# *syn*-Diastereoselective carbonyl allylation by 1- or 3-substituted prop-2-en-1-ols with tin(II) iodide and tetrabutylammonium iodide

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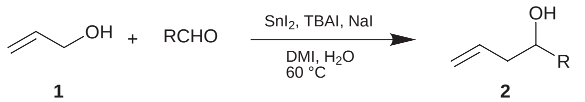
**1-Substituted or 3-substituted prop-2-en-1-ols cause *syn*-diastereoselective carbonyl allylation with tin(II) iodide and tetrabutylammonium iodide *via* the formation of 3-substituted prop-2-enylpolyiodotins to produce *syn*-1,2-disubstituted but-3-en-1-ols.**

Barbier-type carbonyl allylation is one of the most convenient methods for the introduction of allylic functions.[1] Allylic metal reagents in the allylation reaction are generated *in situ* from allylic halides, which are usually prepared from allylic alcohols in advance. Thus, it should be an important aim to generate allylic metal reagents from available and storable allylic alcohols directly. We have already reported carbonyl allylations by allylic alcohols with tin(II) chloride, which need a catalytic amount of palladium complexes such as $PdCl_2(PhCN)_2$, $Pd(PPh_3)_4$ and so on.[2] We here report that allylic alcohols serve as carbonyl allylating agents without the palladium complexes *via* the use of tin(II) iodide and tetrabutylammonium iodide (TBAI),[3] and that the carbonyl allylation by 1- or 3-substituted prop-2-en-1-ols with tin(II) iodide and TBAI exhibits *syn*-diastereoselectivity,[4] in contrast to the palladium-catalysed *anti*-diastereoselective carbonyl allylation by 3-substituted (*E*)-prop-2-en-1-ols with tin(II) chloride in 1,3-dimethylimidazolidin-2-one (DMI).[5]

Prop-2-en-1-ol (**1**) slowly caused allylation of benzaldehyde without palladium catalysts in the presence of tin(II) iodide, TBAI and NaI under the same conditions (namely at room temperature in DMI containing a small amount of $H_2O$) which gave the best results for the carbonyl allylation by allylic halides with tin(II) halides and tetrabutylammonium halides;[4] 15–20 °C, 166 h, 17% yield. When the temperature was raised to 60 °C, prop-2-en-1-ol (**1**) was amenable to the allylation of various aldehydes, as summarized in Table 1. Use of less than 2 equiv. of tin(II) iodide with respect to benzaldehyde lowered the yield ($SnI_2$ (2 mmol), 60 °C, 66 h, 61%). Tin(II) bromide slowed down the allylation of benzaldehyde (72 h, 38%), and no reaction occurred with tin(II) chloride, under the same conditions as those of the allylation with tin(II) iodide.

**Table 1** Carbonyl allylation by **1** with $SnI_2$, TBAI and NaI[a]



**1** **2**

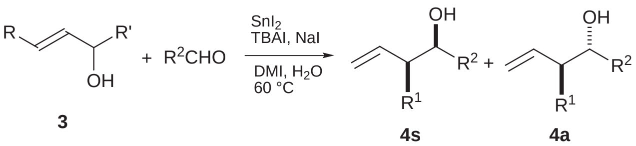
| R | *t*/h | Yield[b] of **2** (%) |
|---|---|---|
| Ph | 41 | 77 |
| 4-$MeC_6H_4$ | 54 | 55 |
| 4-$ClC_6H_4$ | 45 | 79 |
| $PhCH_2CH_2$ | 72 | 64 |
| *c*-$C_6H_{11}$ | 62 | 36 |
| $C_6H_{13}$ | 35 | 52 |
| $CH_2$=$CH(CH_2)_8$ | 46 | 54 |

[a] The allylation of aldehydes (1 mmol) by prop-2-en-1-ol (2 mmol) was carried out with $SnI_2$ (3 mmol), TBAI (0.25 mmol) and NaI (2.5 mmol) in DMI (3 ml) and $H_2O$ (0.1 ml) at 60 °C. [b] Isolated yields.

