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## Simple Procedure for the Aminoselenation of Olefins

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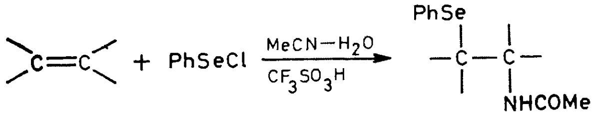
*Summary* The reaction of phenylselenenyl chloride with olefins in acetonitrile in the presence of an acid catalyst and water is a convenient method for the aminoselenation of olefins.

In view of the useful chemistry of organoselenium compounds,[1] the introduction of a nitrogen functional-group into olefins, accompanied by the addition of a phenylseleno-group (aminoselenation of olefins) should provide a valuable method for synthetic strategies. We now report that the reaction of phenylselenenyl chloride with olefins in acetonitrile containing small amounts of organic acid and water affords the $\beta$-aceto-amido-selenide (**1**) in good to excellent yields. Although several methods have been reported which result in the aminoselenation of olefins, some of them[2] require two-pot reactions and/or the preparation of effective selenium reagents, and others[3] can only be applied to special types of olefins, such as olefinic urethanes or Michael acceptors. Our procedure gives a better yield and the reaction is simpler and more general.



(1)

A typical example is as follows. *cis*-But-2-ene was introduced into a stirred dark red solution of phenylselenenyl chloride (5·0 mmol) in acetonitrile (30 ml) until the colour changed to pale yellow. Then, trifluoromethanesulphonic acid (5·0 mmol) and water (25 mmol) were added and the resulting mixture was stirred under reflux for 1 h. After the usual work-up, the product, *threo*-2-acetamido-3-phenylselenobutane (3·7 mmol; 75% yield), was isolated as pale yellow crystals by column chromatography [silica gel, with hexane–chloroform (5:1) as eluent to remove the by-product (diphenyl diselenide) and hexane–ethyl acetate (1:1) to obtain the product].

Table 1. Aminoselenation of olefins.[a]

| Expt. | Olefin | Time/h | Product (**1**) yield[b]/% | M.p. of (**1**) /°C |
|---|---|---|---|---|
| 1 | Hex-1-ene | 3 | 74 (83:17)[c] | — |
| 2 | *trans*-But-2-ene | 1 | 70 | Oil |
| 3 | *cis*-But-2-ene | 1 | 75 | 76—77 |
| 4 | Cyclopentene | 1 | 67 | 72 |
| 5 | Cyclohexene | 1 | 98[d] | 149—150 |
| 6 | Cycloheptene | 1 | 55 | 107—108 |
| 7 | Cyclo-octene | 1 | 42 | 92—93 |

[a] Carried out using phenylselenenyl chloride (5 mmol), olefin (5 mmol), trifluoromethanesulphonic acid (5 mmol), and water (25 mmol) in acetonitrile (30 ml) at reflux temperature. [b] Isolated yield unless otherwise stated. [c] Isomer ratio (see text) was determined by $^{13}$C n.m.r. spectroscopy. [d] Determined by h.p.l.c.

TABLE 2 Effect of organic acid and water [a]

| Expt | Acid (1 mmol) | $H_2O$ (mmol) | Time/h | Yield[b]/% |
|---|---|---|---|---|
| 8 | $CF_3SO_3H$ | — | 1 | 42 |
| 9 | $CF_3SO_3H$ | 1 | 1 | 93 |
| 10 | $CF_3SO_3H$ | 5 | 1 | 98 |
| 11 | — | 1 | 1 | 17 |
| 12 | $p$-$MeC_6H_4SO_3H \cdot H_2O$ | 4 | 3 | 66 |

[a] Carried out using cyclohexene (1 mmol) and phenylselenenyl chloride (1 mmol) in acetonitrile (6 ml) at reflux temperature
[b] Determined by h p l c

The results are shown in Table 1 † This aminoselenation reaction proceeds with *trans*-stereospecificity as for the hydroxyselenation of olefins[4] When the reaction was applied to a terminal olefin (expt 1) the phenylseleno-group was introduced mainly at the terminal carbon atom, but a small amount of the regioisomer was also obtained

As shown in Table 2, the yield of the product (**1**) is not satisfactory when either organic acid or water is omitted (expts 8 and 11) Toluene-*p*-sulphonic acid is also effective as the organic acid, but trifluoromethanesulphonic acid gave better results

This reaction also proceeds smoothly with phenylselenenyl halides generated *in situ* by the reaction of diphenyl diselenide and sulphuryl chloride or bromine in acetonitrile

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† Satisfactory i r and $^1H$ n m r data as well as combustion analytical data, were obtained for all compounds.

[1] For example, D L J Clive, *Tetrahedron* 1978 **34** 1049 H J Reich, *Acc Chem Res* 1979, **12**, 22
[2] D H R Barton, M R Britton-Kelly, and D Ferreira *J Chem Soc Perkin Trans* 1, 1978, 1090, J N Denis, J Vicens, and A Krief, *Tetrahedron Lett* 1979, 2697, D G Garratt, M D Ryan, and M Ujjainwalla, *Can J. Chem* , 1979, **57**, 2145, D G Garratt, *ibid* , 1979, **57**, 2180
[3] H J Reich and J M Renga, *J Org Chem* 1975 **40**, 3313 H J Reich, J M Renga, and J E Trend, *Tetrahedron Lett* , 1976, 2217, D L J Clive, C K Wong, W A Kiel and S M Menchen, *J Chem Soc Chem Commun* , 1978, 379
[4] A Toshimitsu, T Aoai, H Owada, S Uemura and M Okano, *J Chem Soc* , *Chem Commun* , 1980, 412