

# Carbonyl propargylation by 1-substituted prop-2-ynyl mesylates and carbonyl allenylation by 3-substituted prop-2-ynyl mesylates with tin(II) iodide and tetrabutylammonium iodide

Yoshiro Masuyama,\*† Akiko Watabe, Akihiro Ito and Yasuhiko Kurusu

Department of Chemistry, Sophia University, 7-1 Kioicho, Chiyoda-ku, Tokyo 102-8554, Japan

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1-Substituted prop-2-ynyl mesylates cause propargylation of aldehydes with tin(II) iodide, tetrabutylammonium iodide and sodium iodide in 1,3-dimethylimidazolidin-2-one to produce 2-substituted but-3-yn-1-ols, while 3-substituted prop-2-ynyl mesylates cause allenylation of aldehydes under the same conditions as those of the propargylation by 1-substituted prop-2-ynyl mesylates to produce 2-substituted buta-2,3-dien-1-ols.

**Table 1** Allenylation by prop-2-ynyl mesylate with SnI<sub>2</sub> and TBAI<sup>a</sup>

R <sup>3</sup>	Time/h	Yield (%) <sup>b</sup>	
		2 + 3	2:3 <sup>c</sup>
C <sub>6</sub> H <sub>5</sub>	45	85	78:22
ClC <sub>6</sub> H <sub>4</sub>	48	80	75:25
CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	70	74	78:22
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	71	66	66:34
c-C <sub>6</sub> H <sub>11</sub>	72	68	81:19

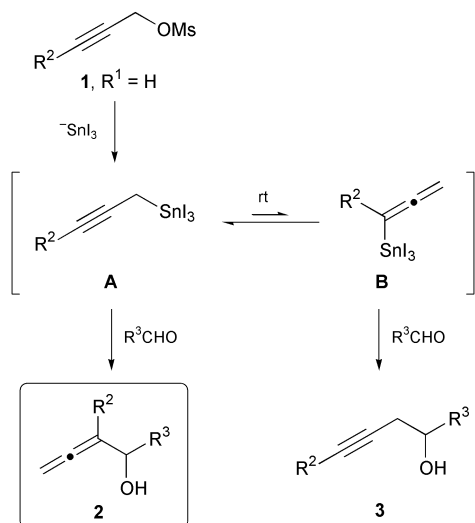
<sup>a</sup> The reaction of prop-2-ynyl mesylate (1.5 mmol) with aldehydes (1.0 mmol) was carried out using SnI<sub>2</sub> (1.5 mmol), TBAI (0.10 mmol) and NaI (1.5 mmol) in DMI (3 ml) at 10 °C. <sup>b</sup> Yields of a mixture of **2** and **3**. <sup>c</sup> The ratio was determined by <sup>1</sup>H NMR analysis (JEOL A-500).

Alkynes and allenes have formed an attractive chemistry for high reactivities with metal complexes or reagents.<sup>1</sup> Thus, the preparation of alkynes and allenes becomes an important theme. Barbier-type carbonyl propargylation or allenylation with propargylic halides is one of the most convenient methods for the introduction of propargyl or allenyl functions.<sup>2–7</sup> However, it is not easy to control selectivity between Barbier-type propargylation and allenylation with propargylic halides. We have established both selective propargylation and allenylation by 1-haloprop-2-yne with tin(II) halide and tetrabutylammonium halide (TBAX) through choice of reaction conditions: carbonyl propargylation occurs with 1-bromoprop-2-yne, SnCl<sub>2</sub> and TBABr at 50 °C in water, while carbonyl allenylation occurs with 1-chloroprop-2-yne, SnI<sub>2</sub> and TBAI at 25 °C in 1,3-dimethylimidazolidin-2-one (DMI).<sup>8</sup> <sup>1</sup>H NMR observations (JEOL A-500) have confirmed that prop-2-ynyltriiodotin (propargyltin), derived from 1-chloroprop-2-yne with SnI<sub>2</sub> and NaI at 25 °C in DMF-d<sub>7</sub>, does not isomerize to propa-1,2-dienyltriiodotin (allenyltin) at 25 °C but does so at 50 °C.<sup>8,9</sup> We thus hoped that this kind of isomerization of propargyltin to allenyltin would be prohibited by the steric effect of a 3-substituent in 1-haloprop-2-yne and be promoted by the steric effect of a 1-substituent in 1-haloprop-2-yne.<sup>10</sup> We here

