Stereospecific Conversion of Epoxides into Olefins

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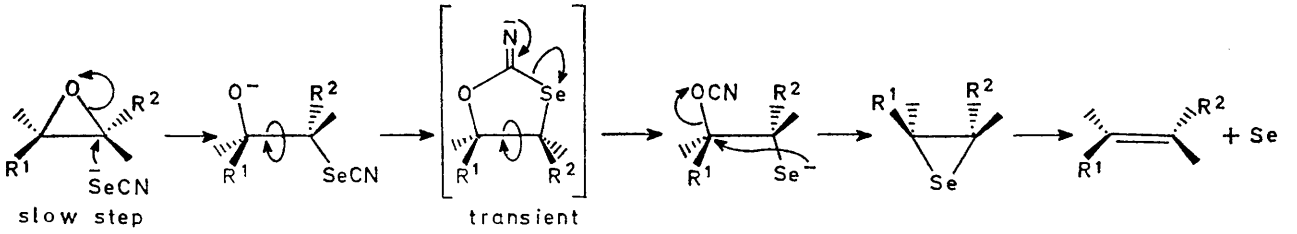
Epoxides can be converted into olefins under slightly alkaline conditions by potassium selenocyanate. Epoxy-groups in straight-chain compounds are so converted in high yields but epoxy-derivatives of cyclic compounds show a remarkable variation in reactivity.

THE use of selenium compounds as reagents in organic synthesis has aroused considerable interest.[1-3] The conversion of epoxides into olefins has been effected by a wide variety of methods,[4] one of which makes use of the instability of episelenides.[5] This reaction seemed to us similar to those in which an epoxide is changed into an episulphide [6] and, like them, is carried out under acidic conditions. Acidic conditions are not always advantageous because undesirable changes may be induced, and in our case we required a reagent to effect the stereoselective conversion of epoxides into olefins under neutral or slightly alkaline conditions. By analogy with the conversion of epoxides into episulphides by potassium thiocyanate,[7] we treated epoxides with the readily available potassium selenocyanate. In aqueous methanolic solution, potassium selenocyanate gives a slightly alkaline solution (pH 8—9) which reacts with epoxides at room temperature to deposit selenium and form an olefin. The course of the reaction can be followed by weighing the precipitated selenium and the rate is greater at higher temperatures. Preliminary kinetic data indicate that the reaction is second-order in epoxide and selenocyanate, and is much slower in t-butyl alcohol. The reaction does not proceed at all in the aprotic solvents dimethyl sulphoxide and dimethylformamide, even at elevated temperatures. Subsequent to this work, our attention was drawn to the use of potassium selenocyanate in attempts to introduce selenium into the pyranoid ring of sugars; in this work treatment of three epoxy-sugars with the reagent gave unsaturated sugars instead of the expected seleno-sugars.[8] A suggested mechanism for the reaction is shown in the Scheme and the Table shows the epoxides which have been converted into olefins.



SCHEME

The Scheme and other data led us to consider that the reaction proceeds *via* a minimum of two half-rotations about the carbon–carbon bond originally part of the epoxide system, and accordingly to examine the behaviour of epoxy-derivatives of cyclic compounds. As shown in the Table, at room temperature the epoxy-derivatives of cyclopentane, cyclo-octane, and cyclododecane were unchanged after 3 days. In contrast, the epoxy-derivatives of cyclohexane and 1-methylcyclohexane were converted rapidly into the respective olefins; that of cycloheptane reacted more slowly. This selectivity is probably due to steric factors preventing the selenocyanate nucleophile from attacking from ' behind ' the epoxide ring; all the epoxides are readily opened

Conversion of epoxides into olefins [a]

Olefin	Yield (%) [b]	Temp. (°C)	Time (h)
Methyl oleate	100	58	18
Methyl elaidate	98	65	18
trans-Stilbene	100	65	2·5 [c]
p-Bromo-β-methylstyrene	100	25	96
Cyclopentene	0 [d]	25	72
Cyclohexene	100	25	72
1-Methylcyclohexene	62 [e]	25	72
Cycloheptene	34 [e]	58	72
Cyclo-octene	0 [e]	60	72
Cyclododecene	0 [e]	65	48
Norborn-2-ene [f]	0 [e]	58	72

[a] Excess of KSeCN in H_2O–MeOH (1 : 10 v/v) was treated with the epoxide. The temperatures and times stated give some idea of the varying rate of reaction. [b] Most of the olefins were liquids and were characterised by spectra (n.m.r., mass, and i.r.) and g.l.c. [c] Also set aside overnight (+18 h). [d] Other products were formed and the epoxide was recovered in 82% yield. [e] Remainder is unchanged epoxide. [f] From mixtures of *exo*- and *endo*-epoxides.

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[2] D. L. J. Clive, *J.C.S. Chem. Comm.*, 1973, 695.

[3] For many examples see D. L. Klagman and W. H. H. Günther, ' Organic Selenium Compounds. Their Chemistry and Biochemistry,' Wiley, New York, 1973.

[4] As examples: O. Ceder, *Acta Chem. Scand.*, 1964, **18**, 126' K. B. Sharpless, M. A. Umbreit, M. T. Nieh, and T. C. Flood; *J. Amer. Chem. Soc.*, 1972, **94**, 6358; C. B. Scott, *J. Org. Chem.*, 1957, **22**, 1118.

[5] D. L. J. Clive and C. V. Denyer, *J.C.S. Chem. Comm.*, 1973, 253.

[6] See, for example, B. Hansen, *Acta Chem. Scand.*, 1957, **11**, 537.

[7] E. E. van Tamelen, *J. Amer. Chem. Soc.*, 1951, **73**, 3444.

[8] T. van Es, *Carbohydrate Res.*, 1967, **5**, 282.

under acidic conditions. Thus, under the slightly alkaline conditions produced by potassium selenocyanate in aqueous media, the selectivity could be used to allow double bonds in different environments, particularly in rings of different sizes, to be differentially protected as epoxides. Use of this reagent in suitable cases makes it possible selectively to convert epoxides into olefins where more than one epoxy-group is present in the same molecule.

EXPERIMENTAL

All epoxides were formed by treating the appropriate olefin with *m*-chloroperbenzoic acid in methylene chloride at room temperature, and were purified by chromatography on silica gel. The purity of the epoxides was checked by g.l.c. and ^{1}H n.m.r. spectroscopy.

Conversion of Epoxides into Olefins.—In a typical experiment, methyl 9,10-epoxystearate (259 mg) was warmed with a solution of potassium selenocyanate (150 mg) in water–methanol (1 : 10; 10 ml) at 65 °C for 18 h. The precipitated selenium was filtered off and washed with methanol. The filtrate was diluted with water and extracted with ether to give methyl oleate; the aqueous solution was made just acidic (AcOH) and extracted with ether to give oleic acid, which was converted into methyl oleate with diazomethane. The total yield of methyl oleate was 245 mg.

We thank Shell Research Ltd. (M. J. W) and the S.R.C. (J. M. B.) for support.

[4/2664 *Received*, 23*rd December*, 1974]