

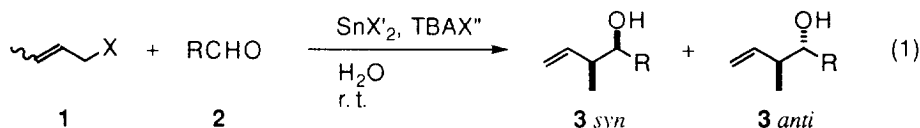
## $\gamma$ -Syn-Selective Carbonyl Allylation by 1-Bromo-2-butene with Tin(II) Iodide and Tetrabutylammonium Bromide

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**Abstract:** (*E*)-rich 1-Bromo-2-butene preferentially caused  $\gamma$ -syn-allylation of aldehydes with tin(II) iodide and tetrabutylammonium bromide (or iodide) in THF-H<sub>2</sub>O or 1,3-dimethyl-2-imidazolidinone-H<sub>2</sub>O to produce 1-substituted syn-2-methyl-3-buten-1-ols. Copyright © 1996 Elsevier Science Ltd

Barbier-type carbonyl allylation by (*E*)- $\gamma$ -substituted allylmetal reagents, derived from (*E*)- $\gamma$ -substituted allylic halides with metals or metal halides, usually makes anti-diastereoselective addition at  $\gamma$ -position of the allylmetal reagents to aldehydes:  $\gamma$ -anti-selective carbonyl allylation.<sup>1</sup>  $\gamma$ -Syn-selective carbonyl allylation by (*E*)- $\gamma$ -substituted allylmetal reagents has only been attained by the addition of (*E*)- $\gamma$ -substituted allylic trialkylsilanes and trialkylstannanes to aldehydes in the presence of Lewis acids.<sup>1</sup> Allylic trichlorotin intermediates, derived from (*E*)- $\gamma$ -substituted allylic alcohols and tin(II) chloride in the presence of a catalytic amount of PdCl<sub>2</sub>(PhCN)<sub>2</sub>, have caused highly controlled  $\gamma$ -anti-addition to aldehydes in polar solvents such as THF-H<sub>2</sub>O and 1,3-dimethyl-2-imidazolidinone.<sup>2</sup> (*E*)-rich 1-Bromo-2-butene has been applied to either  $\alpha$ - or  $\gamma$ -regiocontrolled carbonyl allylation with tin(II) bromide, in which  $\gamma$ -anti-selectivity is lower than that with tin(II) chloride.<sup>3,5</sup> We thus hoped that halogens in  $\gamma$ -substituted allylic tin intermediates, prepared from  $\gamma$ -substituted allylic halides and tin(II) halides, could influence diastereoselection in the  $\gamma$ -regioselective carbonyl allylation. We here report the *first Barbier-type  $\gamma$ -syn-selective carbonyl allylation by (*E*)-rich 1-bromo-2-butene with tin(II) iodide and tetrabutylammonium bromide (or iodide).*



Diastereoselection in the  $\gamma$ -regioselective allylation of benzaldehyde by (*E*)-rich 1-halo-2-butene (**1**)<sup>6</sup> was investigated with tin(II) halides (SnX'<sub>2</sub>) and tetrabutylammonium halides (TBAX'')<sup>3,7</sup> in polar solvents such as THF, DMF and 1,3-dimethyl-2-imidazolidinone (DMI) (eq 1).<sup>8,9</sup> The results are summarized in Table 1. The carbonyl allylation using (*E*)-1-chloro-2-butene (**1**; X=Cl) and SnCl<sub>2</sub> occurred neither with nor without TBACl (entry 1). The carbonyl allylation by (*E*)-rich 1-bromo-2-butene (**1**; X=Br) with SnI<sub>2</sub> proceeded with syn-selectivity (entry 6). The same allylation proceeded with anti-selectivity in the case of SnCl<sub>2</sub> (entry 2).<sup>10</sup>