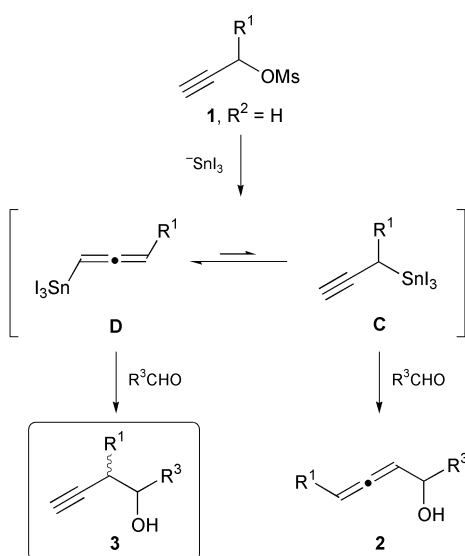
**Table 2** Selective carbonyl propargylation or allenylation mediated by steric effects<sup>a</sup>

R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Time/h	Yield (%) <sup>b</sup>		3 syn:anti <sup>c</sup>
				2 + 3	2:3 <sup>c</sup>	
H	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	48	58	~100:0	
H	CH <sub>3</sub>	ClC <sub>6</sub> H <sub>4</sub>	47	65	~100:0	
H	CH <sub>3</sub>	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	55	52	~100:0	
H	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH=CH	71	21 <sup>d</sup>	94:6	
H	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	51	62	90:10	
H	CH <sub>3</sub>	CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>8</sub>	50	57	89:11	
H	CH <sub>3</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	67	65	90:10	
H	CH <sub>3</sub>	c-C <sub>6</sub> H <sub>11</sub>	79	41	84:16	
H	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	71	81	~100:0	
H	C <sub>6</sub> H <sub>5</sub>	ClC <sub>6</sub> H <sub>4</sub>	63	84	~100:0	
H	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	90	76	~100:0	
H	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	79	56	90:10	
H	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>8</sub>	75	32	98:2	
H	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	70	35	98:2	
H	C <sub>6</sub> H <sub>5</sub>	c-C <sub>6</sub> H <sub>11</sub>	71	48	93:7	
CH <sub>3</sub>	H	C <sub>6</sub> H <sub>5</sub>	71	71	12:88	49:51
CH <sub>3</sub>	H	ClC <sub>6</sub> H <sub>4</sub>	79	83	6:94	48:52
CH <sub>3</sub>	H	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	75	65	6:94	47:53
CH <sub>3</sub>	H	2-Furyl	70	41	0:~100	50:50
CH <sub>3</sub>	H	C <sub>6</sub> H <sub>5</sub> CH=CH	72	75	0:~100	47:53
CH <sub>3</sub>	H	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	70	66	1:99	19:81
CH <sub>3</sub>	H	CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>8</sub>	47	55	1:99	26:74
CH <sub>3</sub>	H	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	71	48	10:90	35:65
CH <sub>3</sub>	H	c-C <sub>6</sub> H <sub>11</sub>	70	44	14:86	— <sup>e</sup>
Pr	H	C <sub>6</sub> H <sub>5</sub>	75	66	2:98	48:52
Pr	H	ClC <sub>6</sub> H <sub>4</sub>	72	85	1:99	50:50
Pr	H	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	75	41	8:92	22:78

<sup>a</sup> The reaction of 1- or 3-substituted prop-2-ynyl mesylates (1.5 mmol) with aldehydes (1.0 mmol) was carried out using SnI<sub>2</sub> (2.0 mmol), TBAI (0.20 mmol) and NaI (2.0 mmol) in DMI (3 ml) at rt. <sup>b</sup> Yields of a mixture of **2** and **3**. <sup>c</sup> The ratios were determined by <sup>1</sup>H NMR analysis (JEOL A-500). For the ratio of syn to anti, see ref. 8. <sup>d</sup> The reaction was carried out in the presence of MS 4Å in THF. <sup>e</sup> The ratio was not confirmed.



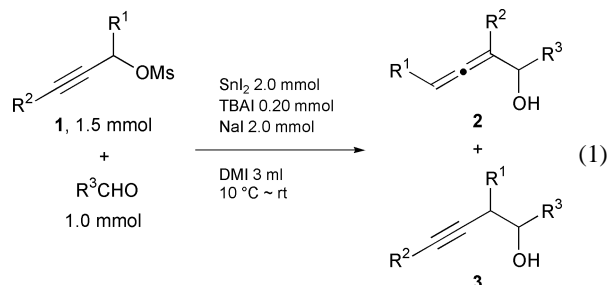
Scheme 1 Allenylation.



