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DIRECT CONVERSION OF OXIRANES TO ALKENES BY CHLOROTRIMETHYLSILANE AND SODIUM IODIDE

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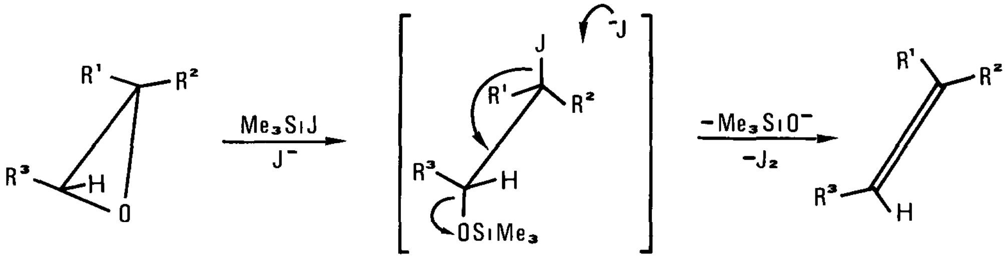
Abstract: *Smooth and quantitative conversion of oxiranes to alkenes is achieved by treatment with in situ generated iodotrimethylsilane.*

In connection with other work concerning hydroxylation of steroidal olefins, we have found that oxiranes can be very fast, smoothly and quantitatively converted to alkenes by treatment with chlorotrimethylsilane and sodium iodide in acetonitrile at room temperature. Indeed, under our experimental conditions, 2α,3α-epoxy-5α-cholestane was quantitatively converted to 5α-cholestane in only half an hour.

The reaction seems to be quite general as shown in the table were a few examples of variously substituted oxiranes are reported. Oxygen elimination is stereoselective according to the last two entries in the table in both of which only the alkene having the same configuration of the starting oxirane is formed.

As far as the reaction pathway is concerned, the conversion of oxiranes to alkenes may be confidently assumed to follow the scheme:



As a matter of fact, H.Sakurai, K.Sasaki and A.Hosomi have recently reported[1] that the reaction of *in situ* generated iodotrimethylsilane with oxiranes in benzene solution leads to quantitative formation of silylated iodohydrins. Under our experimental conditions, the subsequent elimination from the iodohydrin may be well accounted for by further attack of excess iodide ion probably owing to the better solubility of sodium iodide in acetonitrile as well as to the much higher dielectric constant of the latter in comparison with benzene.

In this view, we have therefore prepared in an independent way 2β-iodo-3α-trimethylsilyloxy-5α-cholestane by silylation of the already known[2] iodohydrin. The crude product (P.M.R. δ 3.81, Table. Conversion of oxiranes to alkenes by Me_3SiCl and sodium iodide.

Oxirane	*Time*[a]	*Yield*[b]	*Alkene*
2α,3α-Epoxy-5α-cholestane	30'	96	5α-Cholest-2-ene
4α,5α-Epoxy-cholestane	20'	95	Cholest-4-ene
4β,5β-Epoxy-cholestane	20'	95	Cholest-4-ene
5α,6α-Epoxy-cholestane	20'	97	Cholest-5-ene
2α,3α-Epoxy-3β-methyl-5α-cholestane	15'	96	3-Methyl-5α-cholest-2-ene
cis-1,2-Epoxy-4-*t*Bu-cyclohexane	20'	94	4-*t*Bu-Cyclohexene
trans-1,2-Epoxy-4-*t*Bu-cyclohexane	20'	93	4-*t*Bu-Cyclohexene
Cyclohexene oxide	30'	94	Cyclohexene
(*Z*)-2,2'-Dimethyl-3-hexene oxide	45'	92	(*Z*)-2,2'-Dimethyl-3-hexene
(*E*)-2,2'-Dimethyl-3-hexene oxide	45'	95	(*E*)-2,2'-Dimethyl-3-hexene

[a] *TLC or GLC monitored.* [b] *Yield of crystallized or distilled product. Purity* $\geq$ *95 %.*

4.43) was then directly dissolved in anhydrous acetonitrile, sodium iodide being added to the solution at r.t. (see experimental below). After few minutes the starting material was entirely consumed (TLC) and workup of the reaction mixture gave crude 5α-cholest-2-ene (after crystallization: 93% conversion referred to the starting iodohydrin), thus proving our above assumption.

A typical procedure follows. To a magnetically stirred solution of sodium iodide (3.9 mmol) in anhydrous acetonitrile (5 ml) Me_3SiCl (1.9 mmol) was added dropwise under N_2. After few minutes, to the thus obtained pale yellow suspension a solution of 2α,3α-epoxy-5α-cholestane (1.3 mmol) in anhydrous chloroform (or acetonitrile, when soluble) (1 ml) was slowly added. The stirred solution turned immediately to a red-brown colour and after 30' the reaction was complete (TLC). Usual workup - addition of 5 N aq sodium thiosulphate (20 ml), extraction with Et_2O (3 x 20 ml) and washing of the ethereal layers with water - then led to a crude crystalline product which after one crystallization from hexane had m.p. 74-75°, $|\alpha|_D$ +70° (1.8 mmol; Y. 94%).

It is worth to note how the above results suggest that our experimental conditions might be utilized to convert halohydrins directly to alkenes. Work is already in progress to check the reliability of such a procedure and results will be reported in a forthcoming paper.

REFERENCES

1. H.Sakurai, K.Sasaki and A.Hosomi, *Tetrahedron Letters*, 2329 (1980). See also Ref. 3 for the reaction of oxiranes with chlorotrimethylsilane.
2. R.C.Cookson and J.M.Coxon, *J. Chem. Soc.*, 1466 (1971).
3. O.Ceder and B.Hansson, *Acta Chem. Scand.*, B 30, 574 (1976).

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