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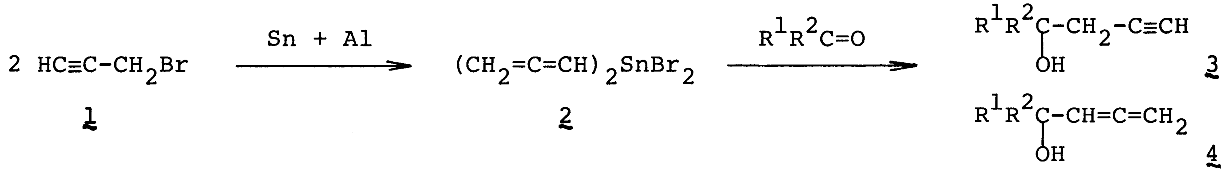
REACTION OF PROPARGYL BROMIDE AND TRIMETHYLSILYLPROPARGYL IODIDE WITH METALLIC TIN, ALUMINUM, AND ALDEHYDES OR KETONES. SELECTIVE SYNTHESIS OF β-ACETYLENE, β-TRIMETHYLSILYLACETYLENE, AND α-TRIMETHYLSILYLALLENE ALCOHOLS

Junzo NOKAMI,* Takashi TAMAOKA, Tadao KOGUCHI, and Rokuro OKAWARA
Okayama University of Science, Ridai, Okayama 700

β-Acetylenic and α-allenic alcohols were synthesized selectively by the reaction of aldehydes and ketones with organotin compounds prepared by treatment of propargyl bromide or trimethylsilylpropargyl iodide with metallic tin and aluminum in a suitable solvent.

Various organometallic compounds have been used to form a C-C bond by the reaction with aldehydes or ketones. However, in these reactions some characteristic differences particular to the metals were also found out. For example, we have reported1) that an allylation of aldehydes and ketones to give homoallyl alcohols can be carried out successfully by allyl bromide and metallic tin in the presence of water, and also an allylation by various allylic bromide is successful in the presence of water by using metallic tin and aluminum. Also, we have succeeded to extend this finding for intramolecular reactions.2) Those interesting findings characteristic to organotin compounds prompted us to investigate further on their reactions. Here, we describe a reaction of propargyl bromide or trimethylsilylpropargyl iodide with metallic tin and aluminum, and their reactions with aldehydes and ketones.

First, we have found out that diallentin dibromide (**2**),3) directly prepared by treatment of propargyl bromide (1) with metallic tin *in the presence of metallic aluminum*4) in dry tetrahydrofuran (THF), reacts with aldehydes and ketones to afford β-acetylene alcohols **3** selectively (Table 1). This result is quite different from that of the reaction of propargyl iodide with aldehyde in the presence of stannous halide (SnX_2) in which α-allene alcohol **4** was reported to be a major product.5)



$$2\ HC{\equiv}C\text{-}CH_2Br \xrightarrow{Sn\ +\ Al} (CH_2{=}C{=}CH)_2SnBr_2 \xrightarrow{R^1R^2C{=}O} \begin{array}{ll} R^1R^2\underset{OH}{C}\text{-}CH_2\text{-}C{\equiv}CH & \mathbf{3} \\ R^1R^2\underset{OH}{C}\text{-}CH{=}C{=}CH_2 & \mathbf{4} \end{array}$$

$\mathbf{1}$ $\qquad$ $\mathbf{2}$

Second, we have found out that trimethylsilylpropargyl iodide (**5**) reacts with metallic tin *in the presence of metallic aluminum*4) in the solvent shown in Table 2 to give bis(trimethylsilylpropargyl)tin diiodide (**6**)6) which in turn reacts with aldehyde to give either α-allenic **7** or β-acetylenic **8** alcohol. For example, the reaction in a mixed solvent of acetonitrile (MeCN) and dimethylsulfoxide (DMSO) gave α-allenic alcohols selectively in good yield. On the other hand, the reaction

Table 1. Reaction of Aldehyde or Ketone with Diallentin Dibromide to β-Acetylene Alcohol 3

Aldehyde or Ketone	Reaction method[a)]	Reaction time/h	3 Yield[b)]/%
Benzaldehyde	A	1.1	94
	B	1.0	70[c)]
n-Heptanal	A	1.0	77
	B	2.0	68
Crotonaldehyde	A	1.0	72
	B	1.5	50
Citral	A	1.0	81
	B	1.5	62
Cyclohexanone	A	1.1	90
	B	1.6	73
2-Octanone	A	1.5	91
	B	2.0	70
Levulinic acid	A	5.0	66[d)]

a) Method A; To a suspension of commercial metallic tin (237 mg, 2 mmol; 325 mesh, 99% purity) and aluminum (54 mg, 2 mmol; 200 mesh, 99.5% purity) in dry THF (2 ml), propargyl bromide (0.36 ml, 4 mmol) was added with vigorous stirring and the stirring was continued for 1 h at room temperature, and then aldehyde or ketone (2 mmol) was added to the reaction mixture. After the stirring was continued as indicated in Table 1, water was added to the reaction mixture. After usual work up (extraction, concentration), the crude product was purified by column chromatography on silica gel.
Method B; Diallentin dibromide was prepared similar to that described in Method A. Aldehyde or ketone (4 mmol) was used.

b) Based on aldehyde or ketone.

c) Mixture of 3 and 4 in the ratio of ca. 3:1 (3:4).

d) 4-Propargyl-4-valerolactone.

in diethylene glycol dimethyl ether (diglyme) gave β-acetylenic alcohols selectively in a satisfactory yield as shown in Table 2. These reactions seem to be unique in the following points, 1) the trimethylsilylpropargyltin compound is easily prepared by using commercial tin and aluminum without any pretreatment for activation of the metals, and 2) either β-acetylenic or α-allenic alcohol can be selectively prepared by the choice of the reaction solvent.[7)]

The following procedure is typical. To a stirred suspension of metallic tin (1.6 mmol) and aluminum (1.6 mmol) in a mixed solvent (4 ml of MeCN, 0.3 ml of DMSO) was added 5 (2.1 mmol) at r.t., and the stirring was continued for 1 h. n-Heptanal (1.0 mmol) was added to the reaction mixture, and the stirring was continued for additional 1 h at r.t. After usual work up, the crude product was purified by column chromatography on silica gel to give pure **7** and **8**.

