Tetrahedron Letters No. 34, pp 3567 - 3569, 1972. Pergamon Press. Printed in Great Britain.

ADDITION OF IODINE THIOCYANATE TO OLEFINS

A NEW SYNTHESIS OF EPISULFIDES

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(Received in USA 18 May 1972; received in UK for publication 21 July 1972)

Although episulfides have been known for many years, synthetic approaches to this ring system are still somewhat limited (1). Conversion of an olefin to the corresponding epoxide followed by subsequent transformation to the episulfide represents a widely used preparative method for these compounds. However, in addition to involving extra steps, this route is unsuccessful in certain cases (e.g., cyclopentene episulfide from cyclopentene oxide with thiourea or potassium thiocyanate) (2). Furthermore, formation of episulfides *via* the epoxide route is not suitable for substrates containing easily oxidized functionality.

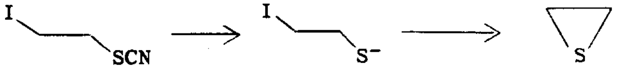
A recently reported (3) episulfide synthesis involves addition of sulfur monochloride to an olefin followed by reduction and dehydrohalogenation of the resulting mixture of chloroalkylmono-, di-, and trisulfides. Unfortunately, the method suffers from a major disadvantage in that a large excess of the alkene must be used. The procedure is therefore unsuited for expensive and/or nonvolatile olefinic starting materials.

In connection with other work, we needed a convenient procedure for converting an olefin directly to the corresponding episulfide. We have therefore examined the basic hydrolysis of ß-iodothiocyanates, obtained directly from olefins and iodine thiocyanate, as a possible new route to episulfides.

Limited spectroscopic evidence (4) suggests that solutions of equimolar amounts of iodine and thiocyanogen contain an appreciable concentration of iodine thiocyanate.

$$I_2 + (SCN)_2 \rightleftharpoons 2ISCN$$

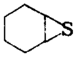
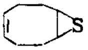
Addition of alkenes to these solutions gives the corresponding ß-iodothiocyanates (5), presumably via addition of iodine thiocyanate to the carbon-carbon double bond (6). Although the stereochemistry of the reaction was not established, it appears reasonable to assume a trans mode of addition based on analogy with the addition of other iodine pseudohalogens to olefins (7,8). It was, therefore, anticipated that treatment of the intermediate iodothiocyanates with base would result in preferential hydrolysis of the thiocyanate moiety followed by rapid ring closure to the episulfide.



This was indeed the case. Treatment of ether solutions of a number of ß-iodothiocyanates with methanolic potassium hydroxide at room temperature resulted in the formation of episulfides in acceptable yields. Some results are shown in Table I.

Table I

Conversion of Olefins to Episulfides

Olefin	Solvent[a]	Product[b]	Yield, %
Cyclopentene	ether		40
Cyclohexene	ether		57
1,5-Cyclooctadiene	ether		26
2-Cholestene	CH_2Cl_2	2ß, 3ß-Epithio-5α-cholestane	46

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[a] Ether appears to be the most generally acceptable solvent. Dichloromethane is also useful although less concentrated solutions are possible because of solubility considerations. Acetonitrile gave considerably less clean reaction mixtures.

[b] All episulfides prepared have been reported previously. The structures of the products in this work were further confirmed by NMR, IR, and mass spectroscopy.

The procedure is particularly convenient in that the intermediate iodothiocyanates need not be isolated. Consequently, the over-all conversion of olefin to episulfide can be carried out in one flask.

Note that this route gives a good yield of the difficultly accessible cyclopentene episulfide directly from the olefin.

Also the method can be selective when applied to polyolefinic starting materials, as shown by the formation of the mono-episulfide from 1,5-cyclooctadiene.

Finally, the direct conversion of 2-cholestene to the corresponding 2β, 3β-episulfide demonstrates that the method is not limited to the use of simple volatile alkene starting materials.

Unfortunately, the procedure does not appear suitable when applied to acyclic olefins. Treatment of a number of iodothiocyanates derived from noncyclic alkenes under the above conditions resulted mainly in mixtures of high boiling malodorous products with no synthetically useful amounts of episulfides being formed.

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