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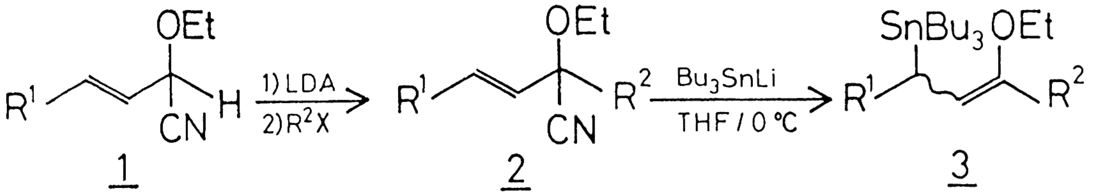
The reaction of 2-ethoxy-3-alkenenitriles with tributylstannyllithium gave the $S_N2'$ product, γ-ethoxyallylstannanes (3), in good yields. When 3 have a trimethylsiloxyl group at δ-position, the corresponding substituted 2-ethoxy-1,3-butadienes were produced by the elimination of trimethylsiloxystannane.

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).

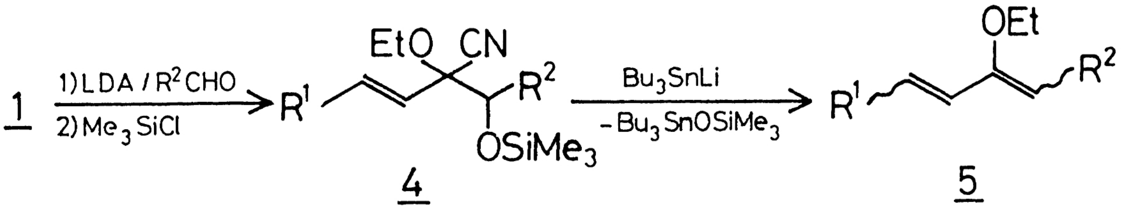
Table 1. Synthesis of γ-ethoxyallylstannane (3)[a)]

| | $R^1$ | $R^2$ | Temp<br>°C | Time<br>h | Yield[b) 6)]<br>% |
|---|---|---|---|---|---|
| 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).

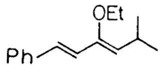


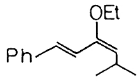
(2)

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 | 5[a)] |
| 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 | 79[b)] |
| 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 $\gamma$-ethoxyallylstannanes (3a and 3b) were hydrolyzed (1 M HCl- EtOH/ r.t./ overnight) to give the corresponding $\beta$-tributylstannyl ketones in 86 and 82% yields, respectively.

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