1 mg, 1.61 mmol) and tri-*n*-butylphosphine (185.1 mg, 0.92 mmol) were added and, after a further period of 1 h at room temperature, the solvent was

evaporated.[49] Chromatography of the residue over silica gel (3 × 10 cm) with CH_2Cl_2 and then over alumina (3 × 15 cm) with hexane gave the crude product. Crystallization from acetone (18 mL) afforded 160.2 mg (11%) of **3**: mp 109–110.5 °C; NMR ($CDCl_3$, 200 MHz) inter alia δ 3.4 (br s, 1 H); exact mass 372.3725 (calcd for $C_{27}H_{48}$ (M − PhSe), 372.3756). Anal. Calcd for $C_{33}H_{52}Se$: C, 75.10; H, 9.93. Found: C, 75.19; H, 10.04.

Dodecyltellurobenzene (27). This experiment was performed in a photographic darkroom equipped with a red safety light. As a matter of routine practice the latter was turned off when not essential.

Diphenyl ditelluride (1.210 g, 2.96 mmol) was tipped into a dry 50-mL three-necked flask which contained a magnetic stirring bar. The flask was immediately fitted with a hose adaptor with tap (which was shut), a reflux condenser closed by a septum carrying inlet and exit needles for nitrogen, and a solid addition tube charged with powdered sodium borohydride (230 mg, 6.08 mol). The apparatus was purged with nitrogen, and absolute ethanol (25 mL) was injected. The magnetic stirrer was turned on and the sodium borohydride was added slowly to the red solution.

By the end of the addition the color had been discharged and at this stage 1-bromododecane (1.5 g, 6.02 mmol) was injected into the flask, residual halide being rinsed from the syringe with absolute ethanol (~2 mL). The nitrogen exit needle was removed and the mixture was refluxed for 3.5 h. (During this period the progress of the reaction was monitored by TLC, samples being removed by syringe through the condenser septum. The plates were developed in the dark but without protection from air.) The reaction mixture was then cooled to room temperature and the nitrogen inlet needle was withdrawn. The solvent was evaporated through the hose adaptor using an oil pump vacuum and the residue was transferred with the aid of a little CCl_4 to the top of a silica gel column (3 × 60 cm) made up with CCl_4. The column was developed with the same solvent. (It is unnecessary to protect the eluate (in the fraction collector) from air.) Appropriate fractions (TLC, silica, CCl_4) were combined and evaporated to yield 1.726 g (76%) of **27** as a homogeneous (TLC, silica CCl_4), pale yellow oil: NMR ($CDCl_3$) δ 0.6–2.0 (m, 23 H), 2.89 (t, J = 7.7 Hz, 2 H), 7.03–7.35 (m, 3 H), 7.60–7.83 (m, 2 H); exact mass 376.1412 (calcd for $C_{18}H_{30}{}^{130}Te$, 376.1410). The material was stored in a refrigerator under nitrogen and with protection from light.

Dichloro(dodecyl)phenyltellurium (28). This experiment was performed in subdued light. A dry 5-mL round-bottomed flask containing a magnetic stirring bar and closed with a septum was flushed with nitrogen and then kept under a slight static pressure of the gas. The flask was wrapped with aluminum foil. Dodecyltellurobenzene (230 mg, 0.615 mmol) was injected and CCl_4 (0.5 mL) was used to rinse all the telluride from the syringe. More CCl_4 (2 mL) was added to the reaction flask and then sulfuryl chloride (182 mg, 1.35 mmol) was injected with stirring. The mixture turned colorless immediately and all the starting telluride had reacted well within 10 min (TLC, silica, benzene). The solvent was evaporated to leave 252 mg (92%) of **28** as a colorless, homogeneous (TLC, silica, benzene) oil: NMR (CCl_4) δ 0.78–2.5 (m, 23 H), 3.62 (t, J = 7.7 Hz, 2 H), 7.42–7.69 (m, 3 H), 8.06–8.37 (m, 2 H); exact mass 411.1101 (calcd for $C_{18}H_{30}{}^{35}Cl^{130}Te$ (M − Cl), 411.1098). Anal. Calcd for $C_{18}H_{30}Cl_2Te$: C, 48.59; H, 6.80; Cl, 15.94. Found: C, 48.56; H, 6.91; Cl, 16.10.

