Tetrahedron Letters Vol. 21, pp 1173 - 1174
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0040-4039/80/0315-1173$02.00/0

REACTION OF OXIRANES WITH LITHIUM: DEOXYGENATION LEADING TO OLEFINS

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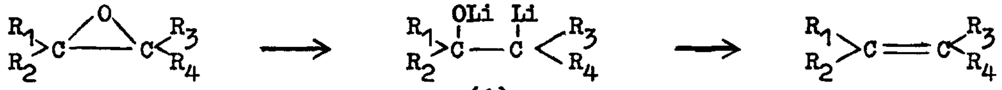
Summary: Mono-, di-, tri- and tetra-substituted epoxides undergo facile deoxygenation yielding olefins when treated with lithium in tetrahydrofuran. Aliphatic epoxides yield olefins with the same stereochemistry as the parent compound.

Apart from some stray reports[1] of reduction of epoxides to alcohols with sodium, there is surprisingly little information on the reaction of epoxides with alkali metals. We have now found that atomised lithium in ether or tetrahydrofuran causes reductive elimination of epoxides yielding olefins in excellent yields. It is interesting to note that while sodium causes reduction to the alcohol stage, lithium causes further elimination, probably due to the more covalent nature of the C-Li and O-Li bonds in the reduction product (1), leading to facile elimination of lithium oxide.



(1)

The reaction is generally carried out by refluxing a solution of the epoxide in tetrahydrofuran with 2.2 g.atom equivalent of atomised lithium; the time taken for the completion of the reaction may vary depending on the substitution. (The reaction is much slower when ether is used as solvent). Inert atmosphere may be created simply by displacing the air with solvent vapours. At the end of the reaction the solvent is removed under suction, the residue treated with cold water and the product extracted into ether. The reaction has been carried out with various substituted epoxides (both cyclic and acyclic) and found to be generally applicable. (See Table). The reaction is stereospecific as evidenced by the fact that oleyl methyl ether epoxide gave oleyl methyl ether and the corresponding <u>trans</u> isomer yielded elaidyl methyl ether. Both <u>cis</u>- and <u>trans</u>-stilbene oxides, however, yielded <u>trans</u>-stilbene and styrene oxide gave essentially polymeric products. The anomalous products from stilbene and styrene oxides are understandable in view of the known reactions of aromatic unsaturated compounds with alkali metals[2].

Table

Epoxide	Time (in hr.)	Product	% Yield (Isolated)
1-Decene oxide	20	1-Decene	97
Cyclohexene oxide	24	Cyclohexene	96
cis-Stilbene oxide	16	*trans*-Stilbene	88
trans-Stilbene oxide	16	*trans*-Stilbene	93
Oleyl methyl ether oxide	36	Oleyl methyl ether	94
Elaidyl methyl ether oxide	36	Elaidyl methyl ether	95
p-Menth-1-ene oxide	76	p-Menth-1-ene	91
Limonene oxide	82	Limonene	86
Terpinolene oxide	98	Terpinolene	75

Deoxygenation of epoxides has attracted enormous attention in recent years because of its utility in organic synthesis and structure elucidation and a variety of reagents have been discovered[3]. Many of them, however, are complex and expensive and often require drastic experimental conditions. The present discovery of a simple procedure to effect the deoxygenation should prove useful. Also, in combination with the known reaction of carbonyl compounds with *gem*-dihalides and lithium yielding epoxides[4], this method may be useful for the synthesis of olefins from carbonyl compounds.

References:

1. F. Kh. Agaev and A. L. Shabanov, Azerb.Khim.Zh.,38(1966); C.A.,**67**,63653u(1967)
2. V. Kalyanaraman and M.V.George, J.Organometal.Chem.,**47**,225(1973)
3. H. Suzuki, T. Fuchita, A. Iwasa and T. Mishina, Synthesis,905(1978) and references 1-20 cited therein.
4. G. Cainelli, N. Tangari and A.U. Ronchi, Tetrahedron,**38**,3009(1972)

(Received in UK 23 January 1980)