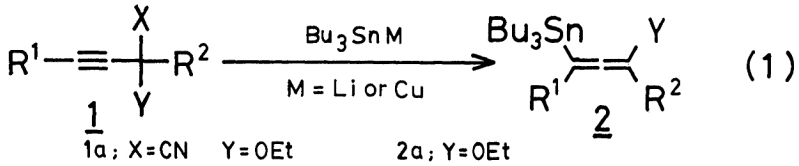
CHEMISTRY LETTERS, pp. 1345-1348, 1987.

Preparation and Reaction of γ-Ethoxy and (Phenylthio)allenylstannanes

Takeshi TAKEDA,* Hiroyuki OHSHIMA, Masami INOUE, Akira TOGO, and Tooru FUJIWARA
Department of Industrial Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184

γ-Ethoxyallenylstannane was obtained by the reaction of 2-ethoxy-3-alkynenitrile or 1-ethoxy-1-(phenylthio)-2-alkyne with tributylstannyllithium in good yield. The reaction of 1,1-bis-(phenylthio)-2-alkyne with tributylstannylcopper(I) reagent gave γ-(phenylthio)allenylstannane which, in turn, was treated with acetal in the presence of $TiCl_4$ to afford the propargyl sulfide derivative predominantly.

Preparation of γ-alkoxyallylstannane and its reaction with carbonyl compounds are the subject of recent interest as a tool for the synthesis of polyhydroxylated natural products.[1] However, little attention have been directed to the γ-heteroatom substituted allenylstannanes. We wish to describe here a convenient method for the preparation of γ-ethoxy and (phenylthio)allenylstannanes (2a and 2b) and the preliminary results of the reaction of 2b with acetals in the presence of $TiCl_4$.



(1)

1a; X=CN Y=OEt
1b; X=SPh Y=OEt
1c; X=SPh Y=SPh

2a; Y=OEt
2b; Y=SPh

Initially we examined the preparation of γ-ethoxyallenylstannane (2a) by the reaction of 2-ethoxy-3-alkynenitrile (1a) with tributylstannyllithium similarly to the method for the synthesis of γ-ethoxyallylstannane which was recently developed by us.[1c] It was found, however, that γ-ethoxyallenylstannanes (2a) were obtained only when 1a possessing an α-alkyl substituent (R^2= alkyl) was employed. Therefore desulfurizative stannylation of monothioacetal (1b) and thioacetal (1c) were then examined in order to prepare γ-phenylthio as well as γ-ethoxyallenylstannanes with no γ-alkyl substituent.

When 1-ethoxy-1-(phenylthio)-2-alkyne was treated with tributylstannyllithium in THF, the reaction was complicated and no stannylated product was obtained like the reaction of 1a which had no α-alkyl group. On the other hand, the displacement of phenylthio group proceeded with allylic inversion to give γ-ethoxyallenylstannane (2a) in good yield by the reaction carried out in the presence of CuBr

Table 1. Preparation of γ-ethoxy and (phenylthio)allenylstannanes (2)

1				Temp	Time	Yield[a]
R^1	R^2	X	Y	°C	h	%
CH_3	$PhCH_2$	CN	OEt	-78	0.7	83
CH_3	$Ph(CH_2)_2$	CN	OEt	-78	1	88
CH_3	$CH_3(CH_2)_7$	CN	OEt	-78	1	85
$CH_3(CH_2)_3$	$PhCH_2$	CN	OEt	-78	0.7	95
$CH_3(CH_2)_3$	$Ph(CH_2)_2$	CN	OEt	-78	0.7	98
$CH_3(CH_2)_3$	CH_3CH_2	CN	OEt	-78	0.5	94
$Ph(CH_2)_3$	$Ph(CH_2)_2$	CN	OEt	-78	1	83
CH_3	H	PhS	OEt	0-r.t.	3	62
$CH_3(CH_2)_3$	H	PhS	OEt	0	2	75
$Ph(CH_2)_3$	H	PhS	OEt	0-r.t.	2	64
CH_3	H	PhS	PhS	-78-0	2	59
$CH_3(CH_2)_3$	H	PhS	PhS	-78-0	2	67
$Ph(CH_2)_3$	H	PhS	PhS	-78-0	2	65

a) All compounds gave satisfactory spectral data.