[(1-Methylundecyl)telluro]benzene (29). With the exceptions noted below the general procedure for **27** was followed using diphenyl ditelluride (409 mg, 1.00 mmol) in absolute ethanol (6 mL), sodium borohydride (78 mg, 2.06 mmol), and 2-bromododecane (500 mg, 2.01 mmol). The mixture was refluxed for 5 h (TLC control) and the solvent was evaporated as before. The residue was stirred with ether and the slurry was filtered through a small pad of anhydrous $MgSO_4$. Evaporation of the ether and chromatography of the resulting oil over silica gel (1.5 × 60 cm) with hexane gave 696 mg (92%) of **29** as a very pale yellow homogeneous (TLC, silica, hexane) oil: NMR ($CDCl_3$) δ 0.7–1.95 [m (incorporating d at 1.62, J = 7 Hz), 24 H], 3.41 (h, J = 7 Hz, 1 H), 7.05–7.43 (m, 3 H), 7.72–7.93 (m, 2 H); exact mass 376.1419 (calcd for $C_{18}H_{30}{}^{130}Te$, 376.1418).

Dichloro(1-methylundecyl)phenyltellurium (30). The procedure for **28** was followed using telluride **29** (350 mg, 0.94 mmol) in CCl_4 (5 mL), sulfuryl chloride (300 mg, 2.23 mmol), and a reaction time of 10 min. The solvent was evaporated and the resulting colorless oil was chromatographed over silica gel (1.5 × 30 cm) with ethyl acetate to give 347 mg (83%) of **30** as a colorless, homogeneous (TLC, silica, ethyl acetate) oil: NMR ($CDCl_3$) δ 0.7–2.38 [m (incorporating d at 1.68, J = 7 Hz), 24 H], 4.13 (s, J = 7 Hz, 1 H), 7.38–7.64 (m, 3 H), 8.1–8.35 (m, 2 H); exact mass 411.1099 (calcd for $C_{18}H_{30}{}^{35}Cl^{130}Te$ (M − Cl), 411.1098). Anal. Calcd for $C_{18}H_{30}Cl_2Te$: C, 48.59; H, 6.80; Cl, 15.94. Found: C, 48.40; H, 6.66; Cl, 15.98.

Dodecyl Methyl Telluride (31). The general procedure for **27** was followed using dimethyl ditelluride (1.420 g, 4.98 mmol) in absolute ethanol (20 mL) and sodium borohydride (435 mg, 11.50 mmol). 1-Bromododecane (2.5 g, 10.03 mmol) was injected into the resulting colorless solution, 0.5 mL of ethanol being used to rinse the syringe. The mixture was refluxed for 3.5 h, at which stage the reaction was complete (TLC control). The solvent was evaporated through the hose connection and the residue was slurried with several portions of CH_2Cl_2 and filtered (using gentle pressure from an argon tank) through a pad of anhydrous $MgSO_4$. Evaporation of the combined filtrates (~45 mL) and distillation of the residue gave 2.62 g (83%) of **31** as a homogeneous (TLC, silica, hexane), pale yellow oil: bp 98–99 °C (0.04 mm); NMR ($CDCl_3$) δ 1.72–1.98 [m (incorporating s at 1.87, 3 H), 26 H], 2.63 (t, J = 7.5 Hz, 2 H); exact mass 314.1255 (calcd for $C_{13}H_{28}{}^{130}Te$, 314.1253).

3α-Phenyltelluro-5α-cholestane (32).[2d] The general technique for **27** was followed using diphenyl ditelluride (204 mg, 0.50 mmol) in absolute ethanol (2 mL) and THF (2 mL), sodium borohydride (39 mg, 1.03 mmol), and 3β-cholestanol 4-methylbenzenesulfonate (543 mg, 1 mmol). The steroid was added in a mixture of absolute ethanol (2 mL) and THF (2 mL). Reaction was complete (TLC control) after a reflux period of 1.5 h. The solvent was evaporated, the residue was stirred with several portions (~45 mL in all) of $CHCl_3$, and the slurries were filtered through a small pad of anhydrous $MgSO_4$. The combined filtrate was evaporated to a brown oil. Chromatography over silica gel (1.5 × 60 cm) with hexane gave 293 mg (50%) of **32** as a pale yellow, crystalline compound: mp 81–82 °C; NMR ($CDCl_3$) δ 0.5–2.15 (m, 46 H), 4.0 (br, $W_{1/2}$ = 11 Hz, 1 H), 7.05–7.35 (m, 3 H), 7.65–7.9 (m, 2 H); exact mass 578.3148 (calcd for $C_{33}H_{52}{}^{130}Te$, 578.3131). Examination by TLC (silica, hexane) revealed trace impurities at the origin and solvent front.