Scheme 2 Propargylation.

report on selective Barbier-type carbonyl propargylation and allenylation mediated by steric effects, using the 1- or 3-substituted prop-2-ynyl mesylates<sup>‡</sup> as Barbier-type propargylating or allenylating reagents, rather than the more usual corresponding halides (1-haloprop-2-ynes), because the mesylates are superior to the halides for ease of preparation and the stability of propargylic substrates.<sup>11</sup>

The reaction of prop-2-ynyl mesylate (**1**;  $R^1, R^2 = H$ ) with some aldehydes was carried out using  $\text{SnI}_2$ , TBAI and NaI under the same conditions as those reported for the carbonyl allenylation by 1-chloroprop-2-yne [eqn. (1)].<sup>8</sup> The results are



summarized in Table 1. Prop-2-ynyl mesylate (**1**;  $R^1, R^2 = H$ ) proved to be as available as 1-chloroprop-2-yne for the selective

carbonyl allenylation with  $\text{SnI}_2$  and TBAI. Thus, we investigated whether the 1- or 3-substituents of prop-2-ynyl mesylates affect the selectivity between propargylation and allenylation under the same conditions as those of prop-2-ynyl mesylate (**1**;  $R^1, R^2 = H$ ) [eqn. (1)]. The results are summarized in Table 2. 3-Substituted prop-2-ynyl mesylates (**1**;  $R^1 = H, R^2 = \text{CH}_3$  and  $R^1 = H, R^2 = \text{C}_6\text{H}_5$ ) caused the same allenylation of various aldehydes as that of **1** ( $R^1, R^2 = H$ ). In particular, with aromatic aldehydes, only allenyl carbinols **2** were obtained. The reaction of cinnamaldehyde in DMI afforded 1-phenylhexa-1,3-dien-5-one derivatives that were probably formed by the hydration of the corresponding allenyl carbinols **2** ( $R^2 = \text{CH}_3, \text{C}_6\text{H}_5$ ) followed by dehydration.<sup>4,8</sup> 1-Substituted prop-2-ynyl mesylate (**1**;  $R^1 = \text{CH}_3, R^2 = H$  and  $R^1 = \text{Pr}, R^2 = H$ ) caused the preferential propargylation of various aldehydes. The selectivity for this propargylation was enhanced by the use of THF– $\text{H}_2\text{O}$  (1 : 1) as a solvent instead of DMI:  $R^1 = \text{CH}_3, R^2 = H, R^3 = \text{C}_6\text{H}_5$ ; rt, 72 h; 92%, **2** : **3** = 0 : ~100, *syn:anti* = 46 : 54.

A plausible mechanism for the allenylation is illustrated in Scheme 1. 3-Substituent  $R^2$  ( $\text{CH}_3$  or  $\text{C}_6\text{H}_5$ ), being bulkier than H, probably prohibits propargyltin intermediate **A** from isomerizing to allenyltin intermediate **B**. Thus allenyl carbinols **2** are produced more selectively than in the allenylation by prop-2-ynyl mesylate (**1**;  $R^1, R^2 = H$ ), via nucleophilic addition of the propargyltin **A** at the  $\gamma$ -position.<sup>8</sup> A plausible mechanism for the propargylation is illustrated in Scheme 2. 1-Substituent  $R^1$  ( $\text{CH}_3$  or Pr) probably promotes the isomerization of the initially prepared propargyltin **C** to allenyltin **D**, even at room temperature, or mediates a direct preparation of allenyltin **D**.<sup>§</sup> The allenyltin **D** then undergoes nucleophilic addition to aldehydes at the  $\gamma$ -position to afford homopropargyl alcohols **3**.

## Notes and references

<sup>†</sup> E-mail: y-masuya@hoffman.cc.sophia.ac.jp

<sup>‡</sup> The 1- or 3-substituted prop-2-ynyl mesylates were prepared from 1- or 3-substituted prop-2-yn-1-ols and methanesulfonyl chloride with triethylamine in ether on an ice-bath. 1-Phenylprop-2-ynyl mesylate was not prepared under the conditions described above: see I. S. Aidhen and R. Braslau, *Synth. Commun.*, 1994, **24**, 789.

<sup>§</sup> It was shown by  $^1\text{H}$  NMR analysis (JEOL A-500) that the reaction of 1-methylprop-2-ynyl mesylate with  $\text{SnI}_2$  and NaI in  $\text{DMF-d}_7$  produced 3-methylprop-1,2-dienyltriiodotin **D** ( $R^1 = \text{CH}_3$ ) at 25 °C;  $\delta$  1.73 (dd,  $J = 7.2, 2.6$  Hz, 3H), 5.21 (quintet,  $J = 6.7$  Hz, 1H), 6.09 (dq,  $J = 5.6, 2.6$  Hz, 1H).

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