**Table 1** Allylation of Benzaldehyde by **1** with Tin(II) Halides<sup>a</sup>

entry	X	X'	X''	solvent	time (h)	<b>3</b> (R=Ph)	
						yield (%) <sup>b</sup>	syn : anti <sup>c</sup>
1	Cl	Cl	Cl	THF	24	N. R.	---
2	Br	Cl	--- <sup>d</sup>	THF	24	63	16 : 84
3	Br	Cl	Br	THF	24	58	52 : 48
4	Br	Br	--- <sup>d</sup>	THF	22	75	42 : 58
5	Br	Br	Br	THF	22	68	77 : 23
6	Br	I	--- <sup>d</sup>	THF	15	55	73 : 27
7	Br	I	Br	THF	15	78	84 : 16
8	Br	I	Br	THF <sup>e</sup>	24	52	51 : 49
9	Br	I	Br	DMF	17	72	84 : 16
10	Br	I	Br	DMI	17	90	81 : 19
11	I <sup>f</sup>	I	I	DMI	17	88	87 : 13

<sup>a</sup>The allylation of benzaldehyde (1 mmol) by **1** (1.5 mmol) was carried out with SnX'<sub>2</sub> (1.5 mmol) and TBAX'' (1.5 mmol) at room temperature in solvent (3 ml)-H<sub>2</sub>O (0.1 ml). <sup>b</sup>Isolated yields. <sup>c</sup>The ratio was determined by <sup>1</sup>H NMR (JEOL GX-270) and by GC (capillary column PEG 20M, 0.25 mm × 30 m). See ref. 12. <sup>d</sup>The reaction was carried out without TBAX''. <sup>e</sup>The reaction was carried out without H<sub>2</sub>O. <sup>f</sup>1-Iodo-2-butene, derived from 1-chloro-2-butene and NaI at 50 °C in DMI, was used *in situ*.

Addition of TBABr enhanced the syn-selectivity in the allylation with any SnX'<sub>2</sub> (entries 2-7).<sup>10</sup> Addition of a bit of water enhanced both the yield and the syn-selectivity (entries 7 and 8).<sup>11</sup> DMI is a superior solvent to THF with regard to yields of **3** (entries 7 and 10). The use of all iodides, namely 1-iodo-2-butene (**1**, X=I), SnI<sub>2</sub>, and TBAI, slightly enhanced the syn-selectivity in DMI (entries 10 and 11).

γ-Syn-selective allylations of various aldehydes were investigated with (*E*)-rich **1** (X=Br), SnI<sub>2</sub>, and TBAX'' at room temperature in THF-H<sub>2</sub>O or DMI-H<sub>2</sub>O, as shown in Table 2. Any aldehyde, such as aromatic aldehydes bearing either an electron-donating group or an electron-withdrawing group, aliphatic aldehydes, and α, β-unsaturated aldehydes, can be used to the syn-selective allylation. Use of TBAI instead of TBABr slightly enhanced both the yield and the syn-selectivity (entries 6 and 7).

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## REFERENCES AND NOTES

- For a review, see: Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207-2293.
- (a) Masuyama, Y. *J. Synth. Org. Chem., Jpn.* **1992**, *50*, 202-212; (b) Masuyama, Y. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, 1994; Vol. 3, pp. 255-303.