1-Phenyltelluro-2-decanol (33). Using the general technique described for **27**, diphenyl ditelluride (3.680 g, 8.99 mmol) in absolute ethanol (45 mL) was treated with sodium borohydride (819 mg, 21.65 mmol). 1,2-Epoxydecane (2.808 g, 17.97 mmol) in ethanol (10 mL) was injected into the resulting colorless solution, 0.5 mL of ethanol being used to rinse the syringe. The mixture was stored at room temperature and the reaction was complete within 15 min (TLC control). The solvent was then evaporated and the residue was slurried with CH_2Cl_2. Filtration through a pad of anhydrous $MgSO_4$ and evaporation of the filtrate (~50 mL) left a yellow oil. Chromatography over silica gel (3 × 60 cm) with 1:1 chloroform–hexane gave 4.410 g of **33.** Rechromatography of the crude fractions gave a further 902 mg of **33.** In all, 5.312 g (81%) of **33** was obtained as a pale yellow, homogeneous (TLC, silica, 1:1 chloroform–hexane) oil: NMR ($CDCl_3$) δ 0.7–1.76 (m, 17 H), 2.22 (br d, J = 4.8 Hz, 1 H), 2.81–3.26 (m, 2 H), 3.69 (br, $W_{1/2}$ = 17 Hz, 1 H), 7.04–7.37 (m, 3 H), 7.64–7.75 (m, 2 H); exact mass 364.1055 (calcd for $C_{16}H_{26}O^{130}Te$, 364.1046). Anal. Calcd for $C_{16}H_{26}OTe$: C, 53.10; H, 7.24; O, 4.42. Found: C, 53.14; H, 7.41; O, 4.38.

1-Phenyltelluro-2-decanol Acetate (34). This experiment was carried out in the darkroom, although the product was noticeably less sensitive than other tellurides to oxidation in the presence of light. Acetic anhydride (1.5 mL) was injected into a stirred solution of **33** (500 mg, 1.50 mmol) in dry pyridine (1 mL). The mixture was kept under a slight static pressure of nitrogen. Acetylation was complete after 18 h (TLC control). The solvents were evaporated at room temperature under oil pump vacuum to yield 520 mg (93%) of **34** as a pale yellow oil: IR (film) 1735 cm^{-1}; NMR ($CDCl_3$) δ 0.73–1.84 (m, 17 H), 1.93 (s, 3 H), 2.9–3.28 (m, 2 H), 5.02 (q, J = 6 Hz, 1 H), 7.05–7.34 (m, 3 H), 7.66–7.89 (m, 2 H); exact mass 406.1153 (calcd for $C_{18}H_{28}O_2{}^{130}Te$, 406.1151). Anal. Calcd for $C_{18}H_{28}O_2Te$: C, 53.51; H, 6.99. Found: C, 53.40; H, 6.99. Analysis of the oil by TLC (silica, 1:1 chloroform–hexane) showed trace impurities. Homogeneous material was obtained by chromatography over silica gel.

5-Phenyltelluro-4-octanol (35). The procedure for **33** was followed using diphenyl ditelluride (409 mg, 1 mmol) in absolute ethanol (4 mL), sodium borohydride (79 mg, 2.09 mmol), and *trans*-4,5-epoxyoctane (256 mg, 1.0 mmol). The epoxide was added in ethanol (3 mL) and the reaction was complete within 1.25 h (TLC control). The solvent was evaporated and the residue was slurried with $CHCl_3$. Filtration through a pad of anhydrous $MgSO_4$ and evaporation of the filtrate (~50 mL) gave a yellow oil. Chromatography over silica gel

(1.5 × 60 cm) with 3:2 chloroform–hexane gave 398 mg (59%) of **35** as a pale yellow, homogeneous (TLC, silica, 3:2 chloroform–hexane) oil: NMR ($CDCl_3$) δ 0.62–2.06 (m, 14 H), 2.2 (br d, J = 7 Hz, 1 H), 3.22–3.78 (m, 2 H), 7.0–7.43 (m, 3 H), 7.64–8.0 (m, 2 H); exact mass 336.0736 (calcd for $C_{14}H_{22}O^{130}Te$, 336.0733).

