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Highly Regioselective Addition of Allylstannanes to Vinyl Epoxides by Lewis Acid Mediation[#]

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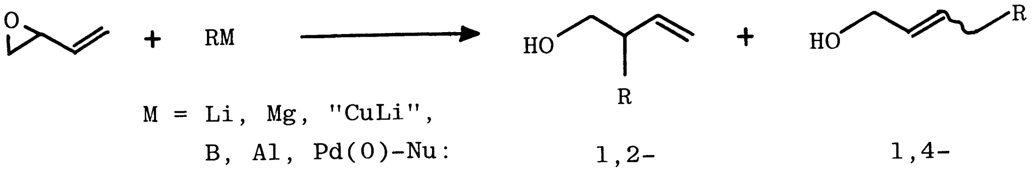
In the presence of $BF_3 \cdot OEt_2$, reaction of allylstannanes with vinyl epoxides gives 1,2 or 1,4 addition products in good yield, depending on the substitution at the olefinic terminus. In either case regioselectivity is extremely high. The 1,2 adduct is applied to the elongation of a prenyl unit in polyprenyl compounds.

Vinyl epoxide is considered to be a substrate of versatile utilities, and nucleophilic addition of organometallic compounds to the substrate gives the products by 1,2 and/or 1,4 attack, depending on the applied reagent, M=Li,[1a,b,d,f] Mg,[1c,d] "CuLi",[1d-n] B,[1o] Al,[1p] Pd(0)-Nu.[1q,r] Selective 1,4 addition was reported with use of copper reagents,[1d-m] while general method providing 1,2 addition product in high selectivity has not been developed except for one special example.[1a] We report herein a successful 1,2 or 1,4 addition of allylstannanes to vinyl epoxides in the presence of $BF_3 \cdot OEt_2$ in high regioselectivity. This method was also applied to elongation of one prenyl unit in the synthesis of polyprenyl alcohols.



The reaction of allylmagnesium bromide with or without copper salt afforded preferentially 1,4 adduct in moderate selectivity (Table 1). However, allylsilane and allylstannane exclusively gave the 1,2 adduct in the presence of Lewis acid. For optimization of the reaction conditions we examined this allylation reaction in the presence of various Lewis acid (Table 1). The reaction was done as follows: to a CH_2Cl_2 solution of vinyl epoxide and allylmetal (1.2 equiv. to the epoxide), Lewis acid (1.1 equiv. to the epoxide) was added at -78 °C and after 0.5 h aqueous workup afforded the crude alcohol, which was purified by column chromatography on silica gel. In every reaction except for the use of Bu_2BOTf, only 1,2 adduct **2** was obtained and allylstannane-$BF_3 \cdot OEt_2$ system showed the highest yield (91% by GLC). In comparison with the low regioselectivity in Friedel-Crafts reaction of vinyl epoxide to aromatic compound,[2] the obtained high yield and high regioselectivity is remarkable.

Under the same reaction conditions, addition reaction between various vinyl

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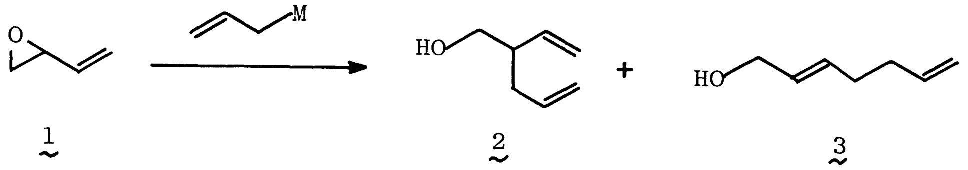
[#] This paper is dedicated to the late Professor Ryozo Goto, Kyoto University.

Table 1. Effect of Lewis Acid on the Allylation of Butadiene Monoxide[a)]



M	Lewis acid	Yield[b)] 2	Yield[b)] 3	M	Lewis acid	Yield[b)] 2	Yield[b)] 3
MgBr[c)]	-	30	70	MgBr(CuI)[c)]	-	19	82
$SiMe_3$	$BF_3 \cdot OEt_2$	0	0	$SnMe_3$	$BF_3 \cdot OEt_2$	91(80)	0
	$AlCl_3$	5	0		$AlCl_3$	52	0
	$TiCl_4$	14	0		$TiCl_4$	14	0
	$SnCl_4$	31	0		$SnCl_4$	0	0
	Bu_2BOTf	21	8		Bu_2BOTf	9	14

a) All reactions except for Grignard reagent were performed according to the method described in the text. b) Yield in parentheses is of isolated product, and others are estimated by GLC. c) Reaction was performed in Et_2O at -78 °C.

