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ALLYLATION REACTIONS BY USING ALLYLSTANNANES IN THE PRESENCE OF A LEWIS ACID

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Allylations of various carbon electrophiles such as carbonyl compounds, acetals, and α,β -enones with allylstannanes promoted by bis(diethyl-aluminum)sulfate or boron trifluoride etherate are described. Merits and demerits of using allylstannanes in syntheses instead of allyl-silanes are also discussed.

In the past several years, we have demonstrated synthetically useful reactions of allylsilanes with a variety of electrophiles promoted by Lewis acids.¹⁾ A general pattern of the reaction can be expressed as:

$$R_{3}^{Si-CR^{1}R^{2}CR^{3}=CR^{4}R^{5} + E-N} \xrightarrow{Lewis acid} R_{3}^{Si-N} + R^{1}R^{2}C=CR^{3}CR^{4}R^{5}-E$$
(1)

Regiospecific allylation, with concomitant rearrangement in the allylic part, is characteristic in the reaction and synthetic applications of allylsilanes along this line attract much attention and are successfully established.²⁾ Regiospecific syntheses of alkyl-substituted allylsilanes such as α, α -dimethylallylsilanes^{1c)} and carbon-functionalized allylsilanes^{1e,f)} have also expanded the scope of the reaction.

The high reactivity and regiospecificity of the reaction can be explained in terms of extensive $\sigma(\text{Si-C})-\pi$ conjugation in allylsilanes.³⁾ Since the $\sigma-\pi$ conjugation exists in allylgermanes and allylstannanes,^{4,5)} allyl transfer reactions may be expected for both allylgermanes and allylstannanes. Moreover, it is reasonably expected that allylstannanes should have more nucleophilic double bond than that of allylsilanes,⁴⁾ because allylstannanes reveal lower first ionization potential than that of the corresponding allylsilanes.⁵⁾ We report here the reaction of allylstannanes which turns out to be a useful reaction of introducing an allyl group into electrophilic carbons.⁶⁾

Like allylsilanes, allylations with allylstannanes (1) proceed very smoothly toward various electrophilic species such as carbonyl compounds, α , β -enones and acetals activated by bis(diethylaluminum)sulfate or boron trifluoride etherate as a Lewis acid to give the corresponding allylated products (2). (eq. 2) The representative results are listed in Table 1.

$$Me_{3}SnCH_{2}CR^{1}C=CR^{2}_{2} + E-N \xrightarrow{\text{Lewis acid}} CH_{2}=CR^{1}-CR^{2}_{2}-E + Me_{3}Sn-Nu \quad (2)$$

$$la, R^{1}=R^{2}=H$$

$$b, R^{1}=viny1; R^{2}=H$$

$$c, R^{1}=H; R^{2}=CH_{2}$$

$$(2)$$

Bis(diethylaluminum)sulfate is quite useful as a Lewis acid for the purpose of activating the electrophilic substrates especially having a carbon-oxygen bond. The reagent is prosperous in that it minimizes side reactions such as polymerization.⁷⁾

The following experimental procedure is typical. To a mixture of an electrophile (1 mmol), an allylstannane (1) (ca. 2 mmol) in benzene (2 ml), a hexane solution (0.5 M) of bis(diethylaluminum)sulfate (2 ml, 1.0 mmol) was added by a syringe. The resulting mixture was stirred at reflux under conditions shown in the Table and then hydrolyzed. After usual work-up, the corresponding allylated product was isolated by the preparative tlc or glc.

The reaction patterns of allylstannanes are the same to those observed for allylsilanes. Homoallyl alcohols are obtained in good yields. Regiospecific allyl transposition is also observed (run 7) and conjugate addition occurs for α,β -enones (runs 8 and 9). The high reactivity of allylstannanes can permit other types of allylation than the Lewis acid catalyzed reaction. Thus, uncatalyzed, ^{8a-c)} free-radical, ^{8d-g)} and transition metal-catalyzed reactions^{8g-k)} are possible. On the other hand, generally low thermal stability of allylstannanes may prevent preparation of regiospecifically functionalized compounds. Therefore, preparation of allylstannanes having any substituents is not easy. In spite of these demerits including the possible toxicity inherent to organostannanes, the high reactivity of allylstannanes are apparently advantageous and may be able to countervail these limitations.

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Run	Allylstannane	Electrophile	Lewis acid	Conditions	Product (%yield) ^{a,b}	
1	Me ₃ SnCH ₂ CH=CH (<u>1</u> a)	₂ Сн ₃ (сн ₂) ₂ сно	BF3.0Et2	rt, 30 min ^{CH} 2 ^{C1} 2	CH ₂ =CHCH ₂ CH(CH ₂) ₂ CH ₃ (OH	91)
2	la 2	сн ₃ (сн ₂) ₂ сно	(Et ₂ Al) ₂ SO ₄	80°C, 16 h PhH-Hexane	Сн ₂ =Снсн ₂ сн (сн ₂) ₂ сн ₃ (он	89
3	Me3 ^{SnCH} 2 ^{C=CH} 2 CH=CH2 (1b)	(CH ₃) ₂ CHCH ₂ CHO	BF ₃ •OEt ₂	-78°C, 20 min CH ₂ Cl ₂	$CH_2 = C - CH_2 CHCH_2 CH (CH_3)$ $CH_2 = CH OH$ (4	с 2 40
4	la 2	PhCHO	BF3.OEt2	-78°C~rt, 2 h CH ₂ Cl ₂	CH ₂ =CHCH ₂ CHPh (6 OH	56)
5	la	PhCHO	(Et ₂ Al) ₂ SO ₄	80°C, 16 h PhH-Hexane	CH ₂ =CHCH ₂ CHPh (7)	79)
6	la	<i>С</i> русно	BF3'OEt2	-78°C, l h CH ₂ Cl ₂	CHCH ₂ CH=CH ₂ (6	58)
7	Me ₃ SnCH ₂ CH=C(CH (1c)	3) ₂ Ph (CH ₂) ₂ CHC O) BF ₃ •OEt ₂ -	-78°C~rt, 3 h CH ₂ Cl ₂	CH ₂ =CHC (CH ₃) 2 ^{CH} (CH ₂) 2 ^H OH (7	?h 77)
8	la	\bigcirc	$(\text{Et}_2\text{Al})_2\text{SO}_4$	80°C, 16 h PhH-Hexane	CH ₂ CH=CH ₂ (4	16)
9	la	PhCH=CHCOCH ₃	$(\text{Et}_2\text{Al})_2\text{SO}_4$	80°C, 16 h PhH-Hexane	CH ₂ =CHCH ₂ CH(Ph)CH ₂ COCH (6	[[] 3 54)
10	la Ph	(CH ₂) ₂ CH(OCH ₃) ₂	$(\text{Et}_2\text{Al})_2\text{SO}_4$	80°C, 18 h PhH-Hexane	CH ₂ =CHCH ₂ CH(CH ₂) ₂ Ph (6 OCH ₃	8)
a Yie is (<u>+</u>	elds after isola	tion by tlc. b aggregation pher	Yields are r omone of bar	ot always opt k beetle, ips	imized. ^C This compoun paraconfusus. ^{2f}	ıđ

Table 1. Reactions of allylstannanes (1) with various electrophilic reagents activated by a Lewis acid.

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