5-(1-Hydroxy-1-methyl-2-phenyltelluroethyl)-2-methylcyclohexanone (36). The procedure for **33** was followed using diphenyl ditelluride (409 mg, 1 mmol) in absolute ethanol (10 mL), sodium borohydride (78 mg, 2.06 mmol), and 6-methyl-3-(2-methyloxiranyl)-cyclohexanone[50] (336 mg, 2 mmol). The epoxide was added in ethanol (5 mL) and the reaction was found to be complete (TLC control) after 40 min at room temperature. The solvent was evaporated and the residue was slurried with $CHCl_3$. Filtration through a pad of anhydrous $MgSO_4$ and evaporation of the filtrate (~50 mL) left a yellow oil. Chromatography over silica gel (2 × 60 cm) with 1:1 ethyl acetate–2,2,4-trimethylpentane gave 530 mg (70%) of **36** as a pale yellow, homogeneous (TLC, silica, ethyl acetate–2,2,4-trimethylpentane) oil: IR (CCl_4) 1708 cm^{-1}; NMR ($CDCl_3$) δ 0.72–2.69 (m, 15 H), 2.94–3.45 (m, 2 H), 6.95–7.35 (m, 3 H), 7.54–7.85 (m, 2 H); exact mass 376.0687 (calcd for $C_{16}H_{22}O_2{}^{130}Te$, 376.0682).

Reduction of Selenides and Selenoacetals with Triphenyltin Hydride. The apparatus consisted of a small, round-bottomed flask containing a magnetic stirring bar and carrying a reflux condenser closed with a septum through which were passed inlet and exit needles for nitrogen. In order to avoid mechanical losses in very small scale experiments it is preferable to have the flask fused to the condenser so that the apparatus is a one-piece unit. The selenide (or selenoacetal) was weighed into the flask, the indicated volume of solvent (toluene or benzene; see Table I) was added from a syringe, and the septum was fixed in place. Nitrogen was swept through the system for about 5 min and then the exit needle was removed so that the contents of the flask were kept under a slight static pressure of nitrogen. The indicated amount (see Table I) of triphenyltin hydride was injected into the mixture and the flask was lowered partially into a preheated oil bath (120–125 °C for toluene). The course of the reaction was monitored by TLC, samples of examination being withdrawn through the condenser septum. Sometimes additional portions of triphenyltin hydride were added at intervals (see Table I). The product was isolated by chromatography and/or distillation.

Reduction of 10. The product had IR (film) 1705 cm^{-1}; NMR ($CDCl_3$) δ 1.14 (d, J = 3.2 Hz), 1.21 (t, J = 7.1 Hz; signals at 1.14 and 1.21 correspond to 6 H), 1.32–2.14 (m, 4 H), 3.32 (br t, J = 6.4 Hz, 2 H), 3.62–4.38 (m, 3 H, incorporating q at 4.1, J = 7.1 Hz); exact mass 157.1111 (calcd for $C_8H_{15}NO_2$, 157.1103). Anal. Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.06; H, 9.48; N, 8.64.

Reduction of 11. The product had IR (film) 1710 cm^{-1}; NMR (CCl_4) δ 1.28 (d, J = 6.1 Hz), 1.34 (t, J = 7 Hz; the signals at 1.28 and 1.34 correspond to 6 H), 2.54 (d of d, J = 15.6, 2.5 Hz, 1 H), 3.31 (d of d, J = 15.6, 9.6 Hz, 1 H), 4.23 (q, J = 7 Hz), 4.49 (m, the signals at 4.23 and 4.49 correspond to 3 H), 6.7–7.81 (m, 4 H); exact mass 205.1101 (calcd for $C_{12}H_{15}NO_2$, 205.1103). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.83. Found: C, 69.90; H, 7.29; N, 6.80.

Reduction of 12. The product[52] had IR (film) 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.65–2.5 (m, incorporating t, J = 7.2 Hz, 11 H), 3.29–3.54 (m, 1 H), 3.99–4.6 (m, incorporating q, J = 7.2 Hz, 3 H), 6.85–7.9 (m, 4 H); exact mass 245.1422 (calcd for $C_{15}H_{19}NO_2$, 245.1415).

Reduction of 13. The product had IR (film) 1700 cm^{-1}; NMR ($CDCl_3$) δ 1.1 (d, J = 6.8 Hz, 3 H), 1.30 (t, J = 7.2 Hz, 3 H), 2.4–3.25 (m, 2 H), 4.04–4.94 (m, 5 H), 7–7.25 (m, 4 H); exact mass 219.1252 (calcd for $C_{13}H_{17}NO_2$, 219.1245). Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.82; N, 6.39. Found: C, 70.98; H, 7.81; N, 6.31.

