

Highly Convenient Method for Hydroxyselenation of Olefins

By AKIO TOSHIMITSU, TOSHIAKI AOAI, HIROTO OWADA, SAKAE UEMURA,* and MASAYA OKANO

(*Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan*)

Summary Reaction of phenylselenenyl chloride with olefins in aqueous acetonitrile affords β -hydroxyselenides (**2**) in excellent yields, providing a most convenient method for the hydroxyselenation of olefins

ADDITION of phenylseleno and hydroxy groups to double bonds (hydroxyselenation of olefins) represents an important route to β -hydroxyselenides which are valuable intermediates in organic synthesis¹ Although several methods have been reported for the hydroxyselenation of olefins,² they are all two-pot reactions and/or they require the preparation of effective phenylselenenyl reagents from

selenium compounds We have now found that a one-flask reaction of commercially available phenylselenenyl chloride with olefins in aqueous acetonitrile at room temperature gives β -hydroxyselenides in excellent yields

In a typical experiment, styrene (0.52 g) in aqueous acetonitrile [MeCN (15 ml) + H₂O (3 ml)] was added to phenylselenenyl chloride (0.96 g) and the resulting yellow solution was stirred at room temperature for 2 h After the usual work-up procedure, the products diphenyl diselenide (0.02 g, 3%) and β -hydroxy- β -phenethyl phenyl selenide (1.34 g, 97%), were separated in a pure form by column chromatography [silica gel with hexane-chloroform (2:1)

as eluent for the former product and hexane-ethyl acetate (5:1) for the latter]. Neither addition of the substrates in reverse order nor stirring of the aqueous acetonitrile solution of phenylselenenyl chloride for 2 h prior to the addition of olefins had any effect on the course of the reaction.

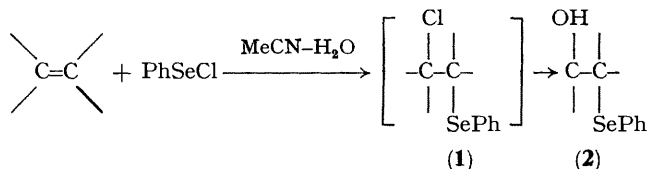
TABLE. Hydroxyselenation of olefins,^a

Expt.	Olefin	Time/h	Product yield ^b /%
1	PhCH=CH ₂	2	97
2	Bu ⁿ CH=CH ₂	24	73 ^e 8 ^e
3	Cyclohex-1-ene	12	96 ^d
4	<i>cis</i> -CHMe=CHMe ^e	24	92
5	<i>trans</i> -CHMe=CHMe ^e	24	89
6	1-Methylcyclohexene	24	73
7	CMe ₂ =CMe ₂ ^f	0.5	70
8	CH ₂ =CHOAc	2.5	82
9	CH ₂ =CMe(OAc)	2	91

^a Carried out using phenylselenenyl chloride (5 mmol) and olefin (5 mmol) in aqueous acetonitrile (18 ml; MeCN:H₂O = 5:1) at room temperature. ^b Isolated yield unless otherwise stated. ^c Yield and isomer ratio are determined by g.l.c. and ¹³C n.m.r., respectively. ^d Determined by g.l.c. ^e Carried out in a pressure bottle using excess butenes (ca. 25 mmol). ^f Carried out at -10 → 25 °C.

The results are shown in the Table.† The products obtained in experiments 3, 4, 5, and 6 showed the *trans*-stereospecificity of this addition reaction. The reaction proceeded well with mono-, di-, tri-, and tetra-substituted olefins, the phenylseleno group adding on to the less substituted carbon atom. Only in the case of hex-1-ene was a small amount of a regioisomer also obtained. From vinyl esters (experiments 8 and 9) the hemiacetal was not detected and instead the hydrolysed aldehyde or ketone was obtained in excellent yield.

When the reaction was applied to norbornene, the phenylselenenyl chloride adduct (1) (*trans*)³ was obtained quantitatively which was, however, found to be reluctant



to hydrolyse, even under reflux temperature, in separate experiments.

(Received, 4th February 1980; Com. 120.)

† Satisfactory i.r. and ¹H n.m.r. data as well as combustion analytical data were obtained for all compounds. The products in experiments 4 and 5 were identical to authentic samples prepared by a known method (ref. 4).

¹ D. L. J. Clive, *Tetrahedron*, 1978, **34**, 1049.

² For example, A. Toshimitsu, S. Uemura, and M. Okano, *J. Chem. Soc., Chem. Commun.*, 1977, 166; D. Laber, A. Krief, and L. Hevesi, *Tetrahedron Lett.*, 1978, 3967; J. N. Denis, J. Vicens, and A. Krief, *ibid.*, 1979, 2697; T. Hori and K. B. Sharpless, *J. Org. Chem.*, 1978, **43**, 1689; D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 1974, 100; H. J. Reich, *J. Org. Chem.*, 1974, **39**, 428; H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow, and D. F. Wendelborn, *ibid.*, 1978, **43**, 1697; K. C. Nicolaou, D. A. Claremon, W. E. Barnette, and S. P. Seitz, *J. Am. Chem. Soc.*, 1979, **101**, 3704.

³ D. Liotta and G. Zima, *Tetrahedron Lett.*, 1978, 4977.

⁴ K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, 1973, **95**, 2697.