A Method for Olefin Inversion *via* Phosphine Oxides

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Summary Treatment of epoxides with Ph_2PLi–THF followed by H_2O_2–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

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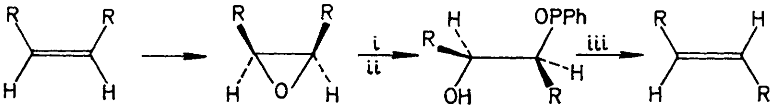
† Exemplified in general terms for transformation of a *cis*-1,2-disubstituted olefin into its *trans*-isomer.



Reagents: i, Ph_2PLi‡–THF; ii, $AcOH–H_2O_2$; 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 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]

TABLE

Epoxide from	Product[a]
cis-Cyclo-octene	*trans*-Cyclo-octene[b] (76)[f]
cis-1-Methylcyclo-octene	*trans*-1-Methylcyclo-octene[b] (63)
cis-cis-Cyclo-octa-1,5-diene[c]	*cis,trans*-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; [f] 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.

The main advantages of the method described here compared with the formally analogous procedure of Vedejs[1b] based on a Wittig-type elimination[4] 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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‡ Obtained by cleavage of PPh_3 with Li in THF.[2]

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