Oxyselenation: Reaction of Olefins with Dimethyl Selenoxide

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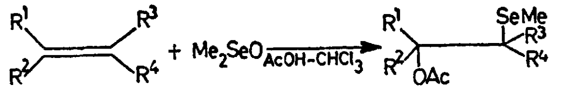
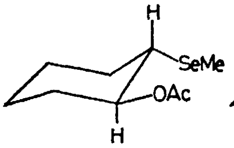
Summary The reaction of olefins with Me_2SeO in AcOH–$CHCl_3$ gave 2-acetoxyalkyl methyl selenides in good yields.

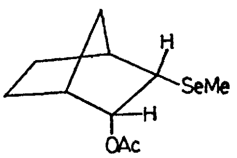
Despite recent interest in organoselenium chemistry,[1] little is known about dimethyl selenoxide.[2] We now report a novel oxyselenation of olefins (I) with Me_2SeO (II) in AcOH–$CHCl_3$ to give 2-acetoxyalkyl methyl selenides (III) (Table), which may be of synthetic importance in view of the work in ref. 1. This reaction has no precedent in dimethyl sulphoxide chemistry. A typical procedure is as follows. The olefin (I) (0·01 mol) in AcOH (10 ml) was added to a solution of Me_2SeO[2b] (II) (0·02 mol) in $CHCl_3$ (30 ml). The mixture was heated at 60° for 42 h to give the 2-acetoxyalkyl methyl selenides (III),† which were isolated by distillation; (IIIa), b.p. 84—87° at 2 mmHg; (IIIb), b.p. 110—111° at 3 mmHg; (IIIc), b.p. 129—132° at 3 mmHg; (IIId), b.p. 93—96° at 4 mmHg.



(I) (II) (III)



(IIIa)



(IIIb)

$PhCH(OAc)CH_2SeMe$

(IIIc)

$Me[CH_2]_3CH(OAc)CH_2SeMe$

(IIId)

Table. Reaction of olefins with Me_2SeO in AcOH–$CHCl_3$

Olefin		Product	Yield/%
Cyclohexene (Ia)	..	(IIIa)	83 (74[a])
Norbornene (Ib)	..	(IIIb)	88
Styrene (Ic) ..	..	(IIIc)	84
Hex-1-ene (Id)	..	(IIId)	87

[a] Reaction in $ClCH_2CH_2Cl$ at 80° for 8 h.

The stereospecific *trans* addition (IIIa and b) and regiospecific addition (IIIc and d) suggests that a species such as MeSeOAc may be the intermediate in this oxyselenation.

(*Received*, *7th February* 1975; *Com.* 142.)

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† All new compounds were adequately characterized by elemental analysis and spectroscopic methods.

[1] For example, see: (a) K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, 1974, **39**, 429; (b) R. A. Zingaro and W. C. Cooper, 'Selenium,' Van Nostrand, New York, 1974, and references therein.

[2] (a) M. L. Bird and F. Challenger, *J. Chem. Soc.*, 1942, 570; (b) G. Ayrey, D. Barnard, and D. T. Woodbridge, *J. Chem. Soc.*, 1962, 2089.