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THE REACTION OF TRIBUTYLSTANNYLLITHIUM WITH 2-ETHOXY-3-ALKENENITRILES. A NEW METHOD FOR THE PREPARATION OF γ-ETHOXYALLYLSTANNANES AND DIENOL ETHERS

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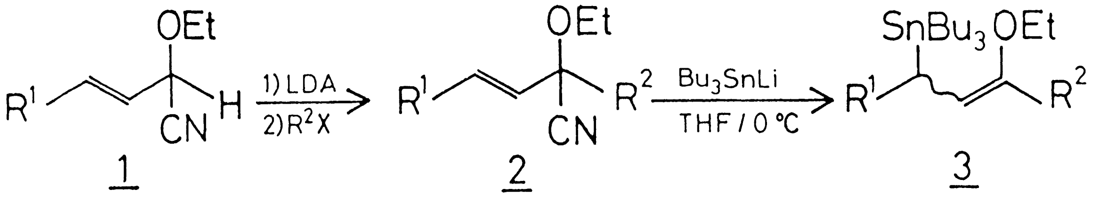
The reaction of 2-ethoxy-3-alkenenitriles with tributylstannyllithium gave the S_N2' product, γ-ethoxyallylstannanes (3), in good yields. When 3 have a trimethylsiloxyl group at δ-position, the corresponding substituted 2-ethoxy-1,3-butadienes were produced by the elimination of trimethylsiloxystannane.

The substitution reactions of allylic halides$^{1)}$ or phosphates$^{2)}$ with trialkylstannyl anion were reported as useful methods for the preparation of substituted allylstannanes, which play an important role in organic synthesis. In this communication, we wish to describe a new method for the preparation of γ-ethoxyallylstannanes (3) by the S_N2' reaction of 2-ethoxy-3-alkenenitriles (2) with tributylstannyllithium and the application of this reaction to the synthesis of dienol ethers (5).

Recently, we showed that the alkylthio group of 2-alkylthioalkanenitrile was reductively removed to give the corresponding α-anion of alkanenitrile by the treatment of tributylstannyllithium.$^{3)}$ We examined the similar reductive lithiation of 2-ethoxy-3-alkenenitrile using tributylstannyllithium as a reducing agent. The expected reductive removal of ethoxyl group, however, was not observed but the nucleophilic displacement of cyano group with tributylstannyl anion proceeded exclusively (Eq. 1).

2-Ethoxy-3-alkenenitriles (1) prepared from the corresponding acetals of α,β-unsaturated aldehyde$^{4)}$ were treated with LDA (THF/ -78 °C) and alkyl halides (-78 °C - r.t.) successively to give the α-alkylated products (2) in good yields (2a; 74%, 2b; 54%, 2c; 86%, 2d; 67%, 2e; 63%).$^{5)}$ When the alkenenitriles 2 were allowed to react with tributylstannyllithium in THF at 0 °C, γ-ethoxyallyl-



(1)

stannanes (3) were produced in good to high yields and no formation of the S_N2 product, α-ethoxyallylstannane, was observed (Table 1).

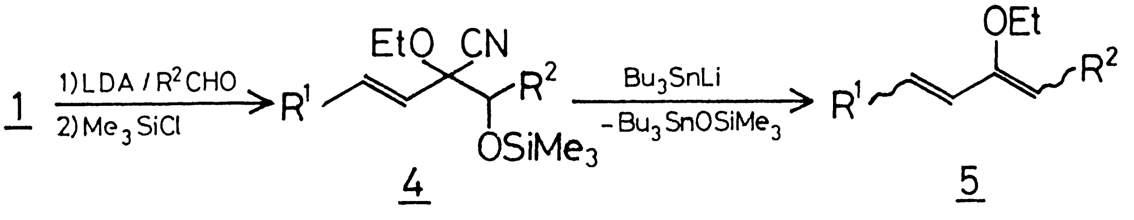
Table 1. Synthesis of γ-ethoxyallylstannane (3)a)

	R^1	R^2	Temp °C	Time h	Yield b) 6) %
a	CH_3	$PhCH_2$	0	2.5	87 7)
b	CH_3	$CH_3(CH_2)_7$	r.t.	1.5	97 7)
c	$CH_3(CH_2)_2$	$PhCH_2$	0	1.5	95
d	$CH_3(CH_2)_2$	$CH_3(CH_2)_7$	0	1.5	84
e	$CH_3(CH_2)_2$	CH_3	0	1.5	89 c)

a) 1.2 equiv. of tributylstannyllithium were used. b) γ-Ethoxyallylstannane was isolated as a mixture of stereoisomers by column chromatography using aluminum oxide deactivated by addition of 6% of water. c) E:Z = 11 : 10. The ratio was determined by HPLC analysis (Merck Si 60; solvent, hexane).

