New Method for Converting Epoxides into Olefins: Use of Triphenylphosphine Selenide and Trifluoroacetic Acid

By Derrick L. J. Clive* and Clive V. Denyer

(*Chemistry Department, University of London King's College, Strand, London* WC2R 2LS)

Summary Triphenylphosphine selenide in the presence of trifluoroacetic acid deoxygenates epoxides stereospecifically.

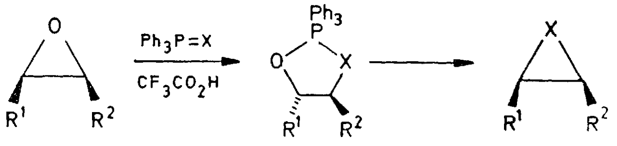
Procedures for deoxygenating epoxides to olefins have important consequences in synthesis[1] and structure determination.[2] We have found that triphenylphosphine selenide[3] and trifluoroacetic acid constitute an effective and mild combination of reagents for carrying out this transformation.[4] The new method is rapid at room temperature and is stereospecific, proceeding in a fashion that preserves the relative stereochemistry about the C–C bond of the epoxide.[5]

Table

Epoxide	Yield of olefin[a] (%)
1,2-Epoxyoctane	71[b]
trans-2-Epoxyoctane ..	68[b]
cis-2-Epoxyoctane	73[b]
cis-Stilbene oxide	*ca.* 71[c]
Cyclohexene oxide ..	53[d]

[a] Products were identified by comparison with authentic samples. [b] G.l.c. analysis of the olefins on silver ion-impregnated columns (*cf.* E. Bendel, B. Fell, W. Gartzen, and G. Kruse, *J. Chromatog.*, 1967, **31**, 531; E. Gil-Av, J. Herling, and J. Shabtai, *ibid.*, 1958, **1**, 508) showed the reaction to be stereospecific. [c] 97·5% *cis*-isomer. [d] Yield refers to the crystalline derivative with 2,4-dinitrobenzenesulphenyl chloride.

Experimentally, the deoxygenation involves addition of trifluoroacetic acid (1 equiv.) in dichloromethane to a solution in the same solvent of the epoxide and an excess (typically 2—3 equiv.) of triphenylphosphine selenide. After a suitable reaction time (1—2·5 h) work-up affords the olefin (see Table).



(1) (2)

Formally, the reaction resembles the conversion[6] of epoxides into episulphides (**1** → **2**; X = S). If the present analogy is valid the olefin must arise by extrusion of selenium from the corresponding episelenide[7] (**2**; X = Se) without loss of stereochemical integrity, an unusual process for which, however, there is precedent in the stereospecific thermolysis of episulphides.[8]

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[1] *E.g.* J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 1959, 112, 2539; S. F. Brady, M. A. Ilton, and W. S. Johnson, *J. Amer. Chem. Soc.*, 1968, **90**, 2882.

[2] *E.g.* D. B. Borders, P. Shu, and J. E. Lancaster, *J. Amer. Chem. Soc.*, 1972, **94**, 2540.

[3] Readily available by the method of A. Michaelis and H. v. Soden, *Annalen*, 1885, **229**, 295.

[4] Metallic and organometallic reagents have recently been introduced for this purpose: K. B. Sharpless, M. A. Umbreit, M. T. Nieh, and T. C. Flood, *J. Amer. Chem. Soc.*, 1972, **94**, 6538; W. P. Giering, M. Rosenblum, and J. Tancrede, *ibid.*, p. 7170; S. M. Kupchan and M. Maruyama, *J. Org. Chem.*, 1971, **36**, 1187. For a survey of older methods see I. T. Harrison and S. Harrison, 'Compendium of Organic Synthetic Methods,' Wiley-Interscience, New York, 1971, p. 502.

[5] The method of E. Vedejs and P. L. Fuchs (*J. Amer. Chem. Soc.*, 1971, **93**, 4070) causes inversion of stereochemistry.

[6] T. H. Chan and J. R. Finkenbine, *J. Amer. Chem. Soc.*, 1972, **94**, 2880.

[7] For spectroscopic detection of episelenides see W. J. R. Tyerman, W. B. O'Callaghan, P. Kebarle, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, 1966, **88**, 4277; A. B. Callear and W. J. R. Tyerman, *Trans. Faraday Soc.*, 1966, **62**, 2760.

[8] E. M. Lown, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *J. Amer. Chem. Soc.*, 1968, **90**, 7164.