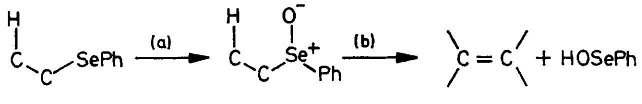
Simple Synthesis of *trans*-Alkenes from Halides by Selenoxide Fragmentation

By Reginald H. Mitchell

(*Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada* V8W 2Y2)

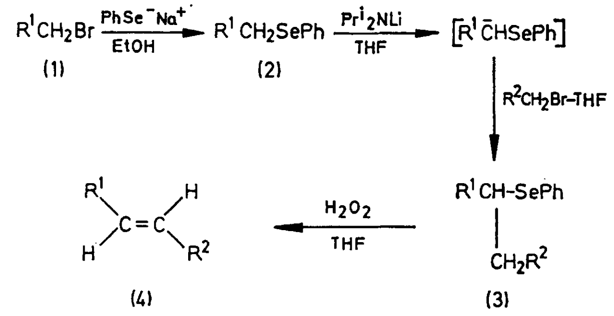
Summary Alkylation of benzyl phenyl selenides (prepared from benzyl halides) with alkyl or arylalkyl halides followed by oxidation to the selenoxide and elimination results in *ca.* 80% yields of *trans*-alkenes.

It has recently been recognized that selenoxide fragmentation [Scheme 1 stage (b)] is a general method for introducing unsaturation into a carbon σ-bond system.[1,2] Both the oxidation, step (a), and the *in situ* fragmentation, step (b), are efficient and they occur under mild conditions with predictable[2] *syn* stereochemistry for the fragmentation.



SCHEME 1

The selenide function might be used not only in the elimination step, but also to build up the carbon skeleton of the final product.† Since selenides are readily available from halides, a synthesis of alkenes starting only from halides‡ would then be available. This approach has been tested successfully using benzyl phenyl selenides [prepared in almost quantitative yield by refluxing an ethanolic solution of the halide (**1**) and $PhSe^-$ for 2 h.[1a]] as shown in Scheme 2.



SCHEME 2

The desired carbon skeleton was obtained by alkylating (room temp.) the anion (prepared using lithium di-isopropylamide in THF)§ of the benzyl selenide (**2**) with a benzyl or alkyl halide to generate the selenide (**3**). Addition of 30% H_2O_2 to the crude mixture yields after 24 h *ca.* 80% yields of pure *trans*-alkenes (**1**). Results for the compounds studied are in the Table.

TABLE

R^1	R^2	Product	Overall yield (%) from (**1**)
Ph	H	$PhCH{=}CH_2$	76
Ph	Me	*trans*-$PhCH{=}CHMe$	80
Ph	Ph	*trans*-$PhCH{=}CHPh$	81
m-Phenylene[a]	Ph	*m*-(*trans*-$PhCH{=}CH)_2C_6H_4$	62

[a] With $R^1 = R^2 =$ *m*-phenylene, no *meta*-cyclophanediene was formed.

For disubstituted alkenes only the *trans* isomer was formed; no trace of the *cis* compound was found by t.l.c. or n.m.r. spectroscopy. This is consistent with a *syn* elimination from an intermediate in which the two R groups are staggered. In the attempted preparation of [2,2]-*meta*-cyclophane-1,9-diene by this procedure, no product could be detected. Apparently the alkylation step proceeded in only poor yield, but the elimination step did not take place at all. Evidently the rotation available in the cyclophane is sufficiently restricted to prevent the two groups from becoming *syn* co-planar around room temperature.¶

I thank the University of Victoria and the National Research Council for financial support.

(*Received, 28th August* 1974; *Com.* 1097.)

---

† Sharpless[2] has seen this possibility as well in his synthesis of α-unsaturated esters.

‡ The synthesis of alkenes by coupling halides is rare (see for example: I. T. Harrison and S. Harrison, 'Compendium of Organic Synthetic Methods,' Wiley-Interscience, New York, 1971, section 205; R. H. Mitchell, *Tetrahedron Letters*, 1973, 4395); more commonly one or two carbonyl compounds are used (*e.g.* in the Wittig and aldol type condensations respectively).

§ Use of BuLi results in ejection of BuSePh, whereas Bu^tOK does not form the anion.

¶ We have observed only very poor yields of products in the analogous elimination of the corresponding sulphoxides, even in refluxing xylene.

[1] K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, 1973, **95**, 2697; H. J. Reich, I. L. Reich, and M. J. Renga, *ibid.*, p. 5813; *J. Org. Chem.*, 1974, **39**, 2133; K. B. Sharpless, M. W. Young, and R. F. Lauer, *Tetrahedron Letters*, 1973, 1979; D. L. J. Clive, *J.C.S. Chem. Comm.*, 1973, 695; 1974, 100.

[2] K. B. Sharpless, R. F. Lauer, and A. Y. Teranishi, *J. Amer. Chem. Soc.*, 1973, **95**, 6137.