Diastereoselective allylation of benzaldehyde (1 mmol) by (*E*)-but-2-en-1-ol (**3**; R = Me, R′ = H, 2 mmol) was investigated with tin(II) iodide (3 mmol) and TBAI (1 mmol) at 60 °C in various solvents containing a small amount of $H_2O$; DMI (19 h, 74%, *syn*:*anti* = 83:17) is superior to other solvents (THF, 26 h, 74%, *syn*:*anti* = 83:17; DMF, 72 h, 18%, *syn*:*anti* = 67:33; $H_2O$, 72 h, 31%, *syn*:*anti* = 89:11; DMI without $H_2O$, 72 h, 25%, *syn*:*anti* = 71:29) for both reactivity and diastereoselectivity. The results in the diastereoselective carbonyl allylation by some 1- or 3-substituted prop-2-en-1-ols† with $SnI_2$, TBAI and NaI in DMI–$H_2O$ are summarized in Table 2. Allylic alcohols bearing an aliphatic group at the α- or γ-position can be applied to the *syn*-diastereoselective carbonyl allylation. In contrast, (*E*)-cinnamyl alcohol bearing an aromatic group at the γ-position exhibits *anti*-selectivity, similar to the palladium-catalysed carbonyl allylation with tin(II) chloride.

The *syn*-diastereoselective carbonyl allylation by 1- or 3-substituted prop-2-en-1-ols, except (*E*)-cinnamyl alcohol, with tin(II) iodide and TBAI probably proceeds *via* (i) the transformation of the prop-2-en-1-ol into 1-substituted 3-iodoprop-1-ene **A**, which is then converted into 3-substituted prop-2-enylpolyiodotin **B**, and (ii) the formation of an acyclic antiperiplanar transition state **C** between 3-substituted prop-2-enylpolyiodotin **B**, in which the tin has no Lewis acidity, and an aldehyde, as shown in Scheme 1.[4]‡ The tin in (*E*)-cinnamylpolyiodotin, derived from (*E*)-cinnamyl alcohol with tin(II) iodide and TBAI, may have Lewis acidity owing to (σ–

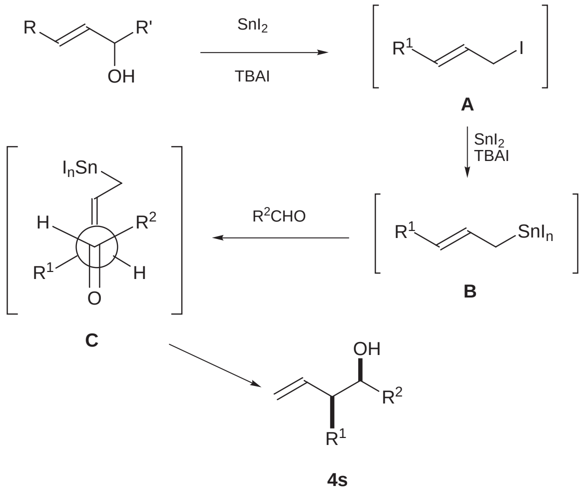
**Table 2** Diastereoselective carbonyl allylation with $SnI_2$, TBAI and NaI[a]



**3** **4s** *syn* **4a** *anti*

| Allylic alcohol | | | Product | | | Ratio[c] |
|---|---|---|---|---|---|---|
| R | R′ | *t*/h | R[1] | R[2] | Yield[b] of **4** (%) | **4s**:**4a** |
| Me | H | 47 | Me | Ph | 76 | 82:18 |
| Me | H | 65 | Me | 4-$MeC_6H_4$ | 50 | 81:19 |
| Me | H | 47 | Me | 4-$ClC_6H_4$ | 79 | 82:18 |
| Me | H | 71 | Me | $PhCH_2CH_2$ | 58 | 67:33 |
| Me | H | 72 | Me | *c*-$C_6H_{11}$ | 37 | 67:33 |
| Me | H | 46 | Me | $C_6H_{13}$ | 61 | 75:25 |
| Me | H | 78 | Me | $CH_2$=$CH(CH_2)_8$ | 56 | 78:22 |
| H | Me | 91 | Me | Ph | 51 | 82:18 |
| H | Me | 87 | Me | $C_6H_{13}$ | 45 | 77:23 |
| Ph | H | 24 | Ph | Ph | 49 | 1:99[d] |
| Pr | H | 48 | Pr | Ph | 80 | 70:30 |