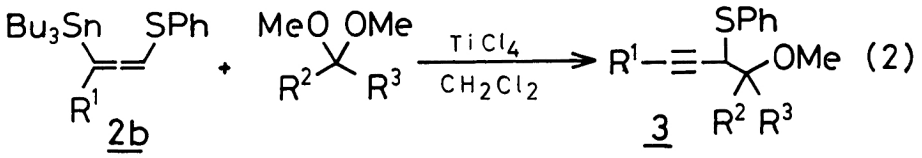
and HMPA.

On the basis of the above observation, thioacetal (1c) was treated with various tributylstannylmetal species to prepare γ-(phenylthio)allenylstannane (2b). After several attempts, tributylstannylcopper(I) reagent[2] was found to be effective for the present transformation and the reaction proceeded regioselectively to give 2b in good to moderate yield (Table 1).

The experimental procedures for the preparation of these allenylstannanes (2a and 2b) are as follows: (i) Preparation of 2a from 1a —— A THF solution of Bu_3SnLi (0.6 mmol) was added to a THF (1.5 ml) solution of 4-ethoxy-5-phenyl-2-hexyne-4-carbonitrile (1a) (107 mg, 0.5 mmol) at -78 °C. After being stirred for 40 min, the reaction was quenched by addition of 5% aq.$NaHCO_3$. The organic material was extracted (ether) and dried (Na_2SO_4). After evaporation of the solvent, 2-ethoxy-1-phenyl-4-(tributylstannyl)-2,3-pentadiene (2a) (198 mg, 83%) was isolated by column chromatography (hexane) using neutral aluminum oxide deactivated by addition of 6% of water. (ii) Preparation of 2a from 1b —— A THF solution of Bu_3SnLi (1 mmol) was added to a THF (3 ml)-HMPA (1 ml) solution of 1-ethoxy-1-phenylthio-2-butyne (1b) (103 mg, 0.5 mmol) and CuBr (144 mg, 1 mmol) at 0 °C. After being warmed up to r.t., the reaction was quenched by addition of sat. aq. NH_4Cl. The work-up and purification procedures descried above gave 1-ethoxy-3-(tributylstannyl)-1,2-butadiene (2a) (120 mg) in 62% yield. (iii) Preparation of (2b) —— A THF solution of Bu_3SnLi (12 mmol) was added to a THF (12 ml) solution of CuBr (1.894 g, 13.2 mmol) and LiBr (1.146 g, 13.2 mmol) at -78 °C. After being stirred for 1 h, 1,1-bis(phenylthio)-2-heptyne (1c) (1.250 g, 4 mmol) in THF (12 ml) was added and the reaction mixture was stirred for 1 h at the same temperature and 1 h at 0 °C. The reaction was quenched by addition of sat. aq. NH_4Cl and organic mate-

rial was extracted with hexane. The extract was dried (Na_2SO_4) and condensed under reduced pressure. 1-(Phenylthio)-3-(tributylstannyl)-1,2-heptadiene (2b) (1.314 g) was isolated in 67% yield by column chromatography (hexane) using silica gel containing 0.1% of hydroquinone.

γ-Ethoxy and (phenylthio)allenylstannane (2a and 2b) are regarded as synthetic equivalents of γ-anions of propargylic ether and sulfide. Then we examined the reaction of 2b with carbonyl compounds and it was found that $TiCl_4$ promoted reaction of 2b with acetal proceeded regioselectively to give the propargylic sulfide (3) (Eq. 2, Table 2).



The following experimental procedure is representative: to a CH_2Cl_2 (2 ml) solution of 3-phenylpropionaldehyde dimethyl acetal (135 mg, 0.75 mmol) was added a CH_2Cl_2 (0.53 ml) solution of $TiCl_4$ (0.5 mmol) and a CH_2Cl_2 (1.5 ml) solution of 1-(phenylthio)-3-(tributylstannyl)-1,2-butadiene (226 mg, 0.5 mmol) successively at -78 °C. After being stirred for 5 min, the reaction was quenched by addition

Table 2. The reaction of γ-(phenylthio)allenylstannane (2b) with acetal

Run	R^1	R^2	R^3	Temp °C	Time min	Yield[d] %	Ratio of stereoisomers
1	CH_3	CH_3	H	-78	10	67	56 : 44[e]
2		$Ph(CH_2)_2$	H	-78	5	71	f)
3		$(CH_3)_2CH$	H	-78	30	54	68 : 32[g]
4		Ph	H	-78	5	62	77 : 23[e]
5[a]		Ph	H	-78	180	67	87 : 13
6[a]		CH_2=CH	H[c]	r.t.	overnight	61	f)
7		CH_3	CH_3	-78	150	56	—
8[b]	$CH_3(CH_2)_3$	CH_3	H	-23	8	65	56 : 44[e]
9		$(CH_3)_2CH$	H	-78	180	55	77 : 23[g]
10[b]		Ph	H	-23	8	54	80 : 20[e]
11[b]	$Ph(CH_2)_3$	CH_3	H	-23	8	61	51 : 49[e]
12[b]		Ph	H	-23	15	54	76 : 24[e]