epoxides and allylstannanes was examined (Table 2). In the reaction with the simple vinyl epoxide, the 1,2 adducts caused by the α attack were exclusively obtained. However, when the olefinic terminus of the vinyl epoxide was substituted either by dimethyl or by phenyl group(s), this reaction lead to the selective formation of the corresponding 1,4 adduct (the γ adduct) in good yield. Thus, the regioselectivity conserning the vinyl epoxides intensively depends on the substitution on the olefinic terminus. These results together with the γ selectivity concerning to the allylstannanes suggest that this reaction includes the nucleophilic addition of the stannyl reagent to the position most capable of stabilizing incipient positive character in the epoxide. The reaction with 3,4-epoxycyclohexene exclusively afforded the corresponding trans-1,2 adduct without formation of the expected 1,4 adduct. This outcome also supports the formation of the BF_3-coordinated intermediate such as 4 .

We applied this methodology to elongation of a prenyl unit. Cope rearrangement[4)] of the adduct (5) at 190-195 °C in the presence of 0.3 equiv. of DBU under argon for 2 h, gave geraniol (6) in quantitative yield (E/Z=58/42). Similarly, the adduct derived from geranyltrimethylstannane gave a mixture of four stereoisomeric farnesols (7) in high yield. This method provids a new route to the synthesis of polyprenyl alcohols.

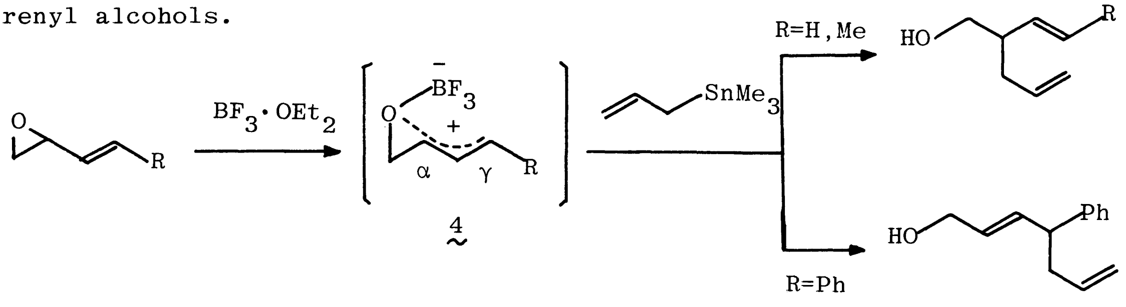
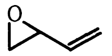
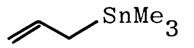
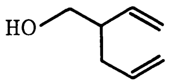
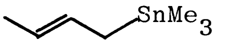
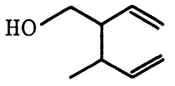
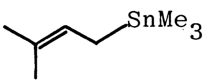
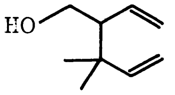
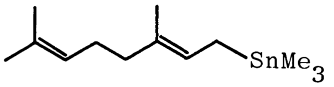
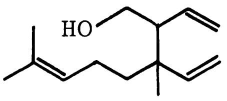
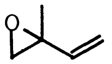
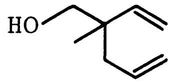
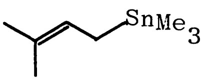
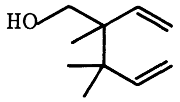
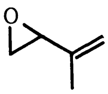
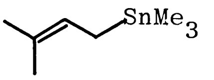
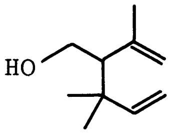
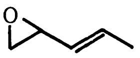
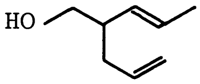
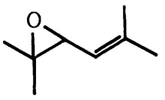
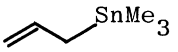
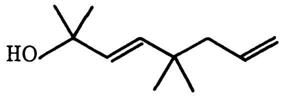
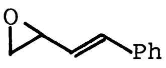
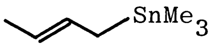
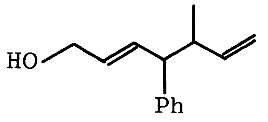
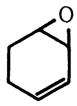
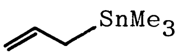
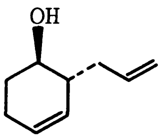
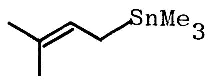
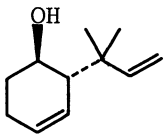
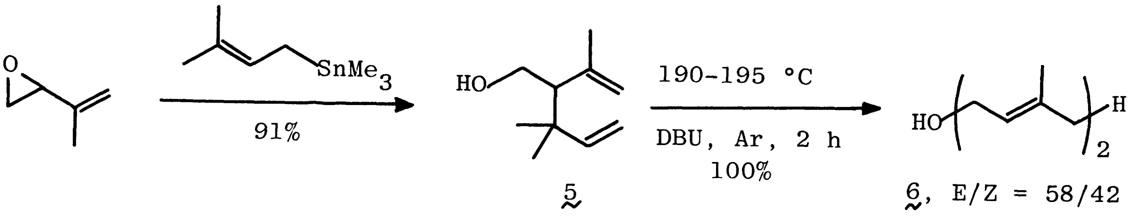
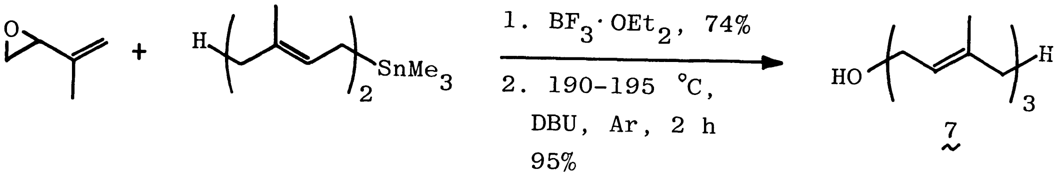