**Table 2**  $\gamma$ -Syn-Selective Carbonyl Allylation by **1** (X=Br) with SnI<sub>2</sub> and TBABr<sup>a</sup>

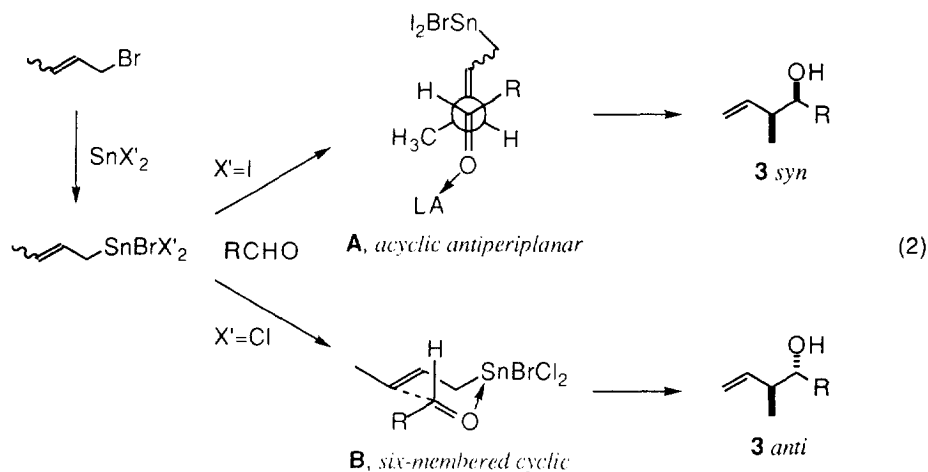
entry	R	solvent	time (h)	<b>3</b> , yield (%) <sup>b</sup>	syn : anti <sup>c</sup>
1	4-MeOC <sub>6</sub> H <sub>4</sub>	THF	64	69	85 : 15
2	4-ClC <sub>6</sub> H <sub>4</sub>	THF	18	65	84 : 16
3	4-MeOOCOC <sub>6</sub> H <sub>4</sub>	THF	24	57	85 : 15
4	4-NCC <sub>6</sub> H <sub>4</sub>	THF	19	73	87 : 13
5	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	THF	17	49	74 : 26
6	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	DMI	24	74	67 : 33
7 <sup>d</sup>	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	DMI	24	84	73 : 27
8	H <sub>2</sub> C=CH(CH <sub>2</sub> ) <sub>8</sub>	THF	19	58	86 : 14
9	( <i>E</i> )-C <sub>6</sub> H <sub>5</sub> CH=CH	THF	16	52	84 : 16
10	( <i>E</i> )-C <sub>6</sub> H <sub>5</sub> CH=CH	DMI	16	73	83 : 17

<sup>a</sup>The allylation of aldehydes (**2**, 1 mmol) by **1** (X=Br, 1.5 mmol) was carried out with SnI<sub>2</sub> (1.5 mmol) and TBABr (1.5 mmol) at room temperature in solvent (3 ml)-H<sub>2</sub>O (0.1 ml). <sup>b</sup>Isolated yields. <sup>c</sup>The ratio was determined by <sup>1</sup>H NMR (JEOL GX-270) and by GC (capillary column PEG 20M, 0.25 mm × 30 m). See ref. 12. <sup>d</sup>TBAI was used instead of TBABr.

- Masuyama, Y.; Kishida, M.; Kurusu, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 1405-1406.
- For carbonyl allylation by allylic bromides with tin(II) chloride or bromide, see: (a) Gambaro, A.; Peruzzo, V.; Plazzogna, G.; Tagliavini, G. *J. Organomet. Chem.* **1980**, *197*, 45-50; (b) Mukaiyama, T.; Harada, T.; Shoda, S. *Chem. Lett.* **1980**, 1507-1510.
- For carbonyl allylation by allylic bromides with tin, see: (a) Mukaiyama, T.; Harada, T. *Chem. Lett.* **1981**, 1527-1528; (b) Nokami, J.; Otera, J.; Sudo, T.; Okawara, R. *Organometallics* **1983**, *2*, 191-193.
- 1-Bromo-2-butene (**1**; X=Br, *E*:*Z*=85:15), which has been purchased from Tokyo Chemical Industry Co., Ltd., contains 14% 3-bromo-1-butene [(*E*)-**1**:(*Z*)-1:3-bromo-1-butene=ca.73:13:14]. (*E*)-1-Chloro-2-butene (**1**; X=Cl) was also purchased from Tokyo Chemical Industry Co., Ltd.
- Masuyama, Y.; Nakata, J.; Kurusu, Y. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2598-2599.
- A typical procedure of  $\gamma$ -syn-selective carbonyl allylation by 1-bromo-2-butene with tin(II) iodide and TBABr is as follows: To a solution of tin(II) iodide (0.56 g, 1.5 mmol) and TBABr (0.48 g, 1.5 mmol) in THF (3 ml) and water (0.1 ml) were added benzaldehyde (**2**; R=C<sub>6</sub>H<sub>5</sub>, 0.11 g, 1 mmol) and 1-bromo-2-butene (**1**; X=Br, 0.20 g, 1.5 mmol). The solution was vigorously stirred at room temperature for 15 h under a nitrogen atmosphere. The reaction mixture was poured into water (30 ml) and extracted with ether-dichloromethane (2/1, 100 ml). The extract was washed first with water and then with brine, and was dried over MgSO<sub>4</sub>. Evaporation of solvents and purification by preparative TLC (Harrison

