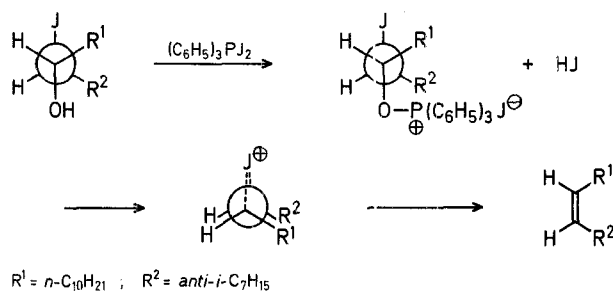
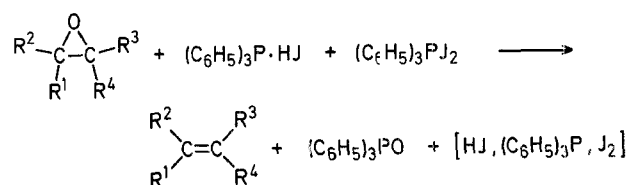


tention in a reaction involving triphenylphosphine dihalides to replace the hydroxy group of an iodohydrin. Triphenylphosphine diiodide, which is not a useful reagent for the preparation of iodides from alcohols², was allowed to react with iodohydrins. The presumed phosphorylated iodohydrin spontaneously decomposed to give an alkene. The reaction proceeds in high yield and is a stereospecific *trans* elimination.



Iodohydrins may be formed by *anti* opening of epoxides with hydrogen iodide³. A convenient method was therefore also determined for the reduction of epoxides to olefins employing 1.1 molar equivalents each of triphenylphosphine hydriodide and triphenylphosphine diiodide. Although the elimination from both diastereomeric iodohydrins was stereospecific if conducted in benzene at room temperature, the cleavage of *cis* epoxides was only ~93% *anti* at that temperature. The epoxide reductions were therefore conducted at 0 °C for 24 h, and then at 25 °C for another 24 h.

The stoichiometry of the overall transformation is such that a net conversion of one equivalent of triphenylphosphine to its oxide has occurred.



A Convenient Stereospecific Reduction of Epoxides and Iodohydrins to Alkenes

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The reaction of *vic*-chlorohydrins with triphenylphosphine dichloride (dibromide) produced *vic*-dichlorides (bromochlorides) with inversion of the hydroxy-bearing carbon¹. Although *erythro*-bromohydrins reacted to form *vic*-dihalides with identical stereochemical consequences, *threo*-bromohydrins produced diastereomeric mixtures of the *vic*-dihalides¹. A rationalization was suggested that involved anchimeric bromine-assisted departure of the phosphorylated hydroxy group to account for the formation of that diastereomeric dihalide in which displacement had occurred with retention of configuration. The greater ability of iodine to donate electron density to an adjacent incipient carbenium ion lead us to expect a greater degree of stereochemical re-

This suggests the possibility of conducting the reaction somewhat more economically. For example, one might consider the hydriodide and diiodide as catalysts in a reduction involving one equivalent each of epoxide and triphenylphosphine. Filtration of the reaction mixture would allow recovery of the hydriodide and diiodide to which another equivalent of an epoxide and triphenylphosphine could be added. Although this notion was attractive, several experiments based thereon failed. The reasons for failure are not clear. Iodoalkanes (3–7%) were occasionally observed as by-products of reduction. This was probably due to addition of free hydrogen iodide to the product alkene [triphenylphosphine hydriodide did not add to (*Z*)-4-octene in benzene, for example], which implied some loss of triphenylphosphine, perhaps by reaction of the diiodide with moisture. In one experiment, addition of 10 mol % excess triphenylphosphine in a reduction of an epoxide caused the formation of secondary alcohol as a major product. Despite the current inability to affect reduction with lessened expenditure of reagents, the procedure is simple, mild, stereospecific, and competitive with other methods.

Table. Reduction of Iodohydrins and Epoxides to Alkenes

Entry	Starting Material	Alkene	Yield ^a [%]	Stereo- specificity ^b [%]	b.p./torr [°C]	
					found	reported
1	<i>threo</i> -7(8)-hydroxy-8(7)-iodo-2-methyloctadecane ^c	(<i>Z</i>)-2-methyl-7-octadecene	96	99	98–101°/0.01	125–129°/0.2 ¹⁰
2	<i>erythro</i> -7(8)-hydroxy-8(7)-iodo-2-methyl-octadecane ^c	(<i>E</i>)-2-methyl-7-octadecene	96	>98	98–101°/0.01	125–129°/0.2 ¹⁰
3	1-eicosene oxide ^d	1-eicosene	95	—	m.p. 26–28°	m.p. 28.5° ¹¹
4	(<i>E</i>)-3-octene oxide ^d	(<i>E</i>)-3-octene	>95 ^c	100	— ^e	— ^e
5	(<i>E</i>)-4-octene oxide ^d	(<i>E</i>)-4-octene	>95 ^c	100	— ^e	— ^e
6	(<i>Z</i>)-4-octene oxide ^d	(<i>Z</i>)-4-octene	>95 ^c	99	— ^e	— ^e
7	(<i>Z</i>)-2-methyl-7-octadecene oxide ^d	(<i>Z</i>)-2-methyl-7-octadecene	91	>98	98–101°/0.01	125–129°/0.2 ¹⁰
8	(<i>Z</i>)-1-acetoxy-7-dodecene oxide ^d	(<i>Z</i>)-1-acetoxy-7-dodecene	93	>99	60–63°/0.01	98–100°/0.5 ¹²
9	(<i>E</i>)-1-acetoxy-4-tridecene oxide ^d	(<i>E</i>)-1-acetoxy-4-tridecene	94	>98	80–82°/0.01	88°/0.08 ¹³
10	(<i>Z</i>)-1-formyloxy-9-tetradecene oxide ^d	(<i>Z</i>)-1-formyloxy-9-tetradecene	93	100	96–100°/0.01	97–100°/0.01 ¹⁴
11	citronellyl formate oxide ^d	citronellyl formate	98	—	128–132°/30	97–100°/10 ¹⁵

^a Yields of isolated product.

