

OXYSELENATION: REACTION OF ACETOXYMETHYL METHYL SELENIDE
WITH OLEFINS IN THE PRESENCE OF HYDROGEN PEROXIDE

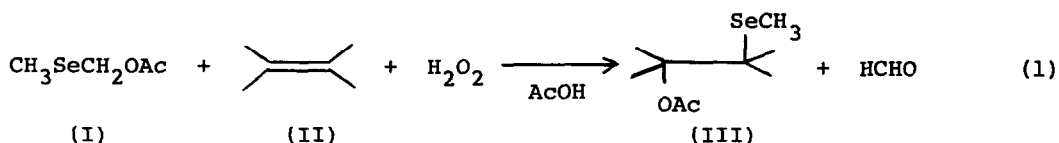
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There has been considerable interest in the chemistry of selenoxides.¹⁾ We have reported previously the acetoxyselenation of olefins with dimethyl selenoxide (DMSeO).²⁾ We now wish to report that acetoxymethyl methyl selenide (I), prepared by the Pummerer reaction of DMSeO with acetic acid,³⁾ reacted with olefins in the presence of hydrogen peroxide to give the corresponding acetoxyselenated products (III) under mild condition in good yield. The reaction was accompanied by elimination of formaldehyde. This new reaction may offer a convenient method of acetoxyselenation of olefins using acetoxymethyl methyl selenide.

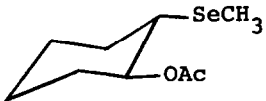
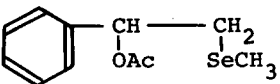


The following experimental procedure is representative; a solution of 11 mmol (1.12 ml) of 30 % hydrogen peroxide in acetic acid (10 ml) was added to a mixture of acetoxymethyl methyl selenide (I) (10 mmol) and cyclohexene (10 mmol) in acetic acid (15 ml) at 0°C with stirring. The resulting solution was stirred for 1 hr at room temperature and then for 3 hr at 80°C for

completion of the reaction. Paraformaldehyde was deposited on the surface of the condenser during the reaction. Evaporation of the solvent under reduced pressure gave a residual yellow liquid, which, on distillation, gave trans-2-acetoxycyclohexyl methyl selenide (1.82 g) in 77 % yield.

The several selenides (III) were synthesized by the similar way. The results are shown in Table 1.

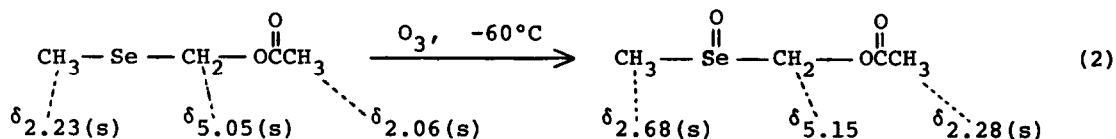
Table 1. Reaction products of olefins with acetoxymethyl methyl selenide in the presence of hydrogen peroxide.^a

Olefin	Product(III)	Yield(%) ^b
Cyclohexene (IIa)		77
1-Hexene (IIb)	$\begin{array}{ccc} \text{CH}_3-(\text{CH}_2)_3-\text{CH}-\text{CH}_2 & & \text{CH}_3-(\text{CH}_2)_3-\text{CH}-\text{CH}_2 \\ & & & \\ \text{OAc} & \text{SeCH}_3 & \text{SeCH}_3 & \text{OAc} \end{array}$ <p style="text-align: center;">(92 : 8)</p>	60 ^c
1-Octene (IIc)	$\begin{array}{ccc} \text{CH}_3-(\text{CH}_2)_5-\text{CH}-\text{CH}_2 & & \text{CH}_3-(\text{CH}_2)_5-\text{CH}-\text{CH}_2 \\ & & & \\ \text{OAc} & \text{SeCH}_3 & \text{SeCH}_3 & \text{OAc} \end{array}$ <p style="text-align: center;">(88 : 12)</p>	72 ^c
Styrene (IId)		74

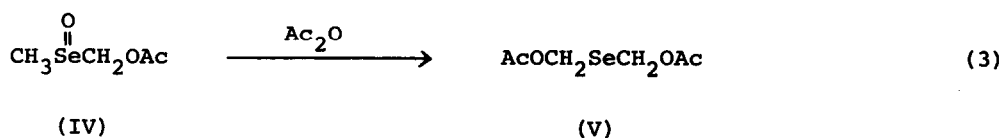
- a) All new compounds were adequately characterized by elemental analysis and spectroscopic methods.
- b) Isolated yields are given.
- c) The ratio of isomers was determined by measurement of NMR spectra in the cases of 1-octene and 1-hexene.

