

Note

An efficient transformation of epoxides into olefins, using potassium iodide, zinc, and phosphorus(V) oxide in *N,N*-dimethylformamide

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The deoxygenation of epoxides into olefins has received considerable attention in organic synthesis^{1,2}. In carbohydrate chemistry, the conversion of epoxides into the corresponding olefinic sugars using potassium selenocyanate has been described³.

During our work on the conversion of vicinal diols into olefins⁴, the possibility of converting epoxides in the hexopyranose series into olefins was also considered. We now report that potassium iodide, zinc, and phosphorus(V) oxide in *N,N*-dimethylformamide at 90° efficiently transforms methyl 2,3-anhydro-4,6-*O*-benzylidene- α -D-hexopyranosides having the *allo* and *manno* configurations into methyl 4,6-*O*-benzylidene-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside in yields of 86 and 83%, respectively. The advantages of this reaction system, apart from the high yields indicated, are the low cost and ready availability of the reagents.

EXPERIMENTAL

General methods were the same as those reported⁵.

Methyl 4,6-O-benzylidene-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside. — A mixture of methyl 2,3-anhydro-4,6-*O*-benzylidene- α -D-*allo*-(or *manno*-)pyranoside⁶ (1.0 g, 3.79 mmol), phosphorus(V) oxide (5.38 g, 37.9 mmol), zinc (2.48 g, 37.9 mmol), and potassium iodide (3.77 g, 22.7 mmol) in *N,N*-dimethylformamide (50 ml) was stirred for 3 h at 90° (15 h for the *manno* compound). The mixture was cooled, and filtered through Celite which was then washed with toluene; the filtrate and washings were combined and extracted exhaustively with saturated, aqueous sodium hydrogencarbonate and then water. The organic phase was dried (MgSO₄), filtered, and concentrated, to yield the title compound (0.81 g, 86%, from the *allo* compound; and 0.78 g, 83%, from the *manno* compound), m.p. 117–119°, $[\alpha]_D +130^\circ$ (*c* 1.0, chloroform); lit.⁷ m.p. 117–119°, $[\alpha]_D +126^\circ$ (chloroform).

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