centrifugal thin-layer chromatotron; Merck Kiesel-gel 60 PF<sub>254</sub> Art. 7749; hexane:ethyl acetate=10:1) and/or HPLC (Japan Analytical Industry Co., Ltd. LC-908; JAIGEL-2H; chloroform) afforded 2-methyl-1-phenyl-3-buten-1-ol (**3**; R=C<sub>6</sub>H<sub>5</sub>, 0.13 g, 78 %, syn:anti=84:16) as a colorless oil.

9. In the palladium-catalyzed allylation of benzaldehyde by (*E*)-2-buten-1-ol with tin(II) halides at room temperature in DMI, tin(II) bromide has lowered the yield (**3**; R=C<sub>6</sub>H<sub>5</sub>, 115 h, 22%, syn:anti=40:60) and tin(II) iodide has not functioned. Thus, allylic alcohols are probably impractical in the carbonyl allylation with tin(II) bromide or iodide.
10. The anti-selection in the use of SnCl<sub>2</sub> suggests a usual six-membered cyclic transition state **B** between (*E*)-2-butenyltin and aldehyde, that is, Lewis acidity of tin in 2-butenylbromodichlorotin (eq 2).<sup>2,12</sup> On the other hand, the syn-selection in the use of SnI<sub>2</sub> does not suggest a six-membered cyclic transition state but rather an acyclic antiperiplanar transition state **A**, because no (*Z*)-2-butenyltin intermediate has been prepared from (*E*)-rich 1-bromo-2-butene (eq 2). That is to say, weak Lewis acidity of tin in 2-butenylbromodiodotin, which is based on low electronegativity of iodine, is probably unable to promote the allylation via the six-membered cyclic transition state.<sup>11</sup> The enhancement of the syn-selection by the addition of TBABr can be explained by no Lewis acidity of the tin in pentacoordinate 2-butenyldibromodiodostannate.<sup>13</sup>



11. Tin(IV) compounds, prepared in the initial stage by the hydrolysis of products, 2-methyl-3-butenyloxybromodiodotins or 2-methyl-3-butenyloxydibromodiodostannate, may function as Lewis acids in the reaction of 2-butenylbromodiodotin or 2-butenyldibromodiodostannate, which is hard to form six-membered cyclic transition states.
12. Takahara, J. P.; Masuyama, Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2577-2586.
13. Pentacoordination of aromatic diolate or fluoride to silicon or tin of allylic silanes and tins usually promotes carbonyl allylations to lead to  $\gamma$ -anti-selection via six-membered cyclic transition states: (a) Sakurai, H. *Synlett* **1989**, 1-8; (b) Denmark, S. E.; Coe, D. M.; Pratt, N. E.; Griedel, B. D. *J. Org. Chem.* **1994**, *59*, 6161-6163, and references cited therein.

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