

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.

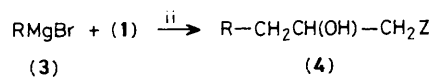
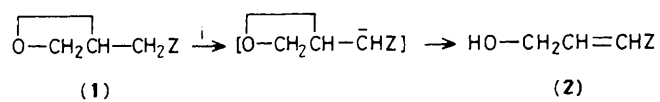
To CuI (1.5 equiv.) in Et₂O a solution of (3) (1.5 equiv.) in tetrahydrofuran (THF) was added under argon at -60 °C, followed by a solution of (1) in Et₂O-THF (v/v 1:1). The reaction was completed in 1 min. After quenching with aqueous NH₄Cl and the usual work-up, column chromatography on silica gel 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 yeast⁷ 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 Et₂O was restricted by the insoluble character of the

Table 1. Reaction of epoxides (1) with Grignard reagents (3) and CuI in Et₂O-THF.^a

(1)	(3); R	% Yield of (4)
(1a)	Me	88
(1a)	[CH ₂] ₆ Me	83 (67 ^b)
(1a)	[CH ₂] ₁₁ Me	72 (34 ^b)
(1a)	[CH ₂] ₂ Ph	80
(1a)	Ph	95
(1a)	Pr ⁱ	50
(1b)	[CH ₂] ₆ Me	80
(1b)	[CH ₂] ₂ Ph	72
(1c)	[CH ₂] ₆ Me	57
(1c)	[CH ₂] ₂ Ph	62
(1c)	Ph	91

^a v/v 1:1. ^b THF solvent.



- a; SO₂Ph
 b; S(O)Ph
 c; CO₂Et

Scheme 1. Reagents: i, base; ii, CuI, Et₂O-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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