

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 synthesis¹ and structure determination.² We have found that triphenylphosphine selenide³ 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
<i>trans</i> -2-Epoxyoctane	68 ^b
<i>cis</i> -2-Epoxyoctane	73 ^b
<i>cis</i> -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.

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.

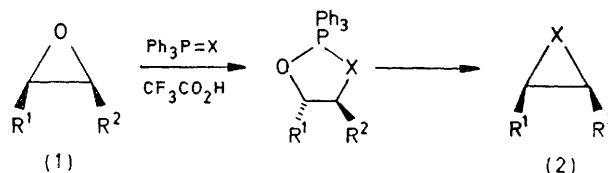
⁵ The method of E. Vedejs and P. L. Fuchs (*J. Amer. Chem. Soc.*, 1971, **93**, 4070) causes inversion of stereochemistry.

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.

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).



Formally, the reaction resembles the conversion⁶ 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 episelenide⁷ (**2**; X = Se) without loss of stereochemical integrity, an unusual process for which, however, there is precedent in the stereospecific thermolysis of episulphides.⁸

We thank Shell Research for support of this work.

(Received, 20th February 1973; Com. 240.)