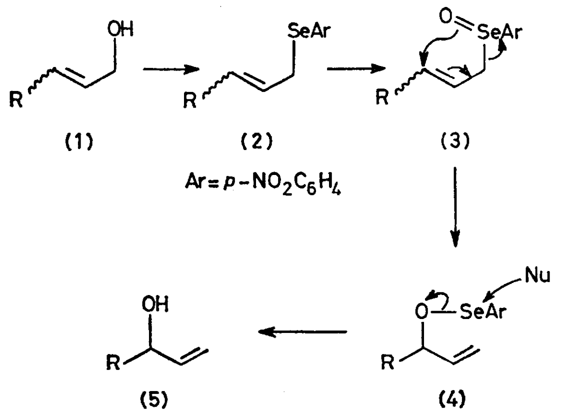
1,3-Transposition of Primary Allylic Alcohols: a New Application of Selenoxide Chemistry

By Derrick L. J. Clive,* Gim Chittattu, Neville J. Curtis, and Steven M. Menchen
(*Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada* T6G 2G2)

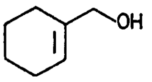
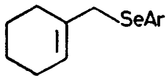
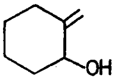
Summary Alk-2-enols undergo efficient contrathermodynamic isomerisation when treated with *p*-$NO_2C_6H_4SeCN$ and Bu^n_3P followed by oxidation with aqueous H_2O_2.

While formation of carbon–carbon bonds and interconversion of functional groups constitute the basis of most synthetic work, the process of functional group transposition[1] is an important supplementary technique.[2] We report a new and efficient procedure for isomerising (*E*) and (*Z*) allylic alcohols of type (**1**; R = alkyl or aryl) to those of type (**5**).[3]



Allylic selenides are known to undergo a very easy 1,3-shift[4] to produce the thermodynamically more stable isomer. Therefore, any S_N2 reaction for converting alcohols (**1**) into selenides should not be complicated by S_N2' processes provided the temperature is high enough for the 1,3-selenoallylic rearrangement.[5] We find that dry pyridine solutions of alcohols (**1**) (*ca.* 0·3 M) and *p*-NO_2-C_6H_4SeCN[6] (1·2 equiv.) can be titrated with Bu^n_3P (1·2 equiv.) at room temperature to give high yields of terminal selenides (see Table).† Very rapid addition of 15% v/v H_2O_2 (20 equiv.) to a pyridine solution of the selenide (**2**) (*ca.* 0·15 M) generates the rearranged alcohol (**5**)‡ which

Table

Alcohol (**1**) R	% Yield of selenide (**2**)	% Yield of rearranged alcohol (**5**)
C_9H_{19} (*cis*)[a]	94[b]	85[c]
C_9H_{19} (*trans*)	95[d]	77[c]
Ph (*cis*)	94[e]	83[c]
Ph (*trans*)	*ca.* 90[d,f]	74[c]
2-Nitro-2-furyl (*trans*)	*ca.* 77	78
Alcohol	Selenide	Rearranged alcohol
		
	(93 %)[g]	(68 %)[c]

[a] Made by semihydrogenation of the corresponding alkyne (m.p. 29—30 °C); *cf.* D. E. Ames, A. N. Covell, and T. G. Goodburn, *J. Chem. Soc.*, 1963, 5889. [b] Free of (*E*) isomer as shown by i.r. spectroscopy. [c] >99% by g.l.c. [d] Free of (*Z*) isomer, as shown by n.m.r. spectroscopy. [e] Little, if any, (*E*) isomer as shown by i.r. spectroscopy, absolute upper limit of 4% (n.m.r.). [f] M.p. 100—102 °C. [g] M.p. 25—29 °C.

---

† Addition of each drop of Bu^n_3P produces a temporary red coloration. The mixture is left for 0·5 h after the end of the addition but the minimum reaction time was not determined. A similar procedure is known to work well with saturated primary alcohols (P. A. Grieco, S. Gilman, and M. Nishizawa, *J. Org. Chem.*, 1976, **41**, 1485).

‡ Experiments run with <1 mmol of selenide.

can be isolated in the yields shown after an arbitrary reaction period of 0·5 h. The alcohol (**5**) is the result of two consecutive and spontaneous processes: [2,3] sigmatropic rearrangement of the selenoxide (**3**) and hydrolysis of the selenenic ester (**4**).[7] The corresponding sigmatropic rearrangement of allylic sulphoxides is not spontaneous[8] so that the use of selenium chemistry[9] permits the contrathermodynamic transformation (**1**) → (**5**) to be carried out under extremely mild conditions.

Satisfactory spectroscopic data and (with the exception of the sensitive furan series) combustion analytical values (±0·3%) were obtained for all new compounds.

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support, and to the National Research Council of Canada, and the University of Alberta.

(*Received*, 3*rd March* 1978; *Com.* 225.)

---

[1] For definition of 'transposition' see P. Brownbridge and S. Warren, *J.C.S. Perkin I*, 1977, 1131.

[2] *E.g.* G. Büchi and J. C. Vederas, *J. Amer. Chem. Soc.*, 1972, **94**, 9128; B. M. Trost, K. Hiroi, and S. Kurozumi, *ibid.*, 1975, **97**, 438.

[3] *Cf.* A. Yasuda, H. Yamamoto, and H. Nozaki, *Tetrahedron Letters*, 1976, 2621; L. Overman and C. B. Campbell, *J. Org. Chem.*, 1976, **41**, 3338; P. S. Wharton and D. H. Bohlen, *ibid.*, 1961, **26**, 3615; J. Tsuji, K. Tsuruoka, and K. Yamamoto, *Bull. Chem. Soc. Japan*, 1976, **49**, 1701.

[4] (a) K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singer, and M. W. Young, *Chemica Scripta*, 1975, **8A**, 9; (b) K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, 1972, **37**, 3973.

[5] In one example studied (see ref. 4b) $t_{1/2} = ca.$ 1·3 h at 52 °C in $CHCl_3$. *Cf.* Thiallylic rearrangement: P. Brownbridge and S. Warren, *J.C.S. Perkin I*, 1977, 2272.

[6] H. Bauer, *Chem. Ber.*, 1913, **46**, 92.

[7] K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Letters*, 1973, 1979; K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, 1972, **94**, 7154; W. G. Salmond, M. A. Barta, A. M. Cain, and M. C. Sobada, *Tetrahedron Letters*, 1977, 1683; H. J. Reich, *J. Org. Chem.*, 1975, **40**, 2570.

[8] D. A. Evans and G. C. Andrews, *Accounts Chem. Res.*, 1974, **7**, 147.

[9] D. L. J. Clive, *Tetrahedron Report No.* 50, *Tetrahedron*, 1978, **34**, 1049.