Ready Nucleophilic Ring Opening of β-Epoxy-sulphone, -sulphoxide, and -ester with Grignard Reagents

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Treatment of β-epoxy-sulphone, -sulphoxide, and -ester with Grignard reagents and copper(I) iodide in diethyl ether–tetrahydrofuran at low temperature leads to rapid ring opening without loss of chirality.

Organometallic compounds such as organocuprates are useful reagents for nucleophilic ring opening of epoxides,[1—3] and the treatment of epoxides containing a carbonyl group at the α-position with organocuprates results in nucleophilic ring opening.[4] However, the epoxides (**1**) containing an electron-withdrawing group Z at the β-position are known to be labile even under mildly basic conditions and to undergo eliminative ring fission giving the allyl alcohols (**2**).[5,6] Here we report the rapid nucleophilic ring opening reactions of (**1**) using Grignard reagents (**3**) and CuI.

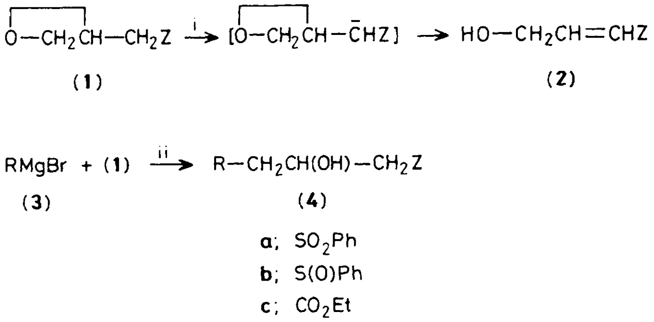
Table 1. Reaction of epoxides (**1**) with Grignard reagents (**3**) and CuI in Et_2O–THF.[a]

(**1**)	(**3**); R	% Yield of (**4**)
(**1a**)	Me	88
(**1a**)	$[CH_2]_6Me$	83 (67[b])
(**1a**)	$[CH_2]_{11}Me$	72 (34[b])
(**1a**)	$[CH_2]_2Ph$	80
(**1a**)	Ph	95
(**1a**)	Pr^i	50
(**1b**)	$[CH_2]_6Me$	80
(**1b**)	$[CH_2]_2Ph$	72
(**1c**)	$[CH_2]_6Me$	57
(**1c**)	$[CH_2]_2Ph$	62
(**1c**)	Ph	91

[a] v/v 1 : 1. [b] THF solvent.

To CuI (1.5 equiv.) in Et_2O a solution of (**3**) (1.5 equiv.) in tetrahydrofuran (THF) was added under argon at −60 °C, followed by a solution of (**1**) in Et_2O–THF (v/v 1 : 1). The reaction was completed in 1 min. After quenching with aqueous NH_4Cl and the usual work-up, column chromatography on silica gel gave the alcohols (**4**), as shown in Table 1. Optically pure (*S*)-(**1a**) [100% enantiomeric excess (e.e.)] was prepared by the stereoselective reduction of 1-chloro-3-phenylsulphonylacetone with baker's yeast[7] and subsequent ring closure with silver oxide.[8] Similar treatment of (*S*)-(**1a**) with heptylmagnesium bromide and CuI afforded (*S*)-1-phenylsulphonyldecan-2-ol (100% e.e.) in 83% yield.

The reaction in THF was accompanied by the formation of (**2**) because of eliminative ring fission, while the experiment using Et_2O was restricted by the insoluble character of the



Scheme 1. *Reagents:* i, base; ii, CuI, Et_2O–THF, −60 °C.

reagents. When the reaction was carried out at room temperature, (**2**) was obtained quantitatively. These findings suggest that the co-ordination of the metal to the oxygen atom at the epoxy group may play an important role in the formation of (**4**).[9] It is interesting to note that the selectivity between these two rapid reactions shown in Scheme 1 can easily be achieved by changes in experimental conditions.

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