^b Determined by G.L.C. analysis of the diastereomeric dibromides or as chlorohydrin trifluoroacetates⁸ using a packed column of Ultrabond II⁹.

^c Reaction with triphenylphosphine diiodide (1.1 equiv).

^d Reaction with triphenylphosphine hydroiodide (1.1 equiv) + triphenylphosphine diiodide (1.1 equiv).

^e Entries 4,5,6 are commercial alkenes whose b.p.'s are in catalogs or on the labels.

Recent interest in epoxide-olefin transformation has been quite intense and has been reviewed⁴. Methods of converting epoxides to olefins related to that described herein are:

- use of diphosphorus tetraiodide (P₂I₄), which seems particularly suited to the preparation of terminal alkenes and α,β -unsaturated systems⁵;
- use of phosphonium iodide (PH₄I), which has been employed for the preparation of 2-alkenoic acids and for which experimental details are unpublished⁶;
- use of triphenyl phosphite methiodide [H₃C—P⁺(OC₆H₅)₃J[−]], which was employed in a 10:1 molar ratio, and also gave good yields of *syn* elimination products from variously substituted epoxides⁷.

I.R. spectra were obtained as dilute solutions in carbon tetrachloride on a Perkin Elmer 467[®] spectrophotometer. ¹H-N.M.R. spectra were obtained in Silanor[®] chloroform using a Bruker WHX-90[®] spectrometer. Mass-spectral data were obtained with a Finnigan Model 105C[®] chemical ionization mass spectrometer that was equipped with a chromatographic inlet (Varian Model 1400[®]) served by a 3% OV-101 column, 3.2 mm × 1.5 m. G.L.C. analyses were performed with a Varian 2400[®] instrument employing a column of Ultrabond II[®] (Supelco supplier), 3.2 mm × 1.5 m that served both for general product analysis as well as for the characterization of alkene geometry based on diastereomeric addition products as mentioned in the Table. The alkenes corresponding to the epoxides listed in the Table were obtained from Farchan Chemical Co. (Willoughby, OH 44094) or Chemical Samples Co. (Columbus, OH 43220): Table, Entry (starting material) 4 (99% *E*), Entry 5 (99% *E*), Entry 6 (96% *Z*), Entry 7 (97.5% *Z*), Entry 8 (97% *Z*), Entry 9 (99% *E*), Entry 10 (97% *Z*). Citronellyl formate was obtained from Givaudan Corp. (Clifton, DE 07014), and 1-eicosene was obtained from Aldrich Chemical Co. Alkenes were epoxidized with 3-chlorobenzoperoxy acid in the usual manner. The iodohydrins (Entries 1 and 2) were prepared from the corresponding *Z*

and *E*-epoxides¹ in the usual manner. Satisfactory spectral data and consistent G.L.C. data were obtained for all compounds. The product alkenes, of course, were compared directly with the commercial samples.

Alkenes from Epoxides; General Procedure:

A mixture of triphenylphosphine hydriodide (1.17 g, 3.0 mmol) and triphenylphosphine diiodide (1.55 g, 3.0 mmol) in benzene (10 ml) + hexane (2 ml) is stirred in a cold room (0°C) for 15 min. A solution of the epoxide (2.5 mmol) in hexane (1 ml) is added to the stirred mixture (which turns canary yellow) and stirring is continued for 24 h at 0°C and for 24 h at room temperature. [The tetra-substituted oxiranes (*trans*-1,2-dialkyl-substituted epoxides) are reduced stereospecifically at room temperature and do not require a reaction period at 0°C]. The mixture is diluted with hexane (15 ml) and suction-filtered to remove triphenylphosphine oxide. The reaction flask is rinsed with hexane (2 × 15 ml), and the rinses are also filtered. The combined filtrate is concentrated using a flash evaporator, and the residue is chromatographed on silica gel (10 g). The alkene is eluted with hexane (50 ml) if it is a hydrocarbon or with 5% ether-hexane (50 ml) if it is an alkenol ester. The eluant is then stripped of solvent to constant weight.

The octenes were not isolated. Instead the yields were determined via dibromide adducts by G.L.C. with tetradecane as internal standard. Derivatization (bromine addition) could be accomplished directly with the hexane-triturated reaction mixture.

Extended reaction times and poor quality triphenylphosphine diiodide appear to favor iodoalkane formation. For example, the epoxide of Entry 7 produced ~6–7% of (presumably) 7- and 8-iodo-2-methyloctadecane; C.I.M.S. (CH₄): *m/e* = 393 (M – 1)⁺, 267 (protonated alkene, i.e., loss of HJ). This same epoxide was reduced in the presence of 10 mol% excess of triphenylphosphine and gave the secondary alcohols, 7- and 8-hydroxy-2-methyloctadecane as a significant by-product [C.I.M.S. (CH₄): *m/e* = 284 (M)⁺, 283, 267 (M – 17)⁺; ¹H-N.M.R. (CDCl₃): δ = 4–18 ppm (m, relative area not meaningful because purity was not 100% and 40H expected in total); I.R. (CCl₄): 3630 cm^{−1}].

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