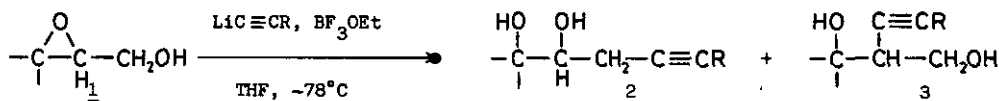


A NOVEL ALKYNYLATION REACTION OF EPOXYALCOHOLS

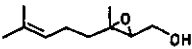
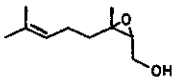
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The ring opening reaction of the epoxyalcohols (1) with various nucleophiles was actively investigated by many authors to afford 1,2- and/or 1,3-diols. Previously, we have reported an efficient method for the synthesis of β -hydroxy-acetylenes by the reaction of lithium acetylides with oxiranes in the presence of a Lewis acid. (M. Yamaguchi and I. Hirao, *Tetrahedron Lett.*, 24, 391 (1983).) We then applied the method to the epoxyalcohols (1) and found a new type of the ring opening product. Thus, lithium acetylides were treated with 1 followed by boron trifluoride etherate at -78°C in tetrahydrofuran to give novel 1,2-diols (2) as well as 1,3-diols (3). The former (2) was considered to be formed by the rearrangement of 1 followed by the ring cleavage at the less hindered site, while the latter by the direct substitution reaction at 2-carbon of 1 (Scheme).



It was also observed that trans-epoxides afforded 2 as the major product and cis-epoxides gave 3 predominantly (Table). All these products are stereochemically pure and the reaction seems to proceed in a highly stereospecific manner.

OXIRANE	ACETYLENE	PRODUCT RATIO <u>2</u> : <u>3</u>	TOTAL YIELD (%)
	PhC $\equiv$ CH	55 : 45	94
	n-AmC $\equiv$ CH	80 : 20	87
	PhC $\equiv$ CH	14 : 86	77
	n-AmC $\equiv$ CH	50 : 50	quant.
	PhC $\equiv$ CH	72 : 28	77
	n-AmC $\equiv$ CH	81 : 19	81
	PhC $\equiv$ CH	42 : 58	82