

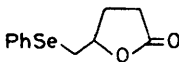
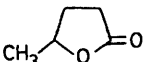
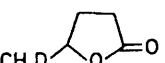
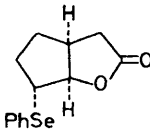
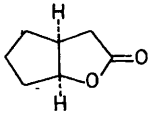
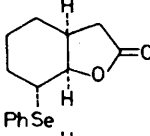
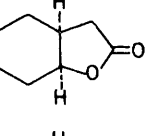
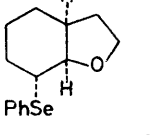
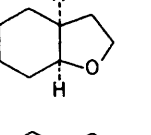
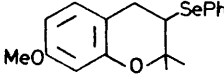
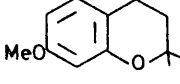
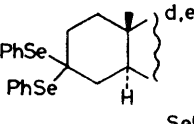
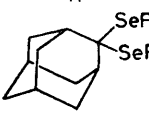
**New Method for Reduction of Ketones and Primary Alcohols to Hydrocarbons:
Reaction of the Derived Selenides with Tin Hydrides**

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Summary Phenyl selenides and selenoacetals are reduced by triphenyltin hydride in a process that constitutes an efficient method for hydrogenolysis of ketone C=O and primary alcohol C-OH bonds.

TABLE^a

Selenide	Equiv. Ph ₃ SnH	Time/h	Product	% Yield
	3	2.5		77
(1)	2.5 ^b	4		ca. 50
	2	2		74
	2.6	1		74
	2	1 ^c		63
	2.3	0.75		84
n-C ₁₂ H ₂₅ SePh	2.5	2.5	n-C ₁₂ H ₂₆	73
	3	1	Cholestane	87
	2	0.75 ^g	Adamantane	91

^a Reactions were carried out in refluxing PhMe except where indicated and volatile products were >99% pure by g.l.c. ^b Ph₃SnD used; ca. 100% D incorporation by n.m.r. spectroscopy. ^c No solvent used because product co-distils with PhMe. ^d Prepared in 91% yield by acidification (dry HCl) of an ether solution of PhSeH and cholestan-3-one. ^e Satisfactory combustion analysis ($\pm 0.2\%$) and mass measurement for (M - PhSe)⁺ were obtained for this compound. ^f M.p. 153–154 °C. Prepared in 83% yield from adamantane-2-one. ^g Reaction in refluxing benzene with an oil bath at 120 °C.

† In our first experiments Bu₃SnH was used in refluxing PhH. Use of Ph₃SnH-PhMe led to shorter reaction times and (with the particular compounds examined) easier chromatographic isolation.

‡ Reaction of secondary alcohols is sluggish.

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³ K. B. Sharpless and M. W. Young, *J. Org. Chem.*, 1975, **40**, 947.

⁴ D. L. J. Clive, G. Chittattu, N. J. Curtis, W. A. Kiel, and C. K. Wong, *J.C.S. Chem. Comm.*, 1977, 725 and references therein.

⁵ P. A. Grieco, S. Gilman, and M. Nishizawa, *J. Org. Chem.*, 1976, **41**, 1485.

⁶ D. Van Ende, W. Dumont, and A. Krief, *Angew. Chem. Internat. Edn.*, 1975, **14**, 700; D. Seebach and A. K. Beck, *ibid.*, 1974, **13**, 806.

⁷ For a summary of other methods of reducing alcohols, see D. H. R. Barton and S. W. McCombie, *J.C.S. Perkin I*, 1975, 1574.

⁸ M. Sevrin, D. Van Ende, and A. Krief, *Tetrahedron Letters*, 1976, 2643.

⁹ L. A. Khazemova and V. M. Al'bitskaya, *J. Org. Chem. (U.S.S.R.)*, 1969, **5**, 1873.

¹⁰ For other reductions by tin hydrides, see H. G. Kuivila, *Synthesis*, 1970, 499; P. J. Smith, *Chem. and Ind.*, 1970, 1025.

THE utility of phenyl selenides is firmly established both for introduction of double bonds into an existing σ -bond framework¹ and for creation of new C-C bonds.¹ However, the synthetic applications of selenides would be extended considerably if efficient and selective methods become available for removing the PhSe-group by reduction. We have discovered that tin hydrides are excellent reagents for this purpose.

The selenides shown in the Table were each treated under N₂ with 2–4 equiv. of Ph₃SnH (usually in refluxing PhMe†) to give the reduction products listed. The second entry shows that the method is also suitable for making deuteriated species.

Under our conditions phenyl sulphides do not appear to be attacked readily.² When n-C₁₀H₂₁SPh was treated with Ph₃SnH in refluxing PhMe we did not detect (g.l.c.) any n-C₁₀H₂₂ even after 2.5 h, but addition of n-C₁₂H₂₅SePh led to rapid production of n-C₁₂H₂₆.

Apart from n-C₁₂H₂₅SePh, which was made³ by displacement of Br⁻ by PhSe⁻, the monoselenides were prepared by cyclofunctionalisation⁴ of appropriate carboxy-, hydroxy-, or phenoxy-olefins. However, selenides can be made directly⁵ from primary alcohols‡ by treatment with PhSeCN and Bu₃P, and selenoacetals are available in high yield by acid-catalysed reaction of a carbonyl compound with a selenol.^{1,6} Therefore the process reported here is a new method for the classical problem of effecting the transformations $\geq C-OH \rightarrow \geq C-H^7$ and $\geq C=O \rightarrow >CH_2$.

In the absence of other structural features sensitive to alkali metal solutions or to hydrogenation (or hydrogenolysis), selenides can be reduced by Li-EtNH₂⁸ and by Raney nickel,^{8,9} respectively. In the few cases where we made a direct comparison with Raney nickel experiments we obtained much higher yields by using Ph₃SnH.¹⁰

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