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Stereo- and regiocontrolled transformations of vinyloxiranes with metal halides

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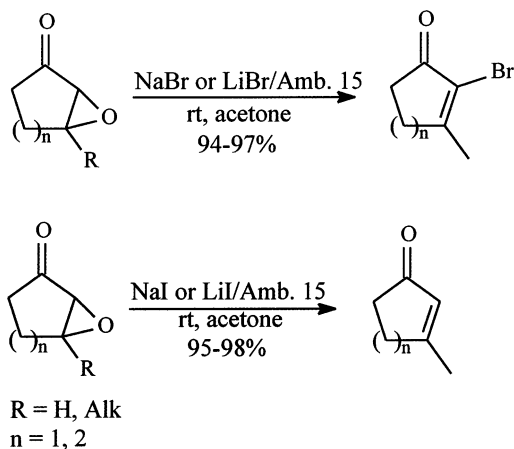
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Abstract

Simple procedures for the transformation of vinyl oxiranes to *trans*, *trans*-dienes and regio- and stereocontrolled unsaturated bromohydrins are reported. © 2000 Elsevier Science Ltd. All rights reserved.

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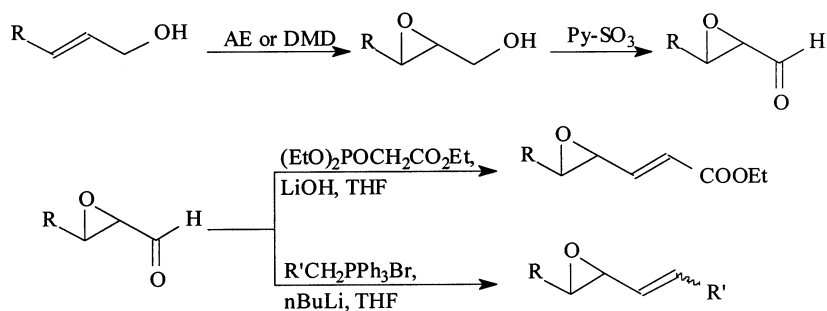
The development of synthetic methodologies to prepare highly functionalised chiral fragments represents an important challenge in organic chemistry. With this purpose, for a few years our research group has studied stereo- and regioselective ring-opening of 2-functionalised epoxides;



Scheme 1.

in fact the possibility of obtaining chiral epoxides through recently introduced methodologies allows access to optically active compounds.¹

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Scheme 2.

While 2,3-epoxy alcohols and esters reacted with metal halides, affording regiocontrolled C-2 or C-3 ring opening,² particular reactivity has been shown by α,β -epoxy ketones, which, when submitted to NaBr or LiBr/Amb. 15 reaction gave the corresponding α -halo- α,β -enones in nearly quantitative yield³ and with NaI or LiI/Amb. 15, the α,β -enones through deoxygenation⁴ (Scheme 1).

Since our hypothesis was that the driving-force for the elimination step in both cases was the restoration of the conjugated system, we decided to explore, under the same reaction conditions, the reactivity of vinyl epoxides where a C=C double bond instead of C=O was present.

Vinyl oxiranes were easily prepared from the corresponding allylic alcohols in three efficient steps: epoxidation of the double bond (by dimethyldioxirane⁵ for racemic compounds, by

Table 1
Deoxygenation of vinyl epoxides with LiI/Amb. 15^a

Vinyl epoxide	Product	Yield %
		80
		83
		78
R, R'= alkyl	Mixture of products	

^a A mixture of 1 mmol of substrate, 4 mmol of LiI and 2.5 mmol of Amb. 15 in 8 mL of acetone was stirred for ~6 h at rt and then filtered on a pad of celite. In the absence of Amb. 15, or with NaI instead of LiI, the reactions gave the starting material.

Sharpless AE⁶ for optically active epoxides), oxidation of the alcohol group and Wittig or Horner–Emmons olefination (Scheme 2).⁷

To study the reactivity of these systems we prepared substrates with various R and R' to investigate the influence of the steric hindrance of R on the oxirane ring and the electronic effects of R' on the double bond.⁸

As shown in Tables 1 and 2, while these compounds gave the deoxygenation products as already found for α,β -epoxyketones with LiI/Amb. 15, with LiBr/Amb. 15 we observed a regio- and diastereoselective opening of the epoxide to give the corresponding *trans*- α -bromo- β -hydroxy olefin derivatives.

Table 2
Ring opening of vinyl epoxides by LiBr/Amb. 15^a

Vinyl epoxide	Product	Yield %
		97
		95
		98
		60
		58
		67

^a A mixture of 1 mmol of substrate, 4 mmol of LiBr and 1 mmol of Amb. 15 (0.5 when R' = alkyl) in 8 mL of acetone was stirred for ~2 h at rt and then filtered on a pad of celite. In absence of Amb. 15 the reactions did not work; with NaBr instead of LiBr chemical yields were lower.

In the case of $R' = \text{CO}_2\text{Et}$, the reaction with LiI/Amb. 15 worked very well, affording the corresponding *trans*, *trans*-diene in high chemical yield, independently of the steric hindrance of R, while for $R' = \text{alkyl}$, a complex mixture of products was obtained.

Also the regio- and stereoselectivity of the oxirane ring opening with LiBr/Amb. 15 did not depend on the size of R (Table 2); the yield of the reaction was very high for $R' = \text{CO}_2\text{Et}$ and quite good for $R' = \text{alkyl}$. The known high reactivity of the allylic position could be responsible for the complete regioselectivity observed, particularly when an electron withdrawing substituent on the double bond makes this position more electron deficient.

In view of the importance of the products obtained, due to the possibility of substituting the halide, and to functionalise further the double bond, the method appears to be of general value. The employment of this methodology in the synthesis of polyhydroxylated chains, subunits present in many naturally occurring compounds, is currently under investigation.

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