[a] The allylation of aldehydes (1 mmol) by allylic alcohols (2 mmol) was carried out with $SnI_2$ (3 mmol), TBAI (0.25 mmol) and NaI (2.5 mmol) in DMI (3 ml) and $H_2O$ (0.1 ml) at 60 °C. [b] Isolated yields. [c] The ratio was determined by $^1H$ NMR spectroscopy (JEOL GX-270 or Λ-500) and/or GC (Capillary column PEG 20M 0.25 mm × 30 m). [d] See ref. 5.



Scheme 1

p)π conjugation between the tin–allylic carbon σ-bond and an electron-deficient olefinic β-carbon in the (*E*)-cinnamyl group.[6] Thus, (*E*)-cinnamylpolyiodotin probably causes *anti*-addition to aldehydes *via* the formation (coordination) of chair-like six-membered cyclic transition states.[2,5]

## Notes and references

† Starting allylic alcohols [prop-2-en-1-ol, (*E*)-but-2-en-1-ol, but-1-en-3-ol (*E*)-cinnamyl alcohol and (*E*)-hex-2-en-1-ol] were purchased from Tokyo Chemical Industry Co., Ltd.

‡ Allylic alcohol are known to cause α-regioselective carbonyl allylation with $Me_3SiCl$, NaI and $H_2O$–Sn (or $SnI_2$). (ref. 3). The tin intermediates in this reaction were assumed to be allylic (μ-iodo)ditin compounds. Since our reaction system contains an excess of iodides, triiodostannate is probably formed, preventing the formation of Sn–I–Sn bonds, and thus allylic (μ-iodo)ditin species. Thus, the thermodynamically stable γ-substituted allylic tin intermediate **B** probably causes the expected γ-addition to aldehyde to produce 1,2-disubstituted but-3-en-1-ol **4**.

1 For a review, see: Y. Yamamoto and N. Asao, *Chem. Rev.*, 1993, **93**, 2207.
2 For reviews of palladium-catalysed carbonyl allylation by allylic alcohols with tin(II) chloride, see: Y. Masuyama, *J. Synth. Org. Chem. Jpn.*, 1992, **50**, 202; Y. Masuyama, in *Advances in Metal-Organic Chemistry*, ed. L. S. Liebeskind, JAI Press, Greenwich, 1994, vol. 3, p. 255.
3 For an α-regioselective carbonyl allylation by allylic alcohols, see: Y. Kanagawa, Y. Nishiyama and Y. Ishii, *J. Org. Chem.*, 1992, **57**, 6988.
4 For a *syn*-diastereoselective carbonyl allylation by allylic halides with $SnI_2$ and TBAI, see: Y. Masuyama, M. Kishida and Y. Kurusu, *Tetrahedron Lett.*, 1996, **37**, 7103; Y. Masuyama, A. Ito and Y. Kurusu, *Chem. Commun.*, 1998, 315.
5 J. P. Takahara, Y. Masuyama and Y. Kurusu, *J. Am. Chem. Soc.*, 1992, **114**, 2577.
6 For *anti*-diastereoselective carbonyl allylation by (*E*)-cinnamyltributyltin or (*E*)-cinnamyltriphenyltin with $BF_3 \cdot Et_2O$ in $CH_2Cl_2$, see: M. Koreeda and Y. Tanaka, *Chem. Lett.*, 1982, 1299.

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