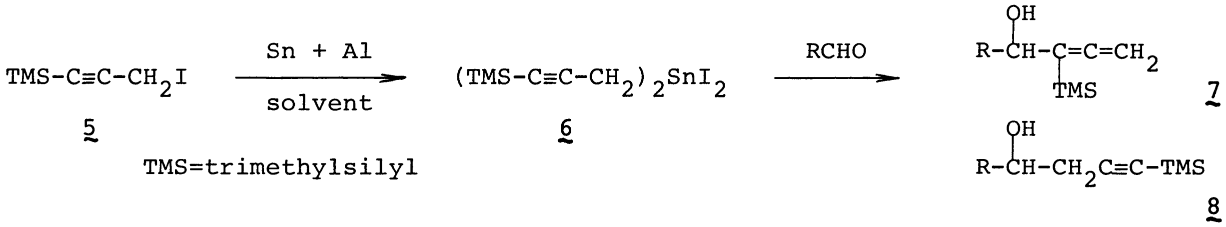


Table 2. Reaction of Aldehyde with Trimethylsilylpropargyltin Compound **6** Derived from Trimethylsilylpropargyl Iodide, Metallic Tin and Aluminum

Aldehyde (mmol)	**5** (mmol)	Metallic Sn and Al (mmol)	Solvent (ml)	Product Yield/%[a] **7**	**8**	(**7**/**8**)
$CH_3(CH_2)_5CHO$						
(1.0)	(2.1)	(1.6)	MeCN-DMSO (4.0-0.3)	84	4	(95/5)
(1.0)	(2.0)	(1.3)	MeCN (3.0)	20	46	(30/70)
(1.0)	(2.0)	(1.5)	diglyme (5.0)	6	69	(8/92)
PhCHO						
(1.0)	(2.0)	(1.2)	MeCN-DMSO (3.0-0.4)	79	9	(90/10)
(1.0)	(2.0)	(1.2)	MeCN (2.0)	57	12	(83/17)
(2.0)	(3.0)	(2.0)	diglyme (3.0)	8	61	(11/89)
$CH_3CH=CHCHO$						
(2.0)	(4.0)	(2.0)	MeCN-DMSO (3.0-2.0)	55	5	(92/8)
(1.0)	(2.0)	(1.6)	MeCN (4.0)	8	53	(13/87)
(1.2)	(2.0)	(2.0)	diglyme (3.0)	6	58	(9/91)
HCHO[b]						
(1.5)	(3.0)	(2.0)	MeCN-DMSO (4.0-1.0)	79	0	(100/0)
(3.0)	(1.0)	(2.0)	diglyme (3.0)	50	3	(95/5)

a) After isolation by column chromatography on silica gel based on aldehyde.
b) Formalin (37 wt. % solution in water).

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2) J. Nokami, S. Wakabayashi, and R. Okawara, Chem. Lett., 1984, 869.

3) After concentration of the supernatant solution, the following spectral data were obtained: NMR (CCl_4) δ 4.70 (2H, dd, J=7 and 15 Hz), 5.40 (1H, dt, J=7 and 13 Hz); IR (neat) 1930 (C=C=C) cm^{-1}.

4) Metallic tin does not react with propargyl bromide or trimethylsilylpropargyl iodide in the absence of metallic aluminum.

5) T. Mukaiyama and T. Harada, Chem. Lett., 1981, 621.

6) We could not isolate the tin compound 6 as a pure compound free from the solvent. However, they were enough stable in the solvent to give the spectral data. The tin compound 6 prepared in MeCN-DMSO was characterized from the following spectral data; NMR δ 0.0 (9H, d, J=2 Hz), 2.2 (2H, t, J=2 Hz); IR 2160 (C≡C) cm^{-1}, and 6 prepared in diglyme was also characterized from the IR spectrum; 2160 cm^{-1}.

7) Many efforts have been paid to obtain either β-acetylenic or α-allenic alcohol selectively. Recent reports on propargylic or allenic metal compounds; allenylsilver(I) compounds, H. Westmijze, H. Kleiji, H. J. T. Bos, and P. Vermeer, J. Organometal. Chem., 199, 293 (1980); 1,3-bis(trialkylsilyl)allenyl metal (Li, Mg), Y. Yamakado, M. Ishiguro, N. Ikeda, and H. Yamamoto, J. Am. Chem. Soc., 103, 5568 (1981); chiral allenylboronic esters, R. Haruta, M. Ishiguro, N. Ikeda, and H. Yamamoto, ibid., 104, 7667 (1982); propargylic titanium reagents, M. Ishiguro, N. Ikeda, and H. Yamamoto, J. Org. Chem., 47, 2225 (1982); Zn and Al mediated condensation of trimethylsilylpropargyl bromide with carbonyl compounds, R. G. Daniels and L. A. Paquette, Tetrahedron Lett., 22, 1579 (1981), and references cited therein.

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