a) $AlCl_3$ was used instead of $TiCl_4$. b) The reaction was carried out by addition of a CH_2Cl_2 solution of $TiCl_4$ to a CH_2Cl_2 solution of 2b and acetal at -23 °C. c) Diethyl acetal. d) The structures of these compounds are supported by IR and NMR spectra. e) Determined by 60 MHz and 200 MHz ^1H NMR spectra. f) The ratio was not determined. g) The two isomers were separated each other by TLC.

of a phosphate buffer solution (pH 7). The usual work-up and purification (silica gel TLC, hexane-AcOEt = 9:1) gave 5-methoxy-7-phenyl-4-(phenylthio)-2-heptyne (110 mg) in 71% yield.

The vicinal coupling constants of the two methine protons α to phenylthio and methoxy groups of 3 obtained by the reaction of isobutyraldehyde (runs 3 and 9) and benzaldehyde (runs 4, 5, and 10) suggest that the major products are the threo adducts (R^1= CH_3, R^2= $(CH_3)_2CH$; 7 Hz (CCl_4), R^1= CH_3, R^2= Ph; 7.1 Hz ($CDCl_3$), R^1= $CH_3(CH_2)_3$, R^2= $(CH_3)_2CH$; 7 Hz (CCl_4), R^1= $CH_3(CH_2)_3$, R^2= Ph; 9 Hz (CCl_4)) and the others are the erythro diastereoisomers (R^1= CH_3, R^2= $(CH_3)_2CH$; 5 Hz (CCl_4), R^1= CH_3, R^2= Ph; 4.4 Hz ($CDCl_3$), R^1= $CH_3(CH_2)_3$, R^2= $(CH_3)_2CH$; 5 Hz (CCl_4), R^1= $CH_3(CH_2)_3$, R^2= Ph; 6 Hz (CCl_4)). The preferential formation of the threo adduct in the present reaction is well explained by assuming the non-cyclic transition states depicted in Fig. 1.

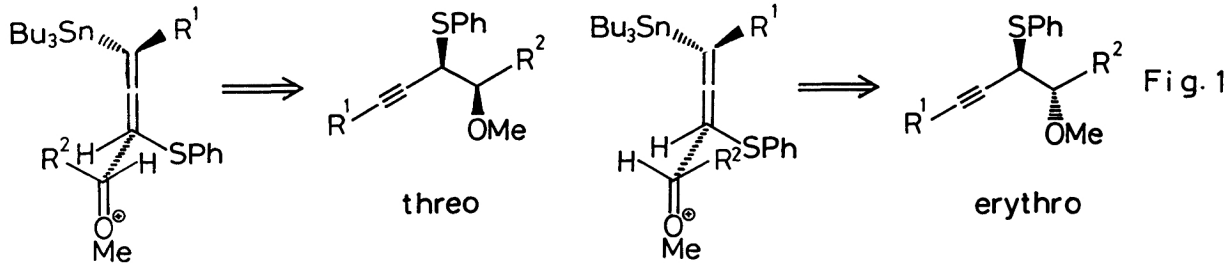


Fig. 1

The authors gratefully acknowledge the financial support of the Saneyoshi Foundation.

References

1) a) J. P. Quintard, B. Elissondo, and M. Pereyre, J. Org. Chem., 48, 1559 (1983); b) M. Pereyre, B. Elissondo, and J. P. Quintard, " Selectivity - a Goal for Synthetic Efficiency," ed by W. Bartman and B. M. Trost, Verlag Chemie, Weinheim (1984), p.201; c) T. Takeda, K. Ando, H. Oshima, M. Inoue, and T. Fujiwara, Chem. Lett., 1986, 345; d) G. E. Keck, D. E. Abbott, and M. R. Wiley, Tetrahedron Lett., 28, 139 (1987); e) M. Koreeda and Y. Tanaka, ibid., 28, 143 (1987).

2) K. Ruitenberg, H. Westmijze, J. Meijer, C. J. Elsevier, and D. Vermeer, J. Organomet. Chem., 241, 417 (1983).

(Received April 17, 1987)