Reduction of 14. The product had IR (CCl_4) 1707 cm^{-1}; NMR ($CDCl_3$, 200 MHz) δ 1.25 (t, J = 7 Hz, 3 H), 1.31–2.1 (m, 8 H), 2.55–2.77 (m, 1 H), 3.20–3.40 (m, 1 H), 3.40–3.67 (br s, 1 H), 4.0–4.27 (m, 3 H, incorporating q (centered at 4.13, J = 7 Hz); exact mass 183.1259 (calcd for $C_{10}H_{17}NO_2$, 183.1258). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.27; H, 9.32; N, 7.37.

Reduction of 15. The product had IR (film) 1675–1700 cm^{-1}; NMR ($CDCl_3$) δ 1.10–2.10 (m, 4 H), ~2.36–~2.9 (br s, 1 H), ~2.9–3.3 (overlapping q of d, J = 3.8, 9.4, 13.8 Hz, 2 H), 3.4–4.04 (m, incorporating s at 3.65, 6 H); exact mass 159.0897 (calcd for $C_7H_{13}NO_3$, 159.0896).

Reduction of 22. A. Without Initiator. Evaporation of solvent and chromatography over silica gel (1 × 15 cm) with 1:1 chloroform–hexane gave the product as white crystals which appeared to be homogeneous by TLC (silica, 1:1 chloroform–hexane) but melted at 142–143 °C, which is below the literature[55] value of 147–148 °C.

B. With AIBN. This reaction was carried out at 100 °C in the presence of ~3 mg of AIBN. Evaporation of the solvent and chromatography over silica gel (1 × 60 cm) with 1:1 chloroform–hexane gave homogeneous (TLC) product (89%), mp 147–148 °C. A portion (45 mg) was recrystallized from 8:2 methanol–chloroform to afford white crystals (37 mg): mp 148–149 °C; IR (CCl_4) 1725 cm^{-1}; $[\alpha]^{25}_D$ −61.16° (c 0.5, $CHCl_3$) [lit.[55] $[\alpha]^{25}_D$ −62° (c 3.66 $CHCl_3$)]; NMR ($CDCl_3$, 400 MHz) δ 0.58–2.1 [m, incorporating s at 0.58, 1.03, 2.04 and t at 0.87 (J = 7.1 Hz), 34 H], 2.32 (m, 1 H), 4.6 (m, 1 H), 5.40 (m, 1 H). If the total product were to have been crystallized with the same efficiency, the yield would have been 73%.

Reduction of 23. Evaporation of the solvent, chromatography over silica gel (3 × 20 cm) and development with chloroform–hexane mixtures [1:49 (100 mL), 1:19 (200 mL), 1:9 (200 mL)] and, finally, with chloroform–hexane (3:7) gave the product. This was recrystallized from a mixture of acetone (3 mL) and methanol (1 mL) to afford pure (TLC, silica, 1:1 chloroform–hexane) material (64% yield): mp 123–125 °C; NMR ($CDCl_3$, 400 MHz) δ 0.78 (s, 3 H), 1.14–1.92 (m, 9 H), 2.0 (m and s, 4 H), 2.07–2.36 (m, 3 H), 2.73 (t, J = 9.6 Hz, 1 H), 2.82 (m, 2 H), 3.78 (s, 3 H), 6.67 (m, 1 H), 6.74 (m, 1 H), 7.24 (d, $J \simeq$ 9.6 Hz, 1 H); exact mass 364.1326 (calcd for $C_{20}H_{28}O^{80}Se$, 364.1324.

Deuteration of 4. The experiment was done by the standard method using triphenyltin deuteride.[20] The product had NMR ($CDCl_3$) δ 1.39 (d of t, J = 6.4, 1.8 Hz, 2 H), 1.56–2.1 (m, 1 H), 2.17–2.67 (m, 3 H), 4.62 (q, br signals, $J \simeq$ 6 Hz, 1 H); exact mass 101.0588 (calcd for $C_5H_7DO_2$, 101.0588).

Deuteration of 18. The product had NMR (CCl_4) δ 0.75–2.3 (m, 13 H), 2.62 (s, 1 H), 3.8 (q, taken to be two overlapping triplets, J_1 = 4.9, J_2 = 9.8 Hz); exact mass 123.1161 (calcd for $C_9H_{13}D$ (M − H_2O), 123.1159).

