

A Method for Olefin Inversion *via* Phosphine Oxides

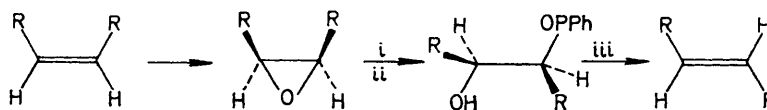
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Summary Treatment of epoxides with $\text{Ph}_2\text{PLi-THF}$ followed by $\text{H}_2\text{O}_2\text{-AcOH}$ gives, by a single inversion, β -hydroxy-diphenylphosphine oxides; the latter can be fragmented stereospecifically to olefins on treatment with an appropriate base.

THE conversion of a *cis*- into a *trans*-olefin or *vice versa* is an important synthetic transformation for which a number of methods have been devised in recent years.¹ We have found that the overall four-step sequence summarised in the Scheme† provides a convenient and efficient new method

† Exemplified in general terms for transformation of a *cis*-1,2-disubstituted olefin into its *trans*-isomer.



Reagents: i, $\text{Ph}_2\text{PLi}^\ddagger\text{-THF}$; ii, $\text{AcOH-H}_2\text{O}_2$; iii, NaH-DMF

SCHEME

for carrying out such an 'olefin inversion' stereospecifically.

In our preliminary investigation of the method, it has been applied to a number of cases (see Table for results) which indicate that it is equally applicable to di-, tri-, or tetra-substituted olefins. Formation of strained *trans*-cyclo-octenes clearly demonstrates the high stereospecificity

TABLE

Epoxide from	Product ^a
<i>cis</i> -Cyclo-octene	<i>trans</i> -Cyclo-octene ^b (76) [†]
<i>cis</i> -1-Methylcyclo-octene	<i>trans</i> -1-Methylcyclo-octene ^b (63)
<i>cis-cis</i> -Cyclo-octa-1,5-diene ^c	<i>cis,trans</i> -Cyclo-octa-1,5-diene ^d (85)
Tetramethylethylene	Tetramethylethylene (53) ^e

^a Figures in parentheses are the percentage yield from β -hydroxyphosphine oxide, the latter being obtainable from epoxide in 75–80% yield after crystallisation; ^b Containing <0.1% *cis*-olefin; ^c Mono-epoxide; ^d Containing 1.0% *cis,cis*-olefin (experiment by P. Newton); ^e Yield low owing to volatility of product; [†] Reaction conditions: (i) Ph_2PLi in THF at 20° for 12 h; (ii) AcOH then H_2O_2 at 0° for 4 h followed by isolation with CHCl_3 , evaporation, and crystallation of the hydroxyphosphine oxide; (iii) NaH-dimethylformamide at 20° for 30 min followed by quenching with water and isolation with light petroleum.

[‡] Obtained by cleavage of PPh_3 with Li in THF.³

¹ (a) A. S. Arora and I. K. Ugi in 'Methoden der Organischen Chemie (Houben-Weyl)', Georg Thieme Verlag, Stuttgart, 1972, vol. 5/1b, p. 728; (b) E. Vedejs and P. L. Fuchs, *J. Amer. Chem. Soc.*, 1973, **95**, 822; (c) J. N. Hines, M. J. Peagram, E. J. Thomas, and G. H. Whitham, *J.C.S. Perkin I*, 1973, 2332.

² A. M. Aguiar, J. Beisler, and A. Mills, *J. Org. Chem.*, 1962, **27**, 1001.

³ E. Vedejs, K. A. J. Snoble, and P. L. Fuchs, *J. Org. Chem.*, 1973, **38**, 1178.

⁴ M. E. Jones and S. Trippett, *J. Chem. Soc. (C)*, 1966, 1090.

⁵ L. Horner, H. Hoffmann, and H. G. Wippel, *Chem. Ber.*, 1958, **91**, 61; L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, *ibid.*, 1959, **92**, 2499; L. Horner, H. Hoffmann, W. Klink, E. Ertel, and V. G. Toscano, *ibid.*, 1962, **95**, 581; L. Horner, W. Klink, and H. Hoffmann, *ibid.*, 1963, **96**, 3133.

⁶ L. Horner, *Fortschr. Chem. Forsch.*, 1966, **7**, 1.

of the reaction; thus the preparation of *trans*-1-methylcyclo-octene uncontaminated with *cis*-isomer contrasts with difficulties reported for an earlier synthesis of this compound.³

The main advantages of the method described here compared with the formally analogous procedure of Vedejs^{1b} based on a Wittig-type elimination⁴ are: (a) the intermediate hydroxyphosphine oxides are highly crystalline and readily purified, and (b) the phosphorus-containing product of the elimination is sodium diphenylphosphinate and hence easily removed.

The olefin-forming elimination is the same as the second step in Horner's 'PO-activated olefination'^{5,6} a much neglected reaction which may owe its neglect to the statement that the more stable olefin is the usual reaction product.⁶ We hope that our observation that thermodynamically unstable alkyl substituted olefins can be obtained *via* the epoxide route will lead to a renaissance of interest in the Horner Reaction.

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