

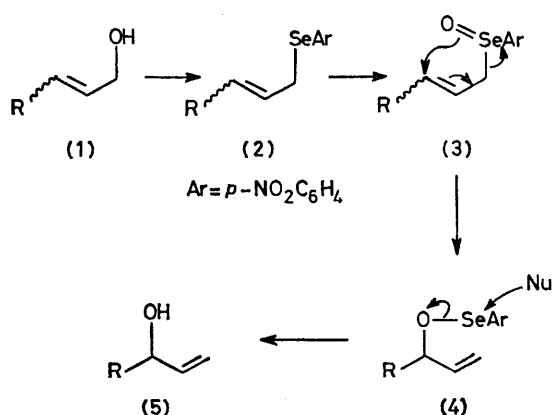
## 1,3-Transposition of Primary Allylic Alcohols: a New Application of Selenoxide Chemistry

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**Summary** Alk-2-enols undergo efficient contrathermodynamic isomerisation when treated with  $p\text{-NO}_2\text{C}_6\text{H}_4\text{SeCN}$  and  $\text{Bu}^n_3\text{P}$  followed by oxidation with aqueous  $\text{H}_2\text{O}_2$ .

WHILE formation of carbon-carbon bonds and interconversion of functional groups constitute the basis of most synthetic work, the process of functional group transposition<sup>1</sup> is an important supplementary technique.<sup>2</sup> 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).<sup>3</sup>

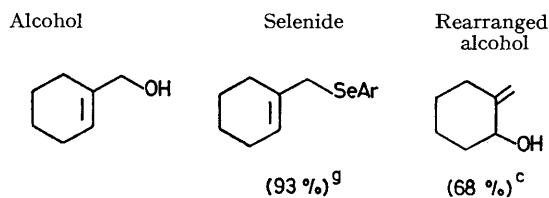


Allylic selenides are known to undergo a very easy 1,3-shift<sup>4</sup> to produce the thermodynamically more stable isomer. Therefore, any  $\text{S}_{\text{N}}2$  reaction for converting alcohols (1) into selenides should not be complicated by

$\text{S}_{\text{N}}2'$  processes provided the temperature is high enough for the 1,3-selenoallylic rearrangement.<sup>5</sup> We find that dry pyridine solutions of alcohols (1) (ca. 0.3 M) and  $p\text{-NO}_2\text{-C}_6\text{H}_4\text{SeCN}$ <sup>6</sup> (1.2 equiv.) can be titrated with  $\text{Bu}^n_3\text{P}$  (1.2 equiv.) at room temperature to give high yields of terminal selenides (see Table).<sup>†</sup> Very rapid addition of 15% v/v  $\text{H}_2\text{O}_2$  (20 equiv.) to a pyridine solution of the selenide (2) (ca. 0.15 M) generates the rearranged alcohol (5)<sup>‡</sup> which

TABLE

| Alcohol (1)<br>R                                      | % Yield of<br>selenide (2) | % Yield of<br>rearranged<br>alcohol (5) |
|---|----------------------------|---|
| $\text{C}_8\text{H}_{19}$ ( <i>cis</i> ) <sup>a</sup> | 94 <sup>b</sup>            | 85 <sup>c</sup>                         |
| $\text{C}_8\text{H}_{19}$ ( <i>trans</i> )            | 95 <sup>d</sup>            | 77 <sup>c</sup>                         |
| Ph ( <i>cis</i> )                                     | 94 <sup>e</sup>            | 83 <sup>c</sup>                         |
| Ph ( <i>trans</i> )                                   | ca. 90 <sup>d,†</sup>      | 74 <sup>c</sup>                         |
| 2-Nitro-2-furyl ( <i>trans</i> )                      | ca. 77                     | 78                                      |



<sup>a</sup> 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. <sup>b</sup> Free of (*E*) isomer as shown by i.r. spectroscopy. <sup>c</sup> >99% by g.l.c. <sup>d</sup> Free of (*Z*) isomer, as shown by n.m.r. spectroscopy. <sup>e</sup> Little, if any, (*E*) isomer as shown by i.r. spectroscopy, absolute upper limit of 4% (n.m.r.). <sup>†</sup> M.p. 100–102 °C. <sup>g</sup> M.p. 25–29 °C.

<sup>†</sup> Addition of each drop of  $\text{Bu}^n_3\text{P}$  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).

<sup>‡</sup> 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).<sup>7</sup> The corresponding sigmatropic rearrangement of allylic sulphoxides is not spontaneous<sup>8</sup> so that the use of selenium chemistry<sup>9</sup> 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 ( $\pm 0.3\%$ ) were obtained for all new compounds.

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<sup>1</sup> For definition of 'transposition' see P. Brownbridge and S. Warren, *J.C.S. Perkin I*, 1977, 1131.

<sup>2</sup> 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.

<sup>3</sup> 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.

<sup>4</sup> (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.

<sup>5</sup> In one example studied (see ref. 4b)  $t_{1/2} = ca. 1.3$  h at 52 °C in CHCl<sub>3</sub>. Cf. Thiallylic rearrangement: P. Brownbridge and S. Warren, *J.C.S. Perkin I*, 1977, 2272.

<sup>6</sup> H. Bauer, *Chem. Ber.*, 1913, **46**, 92.

<sup>7</sup> 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.

<sup>8</sup> D. A. Evans and G. C. Andrews, *Accounts Chem. Res.*, 1974, **7**, 147.

<sup>9</sup> D. L. J. Clive, *Tetrahedron Report No. 50, Tetrahedron*, 1978, **34**, 1049.