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A NOVEL SYNTHESIS OF EPOXIDES AND ALLYLIC ALCOHOLS FROM CARBONYL COMPOUNDS THROUGH α,β-EPOXY SULFOXIDES[1]

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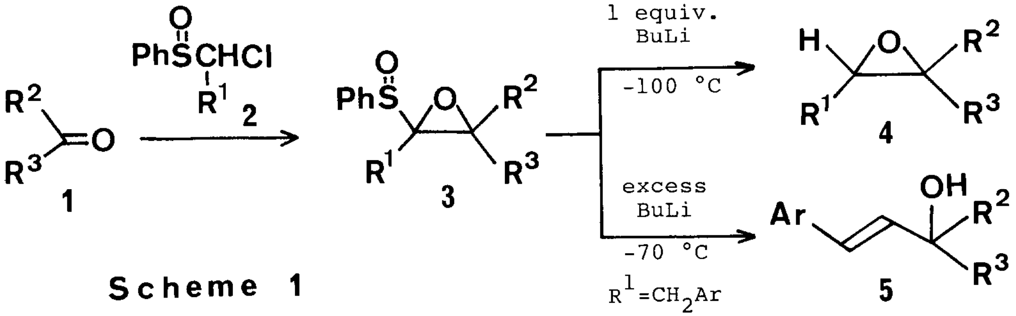
Summary Treatment of α,β-epoxy sulfoxides, easily prepared from carbonyl compounds with 1 equivalent of n-butyllithium at -100 °C gave the desulfinated epoxides in good yields. The similar α,β-epoxy sulfoxides having arylmethyl group at α-position, on treatment with excess n-butyllithium at -70 °C afforded 3-aryl allylic alcohols.

Epoxides are very important compounds in organic synthesis. The preparation of epoxides are usually classified into two categories. One is the oxidation of double bond with peracids, peroxides[2] or with NBS in the presence of excess water followed by treatment with alkaline.[3] The other is from ketones via the Darzens type condensation[4] including sulfur ylides[5] or arsonium ylides.[6]

α,β-Epoxy sulfoxides (3) are very easily prepared in high yields from carbonyl compounds (1) and 1-chloroalkyl phenyl sulfoxides (2) by the Darzens type condensation.[7] We have reported that the β-carbon of α,β-epoxy sulfoxides (3) is highly reactive toward nucleophiles such as selenolates, thiolates, and amines giving dialkyl ketones,[8a,c] α-sulfenylated ketones,[8a,d] and α-amino ketones,[8b] respectively, in good yields. In the course of the studies for the new synthetic methods through α,β-epoxy sulfoxides here we report a novel and efficient synthesis of epoxides and allylic alcohols from

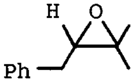
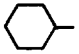
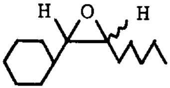
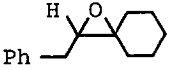
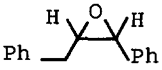
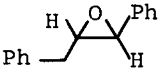
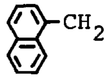
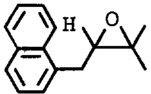
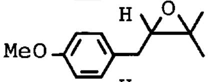
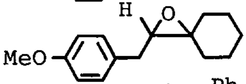
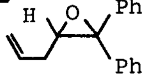
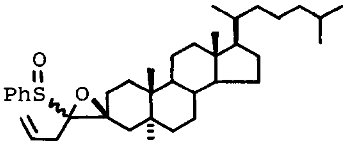
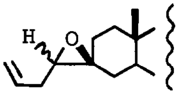
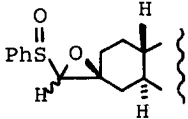
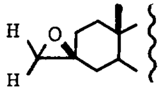


Scheme 1

ketones through α,β-epoxy sulfoxides on treatment with n-butyllithium (BuLi) as shown in Scheme 1.

