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STEREOSPECIFIC DEOXYGENATION OF EPOXIDES WITH SODIUM(CYCLOPENTADIENYL)DICARBONYLFERRATE. INVERSION OF OLEFIN STEREOCHEMISTRY.

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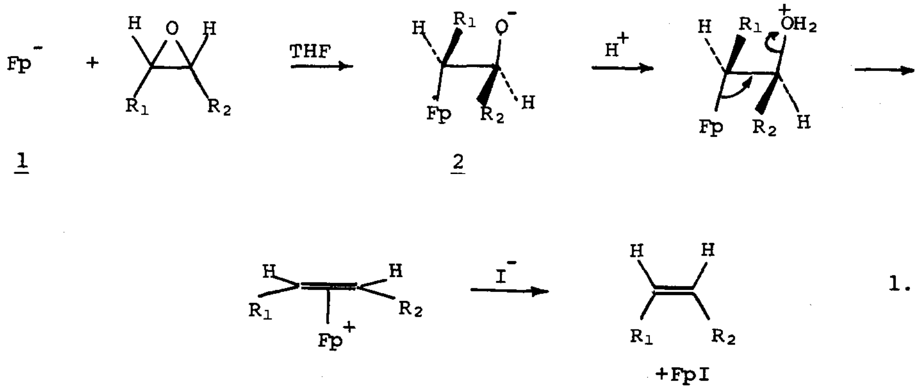
The deoxygenation of epoxides constitutes a process of importance both in structure determination[1] and in synthesis. Applications in synthesis abound, and are exemplified by sequences in which the epoxide is employed either as a protecting group[2] or as a key intermediate in the stereochemical inversion of an olefin. While several methods are available for deoxygenation of epoxides which are nonstereospecific,[3,4a] or proceed with retention of stereochemistry,[4] fewer methods exist by which such reduction may be achieved with inversion of olefin stereochemistry.[5] Moreover, such stereospecificity is often low.[5a,b,d]

We recently reported a new method for deoxygenating epoxides, using the complex anion $C_5H_5Fe(CO)_2^-$ (designated by the symbol Fp^-), which gave olefins of retained stereochemistry.[4d] This sequence, which can be effected without isolation of intermediates, is summarized by eq. 1.



1.

We now find that a simple variant of this scheme, in which the intermediate alkoxide (**2**) is thermally decomposed, yields the olefin of inverted stereochemistry (eq. 2).

2.

Decomposition may be effected either by refluxing THF solutions of **2** (method A), by removal of solvent from these solutions *in vacuo* and heating the solid briefly at 130-150° (method B), or by passing solutions of **2** through a heated tube (240°, contact time *ca*. 3 sec) (method C).

The ease and convenience of the method are illustrated by the interconversions of *cis*- and *trans*-stilbene through their epoxides. Thus, *cis*-stilbene oxide was treated with a molar equivalent of NaFp in THF at room temperature for 16 hr. The resulting dark green solution was then refluxed for 1 hr. Solvent was removed, and the residue, after chromatography on alumina, gave *trans*-stilbene in 96% yield. No *cis*-stilbene was detectable on glc analysis. (5% Se-30)

Similarly, *trans*-stilbene oxide in THF was allowed to react with **1** at room temperature for 6 hr. Solvent was removed *in vacuo*, and the residue was first heated at 130° for 15 min in a nitrogen atmosphere and then extracted with Skelly-B. Purification of the product by chromatography on alumina gave 92% of stilbene, shown by glc analysis to be 94% *cis*- and 6% *trans*-stilbene. For volatile olefins, the alkoxide (**2**) was heated *in vacuo* and the olefin was allowed to continuously distill.

Results obtained with several other epoxides are summarized in the Table.

The detailed mechanism of the decomposition reaction has not been established, but must involve a *cis*-elimination, since epoxide opening by **1** has been shown to occur with inversion.[4d] The elimination step is reminiscent of the thermal decomposition of betaines derived from β-hydroxy phosphonium salts,[5a,c,6] and may proceed either by direct attack of the oxygen anion at the metal center or through initial addition to a carbonyl ligand.[7]

The reaction sequence appears to be particularly well suited to diaryl and dialkyl epoxides, and is not complicated by the presence of an olefinic group in the substrate. It is less effective with α,β-epoxy carbonyl compounds. *Cis*-olefins derived from these substances would be expected to be especially sensitive to base catalyzed isomerization. Although 1 itself does not catalyze this change, the alkoxide (2) or its decomposition products may be responsible. Attempts to overcome this difficulty by continuously distilling the olefin *in vacuo* (method B) or by employing a flow method (method C) led to an appreciably higher proportion of *cis*-ester from ethyl cinnamate epoxide, but the increase in *cis*-isomer from ethyl crotonate epoxide was smaller (Table). The importance of rapidly removing product olefin from organometallic decomposition products is suggested by results with the lower boiling 3-pentene-2-one epoxide, which gave a relatively high yield of *cis*-isomer.

Further variants and applications of this sequence are being examined.

Table I

Deoxygenation of Epoxides with $C_5H_5Fe(CO)_2^-$

Epoxide	Method	Olefin Yield[a]	Stereochemistry	
		(%)	*cis* (%)	*trans*
cis-stilbene	A	96	< 1	> 99
trans-stilbene	B	92	94	6
cis-2-butene	B	86	< 1	> 99
trans-2-butene	B	69	99	1
cis-2-pentene	B	61	< 1	> 99
trans-2-pentene	B	63	> 99	< 1
trans,trans-2,4-hexadiene (monoepoxide)	B	62	94 (c,t)	6 (t,t)
trans,trans-2,4-hexadiene (diepoxide)	B	51	45 (c,c) 48 (c,t)	7 (t,t)
trans-3-pentene-2-one[b]	B	54	85[c]	15[c]
trans-ethyl crotonate	A	--	52	48
	B	93	53	47
	B[d]	81	61	39
	C	76	57	43
trans-ethyl cinnamate	B	61	21	79
	C	53	37	53

[a] based on epoxide [b] 72% *trans*, 28% *cis* [c] values corrected for presence of *cis*-pentenone epoxide [d] alcohol was isolated by quenching 2 with water, purified by chromatography, and then reconverted to 2 with NaH.

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