Deuteration of 26. A portion of the product was isolated by chromatography (alumina, hexane) and identified by its spectral properties: NMR ($CDCl_3$) δ 1.3 (br s, 3 H), 7.2–7.95 (m, 7 H); exact mass 158.1065 (calcd for $C_{12}H_{10}D_2$, 158.1065).

Reduction of Tellurium Compounds. The general technique was the same as used for selenium compounds (see above) except that (1) benzene was employed as solvent, (2) reactions were carried out at room temperature or at reflux temperature, and (3) the reactions were set up in a well-darkened laboratory (by the illumination from a red safety lamp) and were allowed to proceed under these conditions (which are less stringent than the darkroom procedure needed for preparing the tellurides). For reductions of **27**, **28**, and **31**, appropriate reaction times (at 31 °C) were established by reactions run in an NMR spectrometer.

Reduction of 36. The product had IR (CCl_4) 3610, 1707 (split) cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.6 [m, incorporating d at 0.99 (J = 6.4 Hz), and s at 1.19]; exact mass 170.1310 (calcd for $C_{10}H_{18}O_2$, 170.1307). The spectral characteristics agree with the published data.[56]

4-Oxa-6-phenylselenohex-1-ene (41). Sodium borohydride (256 mg, 6.77 mmol) was added from a side arm solid addition tube to a stirred solution of diphenyl diselenide (1.172 g, 3.75 mmol) in absolute ethanol (25 mL), the mixture being kept under a nitrogen atmosphere with provision for escape of gases. The resulting colorless solution was cooled in an ice bath and ethylene oxide (~6 mL) was added dropwise. Stirring was continued for 30 min after the end of the addition and the mixture was then poured into hydrochloric acid (1.2 N, 25 mL) and extracted with ether. The ether layer was washed with saturated aqueous $NaHCO_3$ and then with brine. The organic extract was dried (Na_2SO_4) and evaporated. Chromatography of the resulting oil over silica gel (1 × 30 cm) with 1:1 hexane–chloroform gave 1.410 g (93%) of 2-hydroxyethyl phenyl selenide.[57]

A portion (201 mg, 1 mmol) of 2-hydroxyethyl phenyl selenide was dissolved in dry toluene (2 mL) in a flask carrying a reflux condenser closed by a septum which carried inlet and exit needles for nitrogen. Sodium hydride (75 mg of 50% w/w oil suspension, 1.56 mmol) was added to the mixture with stirring and, after 5 min, allyl bromide (126 mg, 1 mmol) was injected. The mixture was heated at 100 °C for 10 min (TLC control), cooled, and partitioned between water (5 mL) and ether. The organic extract was dried (Na_2SO_4) and evaporated. Chromatography of the residue over silica gel (1 × 30 cm) with 3:7

chloroform–hexane gave 98 mg (40%) of **41** as a pale yellow, homogeneous (TLC, silica, 3:7 chloroform–hexane) oil: NMR ($CDCl_3$) δ 3.05 (t, J = 7 Hz, 2 H), 3.67 (t, J = 7.1 Hz, 2 H), 3.98 (d of t, J = 6, 1.5 Hz, 2 H), 5.04–5.41 (m, 2 H), 5.65–6.15 (m, 1 H), 7.09–7.39 (m, 3 H), 7.39–7.71 (m, 2 H); exact mass 242.0207 (calcd for $C_{11}H_{14}O^{80}Se$, 242.0210). Anal. Calcd for $C_{11}H_{14}OSe$: C, 54.78; H, 5.85; O, 6.63. Found: C, 54.47; H, 5.84; O, 6.81.

Reduction of 4-Oxa-6-phenylselenohex-1-ene (41). The selenide **41** (2.650 g, 10.99 mmol) was heated (120 °C) in the usual way under nitrogen with triphenyltin hydride (3.988 g, 11.36 mmol). No solvent was used. After an overnight period a trace of the starting selenide (**41**) remained (TLC). The mixture was cooled and volatile material was distilled under oil pump vacuum directly into a cold trap cooled in liquid nitrogen. The distillate, which was a colorless liquid, weighed 635 mg and was composed of three components as judged by VPC (relative peak areas): 3-methyltetrahydrofuran (46.5), allyl ethyl ether (36.6), and benzene (16.1). Portions of the two ethers were isolated by preparative VPC and identified by spectral comparison with authentic standards.

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