It has already been reported that the treatment of sulfoxides with alkylmetal takes place carbon-sulfur bond cleavage.[9] Actually when the α,β-epoxy sulfoxide (3a) was treated with 1 equivalent of BuLi in THF at -70 °C, 3a disappeared within 1 min to afford the epoxide (4a) in 89% yield. It is worth-

Table 1. Preparation of Epoxides from α,β-Epoxy Sulfoxides

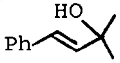
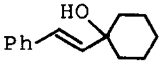
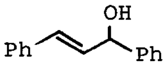
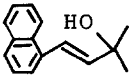
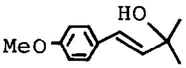
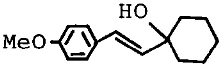
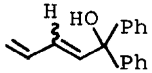
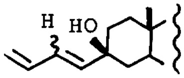
Epoxy sulfoxides (3) R^1	R^2	R^3		Temp. (°C)	Epoxide (4)		Yield[a)] %
$CH_3(CH_2)_5$	—$(CH_2)_5$—		(3a)	-70		(4a)	89
$PhCH_2$	CH_3	CH_3	(3b)	-100		(4b)	71
	$CH_3(CH_2)_5$ or H		(3c-L) (3c-P)	-70 -70		(4c-L) (4c-P)	86 97
$PhCH_2$	—$(CH_2)_5$—		(3d)	-100		(4d)	65(91)
$PhCH_2$	H	Ph	(3e-L)	-100		(4e-L)	79
$PhCH_2$	Ph	H	(3e-P)	-100		(4e-P)	90
	CH_3	CH_3	(3f)	-100		(4f)	49(62)
	CH_3	CH_3	(3g)	-100		(4g)	69
	—$(CH_2)_5$—		(3h)	-100		(4h)	78
CH_2=CH-CH_2	Ph	Ph	(3i)	-100		(4i)	85
			(3j)	-100		(4j)	83
			(3k)	-100		(4k)	27

a) Isolated yields after silica gel column chromatography. The yields in parenthesis are calculated from consumed starting material.

while noting that in this case the cleavage was not the bond of S-Ph but S-CO. Of the alkylmetal examined (MeLi, BuLi, ^{t}BuLi, EtMgBr) BuLi was the most effective in this reaction. On the other hand, the treatment of 3b with 1 equiv. of BuLi at -70 °C gave the epoxide (4b) and the allylic alcohol (5b) in 25% and 62% yields, respectively, along with reasonable amount of phenyl butyl sulfoxide. This result indicated that the epoxide (4) having acidic hydrogens in its α-position of the substituents should be apt to be isomerized into an allylic alcohol by bases. On the basis of this consideration this reaction was carried out at -100 °C for 5 min. In this reaction 71% of the desired epoxide (4b) was isolated and almost no allylic alcohol was observed. Representative results of the treatment of α,β-epoxy sulfoxides with 1 equivalent of BuLi are listed in Table 1. As shown in Table 1, quite good results were obtained except from 3k. As E- and Z-epoxy sulfoxides (3e-L) and (3e-P) gave Z- and E-epoxides (4e-L) and (4e-P),[10] respectively, without any contamination of their isomers this reaction is stereospecific.

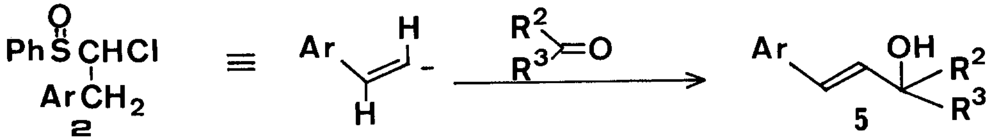
To get the allylic alcohols (5), excess BuLi (3-5 equivalents) and higher temperature (-70 °C) was used in this reaction and the results are summarized

Table 2. Preparation of Allylic Alcohols from α,β-Epoxy Sulfoxides

Epoxy sulfoxides (3)	BuLi (eq)	Allylic Alcohol (5)		Yield a) %
3b	3		(5b)	76
3d	3		(5d)	87
3e-L	3		(5e)	16
3e-P	3	5e		58
3f	3		(5f)	69
3g	3		(5g)	72
3h	3		(5h)	71
3i	5		(5i)	85
3j	3		(5j)	68

a) Isolated yields after silica gel column chromatography.

in Table 2. All α,β-epoxy sulfoxides having arylmethyl group (including allyl group) at α position afforded 3-aryl allylic alcohols (5) in good yield except the result from 3e-L. In this reaction when R^1 was simple alkyl group no allylic alcohol was obtained. It is worthy of note that in this reaction 1-chloroalkyl phenyl sulfoxides (2; R^1=CH_2Ar) acted as β-arylvinyl carbanion equivalent.



We are currently studying the scope and mechanistic aspects of these reactions.

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