Table 2. Regioselective Allylation of Vinyl Epoxides[a]

Vinyl epoxide	Allylstannane	Product	Yield/%[b]
			91(80)
			(77)[c]
			(98)
			80(79)[c]
			92(40)
			(40)
			(91)
			(81)
			(63)
			(65)[c,d]
			(55)[e]
			(82)[e]

a) All reactions were performed in 3.0 mmol scale according to the method shown in the text. b) Yield in parentheses is of isolated product by column chromatography, and others are evaluated by GLC. c) Erythro:threo = 1:1. d) Only a trace amount of 1,2 adduct was detected by ^{1}H-NMR. e) 100% trans, for the determination of the stereochemistry, see Ref. 3.





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1) a) G.Stork, C.Kowalski, and G.Garcia, J. Am. Chem. Soc., 97, 3258 (1975); b) M.Tamura and G.Suzukamo, Tetrahedron Lett., 22, 577 (1981); c) R.J.Anderson, J. Am. Chem. Soc., 92, 4978 (1970); d) R.W.Herr and C.R.Johnson, ibid., 92, 4978 (1970); e) J.Staroscik and B.Rickborn, ibid., 93, 3046 (1971); f) D.M.Wieland and C.R.Johnson, ibid., 93, 3047 (1971); g) C.Cahiez, A.Alexakis, and J.F. Normant, Synthesis, 1978, 528; h) A.Alexakis, G.Cahiez, and J.F.Normant, Tetrahedron Lett., 1978, 2027; i) F.E.Ziegler and M.A.Cady, J. Org. Chem., 46, 122 (1981); j) M.F.Schlecht, J. Chem. Soc., Chem. Commun., 1982, 1331; k) J.P. Marino and D.M.Floyd, Tetrahedron Lett., 1979, 675; l) J.P.Marino, and H. Hatanaka, J. Org. Chem., 44, 4467 (1979); m) P.M.Savu and J.A.Kazenellenbogen, ibid., 46, 239 (1981); n) D.L.J.Clive, V.Farina, and P.L.Beaulieu, ibid., 47, 2572 (1982); o) A.Suzuki, N.Miyaura, M.Itoh, H.C.Brown, G.W.Holland, E. Negishi, J. Am. Chem. Soc., 93, 2792 (1971); p) L.E.Overman and L.A.Flippin, Tetrahedron Lett., 22, 195 (1981); q) J.Tsuji, H.Kataoka, and Y.Kobayshi, ibid., 22, 2575 (1981); r) B.M.Trost and G.A.Molander, J. Am. Chem. Soc., 103, 5969 (1981).

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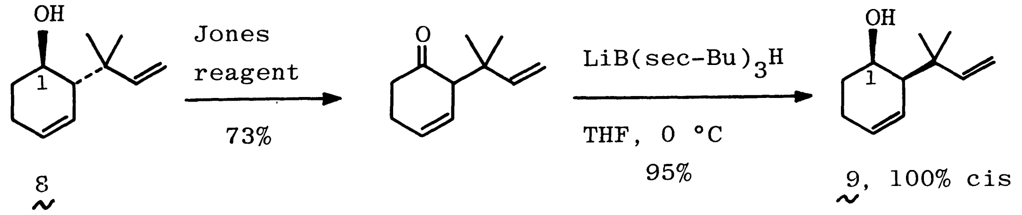
3) Trans stereochemistry of the adduct (8) was determined by comparison of the spectroscopic and GLC data of the product 8 with the corresponding cis isomer (9) derived from 8 according to the following scheme. In ^{1}H-NMR spectra, H^1 of 9 showed the signal at δ 3.70(J=3, 3, 7 Hz), compared with that of 8, δ 4.15 (br). 8 and 9 showed different retention time on GLC analysis. The allyl adduct was also assigned to be the trans isomer from ^{1}H-NMR.



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