In order to clarify the role of oxidizing agent, i.e. hydrogen peroxide or peracetic acid, in the present acetoxyselenation, the following experiments were carried out. In the absence of hydrogen peroxide, the acetoxyselenation did not take place and all the reactants were recovered unchanged. Hydrogen peroxide could oxidize cyclohexene to give cyclohexene oxide. However, acetoxymethyl methyl selenide (I) did not react with cyclohexene oxide under the present reaction conditions. These facts suggested that oxidation of acetoxymethyl methyl selenide (I) to the corresponding selenoxide (IV) took place at the initial step of the reaction. Direct isolation of the reaction intermediate of the present acetoxyselenation was unsuccessful, but it was shown by controlled experiments that the acetoxyselenation proceeded via acetoxymethyl methyl selenoxide (IV).

The oxidation of (I) with ozone was successfully performed in chloroform solution at -60°C , and the evidence for the formation of acetoxymethyl methyl selenoxide (IV) was obtained by measurement of the NMR spectrum. The sharp singlet (δ 5.05) due to two methylene protons of (I) was changed by the oxidation into an AB type quartet centered at δ 5.15, as shown in eq (2).



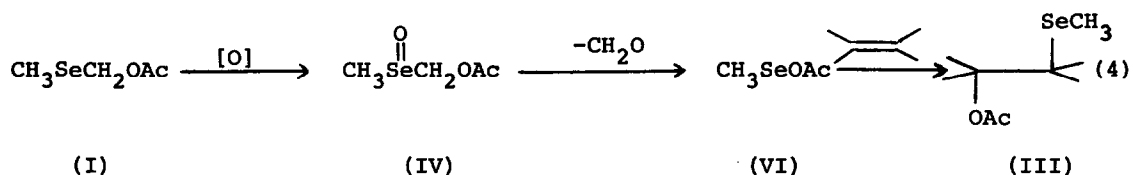
A chemical evidence for the formation of acetoxymethyl methyl selenoxide (IV) was also obtained. Although attempts to isolate the selenoxide (IV) were unsuccessful due to its thermal instability, α, α' -diacetoxymethyl selenide (V), Pummerer reaction product from (IV), was obtained on treatment of the solution of (IV) with acetic anhydride.



The reaction of an olefin with (IV) did give the acetoxyselenated product (III). Addition of cyclohexene (1 equiv.) to the chloroform solution of (IV) resulted in the formation of (IIIa) in 64 % yield, and the generation of formaldehyde was also observed.

The feature of the present acetoxyselenation, the structure of the products above all, suggests the generation of electrophilic species such as methylselenenyl acetate (VI) in the course of the reaction. Consequently, it seems likely that the present acetoxyselenation (eq. 1) involves a sequence of reactions postulated in eq (4).

The details of the reaction are now under investigation.



References

- 1) See, e.g., (a) K.B. Sharpless, K.M. Gordon, R.F. Lauer, D.W. Patrick, S.P. Singer, and M.W. Young, *Chem. Scripta*, **8A**, 9 (1975)., (b) H.J. Reich, J.M. Renga, and I.L. Reich, *J. Amer. Chem. Soc.*, **97**, 5434 (1975).; references cited therein.
- 2) N. Miyoshi, S. Furui, S. Murai, and N. Sonoda, *J. C. S. Chem. Comm.*, 293 (1975).
- 3) Dimethyl selenoxide (25 mmol) was heated in acetic acid (100 ml) at 60°C for 24 hr, acetoxymethyl methyl selenide (I) was obtained by distillation (bp. 51-52°/10mm) in 29.2 % yield.