Concerning the preparation of γ-ethoxyallylstannane (3), Quintard et al. reported that 3 was produced by the acid-catalyzed isomerization of α-ethoxyallylstannane which was synthesized by the reaction of chloroethoxymethylstannane with vinylmagnesium reagent.8) It should be noted that the present method is apparently advantageous to the preparation of 3.

Next, the synthesis of dienol ethers (5) from 2-ethoxy-3-alkenenitriles (1) was examined on the basis of the above observation. The trimethylsiloxyalkenenitriles (4) were synthesized by the reaction of lithium salts of 1 with aldehydes followed by the treatment with chlorotrimethylsilane. The substituted 2-ethoxy-1,3-butadidenes (5) were obtained in good yields by the simple treatment of the trimethylsilyl ethers (4) with tributylstannyllithium in THF (Eq. 2).



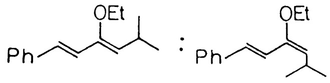
(2)

The following experimental procedure is representative: To a THF (1.5 ml) solution of LDA (diisopropylamine (132 mg, 1.3 mmol) and butyllithium (1.2 mmol)) was added a THF (1 ml) solution of 2-ethoxy-3-hexenenitrile (153 mg, 1 mmol) at -78 °C. After stirring for 30 min, 3-phenylpropionaldehyde (161 mg, 1.2 mmol) in THF (1 ml) was added at -78 °C and the reaction mixture was gradually warmed up to 0 °C. Then chlorotrimethylsilane (0.19 ml, 1.5 mmol) was added to the reaction mixture and the mixture was stirred overnight. The reaction was quenched by the addition of a phosphate buffer solution (pH 7) and organic material was extracted with AcOEt. The extract was dried (Na_2SO_4) and condensed under reduced pressure. The residue was chromatographed on silica gel (hexane-AcOEt) and 4-ethoxy-1-phenyl-3-trimethylsiloxy-5-nonene-4-carbonitrile (4c, 288 mg) was isolated in 80% yield. A THF solution of tributylstannyllithium (2.1 mmol) was added to 4c (360 mg, 1 mmol) in THF (2 ml) at 0 °C and the mixture was stirred for 2 h. After addition of a 5% $NaHCO_3$ aqueous solution, organic material was extracted with ether and dried over Na_2SO_4. The solvent was removed and the crude dienol ether was purified by column chromatography (aluminum oxide deactivated by 6% of water / hexane) and 5-ethoxy-1-phenyl-4,6-decadiene (5c) (146 mg) was obtained in 60% yield.

Table 2. Preparation of dienol ether (5)

	R^1	R^2	Yield/%6) 4	 5a)
a	CH_3	$(CH_3)_2CH$	67	73
b	CH_3	$Ph(CH_2)_2$	74	86
c	$CH_3(CH_2)_2$	$Ph(CH_2)_2$	80	60
d	$CH_3(CH_2)_2$	$CH_3(CH_2)_7$	67	72
e	Ph	$(CH_3)_2CH$	86	79b)
f	Ph	$Ph(CH_2)_2$	83	63

a) Isolated as a mixture of stereoisomers. The ratio was determined by NMR analysis. b)



= 6 : 5.

In a similar manner, several dienol ethers (5) were synthesized as shown in Table 2.

It is known that the primary conventional route to 2-alkoxy-1,3-butadienes (5) is the pyrolysis of γ-alkoxyacetals.9) However, it generally affords low yieldes because of the rather vigorous reaction conditions employed. The present reaction provides a convenient method for the preparation of 2-ethoxy-1,3-butadienes utilizing two different aldehydes ($R^1CH=CHCHO$ and R^2CHO).

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5) The yields are not necessarily optimum.

6) All compounds exhibited IR and NMR spectral data in accordance with assigned structures.

7) The γ-ethoxyallylstannanes (3a and 3b) were hydrolyzed (1 M HCl- EtOH/ r.t./ overnight) to give the corresponding β-tributylstannyl ketones in 86 and 82% yields, respectively.

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