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DEOXYGENATION OF EPOXIDES TO OLEFINS WITH $FeCl_3$ — n-BuLi SYSTEM

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Deoxygenation reaction of epoxides with iron(III) chloride-n-butyllithium system gave olefins in high yields under mild reaction conditions.

Deoxygenation reaction of epoxides to olefins has applicabilities to some extent to synthetic chemistry. Cornforth et al. reported a general stereoselective synthesis of olefins via epoxides as intermediates.1) Several steroids were prepared by the reductive elimination of α,β-epoxy ketones.2) As the reagents for transformation of epoxides to olefins, trivalent phosphorus compounds have been often employed.3) For metallic reagents, chromium(II) salts and complexes were used by Julian et al.2) and Kochi et al.4) for the deoxygenation of several epoxides. Zinc-copper couple in ethanol was also used successfully for the same reductive process by Kupchan and Maruyama.5) Sharpless et al. have reported the deoxygenation reaction of carbonyl compounds and epoxides using lower valent tungsten halides.6) We wish to report here a new deoxygenation method of epoxides to olefins by means of iron(III) chloride-n-butyllithium system, which has advantages in the availability of reagents and the mildness of reaction conditions.

We have already reported the deoxygenation reaction of thiolsulfonate esters to disulfides with reduced iron.7) To extend the scope of the deoxygenation process utilizing the strong affinity of iron to oxygen, we applied the reaction to epoxides. However, the heating of cyclohexene oxide with reduced iron at 150-200°C under several reaction conditions gave unfortunately only 13% of the maximum yield of cyclohexene, although a large portion of the epoxides had been consumed. To attain more effective and milder reaction conditions, we focussed our attention on "soluble iron" species, which was prepared by the addition of n-butyllithium into a solution of iron(III) chloride in tetrahydrofuran. The resultant black solution of iron was found to reduce styrene oxide smoothly to give styrene at room temperature. The ratio of iron(III) chloride to n-butyllithium seriously affected the course of the reaction. The use of two or three equimolar of n-butyllithium toward iron(III) chloride gave a good result, and the preferable ratio of iron(III) chloride toward the epoxide for the formation of the olefin was found to be 3:1. n-Hexane, which was inevitably contained in the reaction mixture as the solvent of n-butyllithium, decreases the deoxygenation ability. The deoxygenation reaction was most advantageously carried out by the removal of the solvent from the reaction mixture of iron(III) chloride and n-butyllithium, followed by the addition of small amount of tetrahydrofuran. The suppression of the side-reaction giving polymeric substances was achieved by the slow addition of the epoxide to the reaction mixture of iron(III) chloride and n-butyllithium. This resulted in a formation of styrene in a high yield of 78%. Various types of epoxides are found to be deoxygenated by this new process, as shown in the Table.

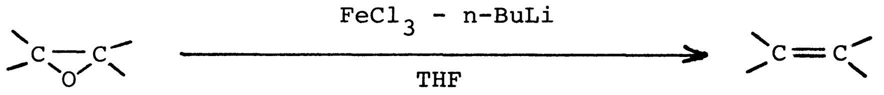


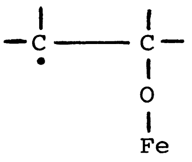
Table Deoxygenation of Epoxides[a]

Epoxide	Reaction		Yield of Olefin(%)[b]
	Temp.(°C)	Time(hr)	
Styrene oxide	r.t.	1	78
β-Methylstyrene oxide	reflux	1	92
trans-Stilbene oxide	reflux	5	81[c]
cis-Stilbene oxide	r.t.	2	86[d]
Indene oxide	r.t.	1.5	84
Cyclohexene oxide	reflux	3	85
1-Octene oxide	reflux	4	57

[a] n-Butyllithium (12 mmol), and iron(III) chloride (6 mg-equivalent) were used for epoxide (2 mmol) in tetrahydrofuran (5 ml) as solvent. [b] Yields were determined by glpc. [c] trans/cis = 94:6 [d] trans/cis = 89:11

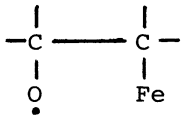
While styrene oxide is deoxygenated at room temperature, β-methylstyrene oxide required refluxing in tetrahydrofuran solution to form β-methylstyrene in a high yield, and further, it is necessary to heat longer time in the case of trans-stilbene oxide. These facts indicate that the steric hindrances may have an important effect on the reactivities of epoxides. The delocalization energy of resultant double bond in the formed olefin also accelerates the reaction, as is obvious when one compares the reactivities of aromatic epoxides with these of aliphatic ones.

As shown in the Table, trans-stilbene oxide and cis-stilbene oxide formed trans- and cis-stilbenes in the ratio of 94:6 and 89:11, respectively. It seems that cis-stilbene oxide does not isomerize to the trans-isomer under the reaction conditions, because the reaction rate of the former is extremely faster than that of the latter. A control expriment revealed that no isomerization of cis-stilbene to the trans-isomer had been occurred under the reaction conditions. Accordingly, the formation of trans-stilbene from cis-stilbene oxide indicates that the reaction proceeds by a stepwise mechanism. Although it is not clear what kind of lower valent iron species are formed in these reactions, essentially two intermediates can be supposed, on the analogy of similar reactions using other metallic reagents.[4), 5)] It is possible to consider that a low valent iron species attacks at oxygen or carbon to generate either of two isomeric radicals, I or II, respectively. The much greater reactivity of styrene oxide compared to cyclohexene oxide or octene oxide is considered due to the stabilization of the intermediate radicals. The C-centered radical I should be much more susceptible to stabilization by a phenyl group on the α-carbon than the O-centered radical II. The strong affinity of iron to the oxygen atom may also favour the formation of the radical I. Thus the radical I is preferred as the reaction intermediate.



I

or



II

The typical experimental procedure is as follows. To a solution of iron(III) chloride (0.97 g, 6 mg-equivalent) in tetrahydrofuran (12 ml) was added a solution of n-butyllithium in n-hexane (7.1 ml, 12 mmol) stirring at -78°C under an atmosphere of argon. The reaction mixture was allowed to warm to room temperature, the solvent was removed in vacuo, and argon gas was again introduced. After the addition of tetrahydrofuran (5 ml), styrene oxide (2 mmol, in 5 ml of tetrahydrofuran) was added dropwise at room temperature. The reaction mixture was stirred for 1 hr and then treated with 2N aqueous solution of sodium hydroxide. Formed styrene was extracted with ether and dried over anhydrous magnesium sulfate. The yield was determined by glpc.

This method of deoxygenation of epoxides using iron(III) chloride-n-butyllithium system has advantages of high yield of olefins under mild reaction conditions, and of availabilities of iron compound used as reducing reagent.

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