

Either γ -*syn*- or γ -*anti*-selective palladium-catalysed carbonyl allylation by mixed (*E*)- and (*Z*)-1,3-dichloropropene with tin(II) halides

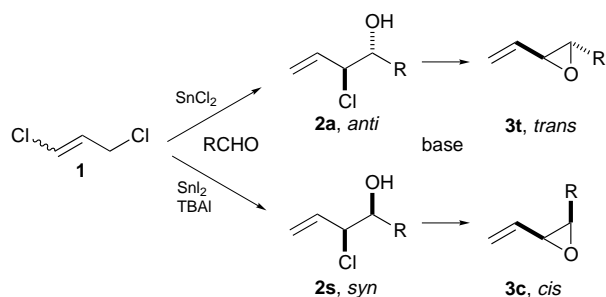
Yoshiro Masuyama,* Akihiro Ito and Yasuhiko Kurusu

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

Palladium-catalysed carbonyl allylations by mixed (*E*)- and (*Z*)-1,3-dichloropropene with $\text{SnI}_2\text{-Bu}_4\text{NI}$ and SnCl_2 diastereoselectively produce *syn* and *anti* 1-substituted 2-chlorobut-3-en-1-ols, respectively. These are transformed into *cis* and *trans* 1-substituted 2-vinyl epoxides.

Barbier-type carbonyl allylations by (*E*)- γ -substituted allylic metal reagents, derived from (*E*)- γ -substituted allylic halides with metals or metal halides, usually add *anti*-diastereoselectively at the γ -position of the allylic metal reagents to aldehydes; γ -*anti*-selective carbonyl allylation.¹ γ -*syn*-Selection is difficult for the Barbier-type carbonyl allylations by (*E*)- γ -substituted allylic metal reagents. We have found that halogens on the tin of but-2-enyltin reagents, prepared from (*E*)-rich 1-bromobut-2-ene and tin(II) halides, affect the diastereoselectivity in the γ -regioselective carbonyl allylation in THF–H₂O at room temperature; *anti*-selection with tin(II) chloride and *syn*-selection with tin(II) iodide–tetrabutylammonium bromide (or iodide).² We thus hoped that palladium-catalysed carbonyl allylation³ by (*E*)-rich 3-chloroprop-2-enyltin reagents, derived from (*E*)- and (*Z*)-mixed 1,3-dichloropropene (**1**)† with SnCl_2 or $\text{SnI}_2\text{-Bu}_4\text{NI}$ via the formation of 1-chloro-*syn*- π -allylpalladium complex, could lead to halogen-coordination controlled diastereoselectivity to produce diastereo-defined 1-substituted 2-chlorobut-3-en-1-ols, which could be transformed into the corresponding 1-substituted 2-vinyl epoxides (Scheme 1).⁵

Diastereoselectivity in the allylation of benzaldehyde by (*E*)- and (*Z*)-mixed 1,3-dichloropropene (**1**) in 1,3-dimethylimidazolidin-2-one (DMI)–H₂O‡ was investigated with tin(II) halides (SnX_2) and tetrabutylammonium halides (TBAX'). To a solution of SnX_2 (2.0 mmol) and TBAX' (2.0 mmol) in DMI (3 ml)–H₂O (0.1 ml) in the presence or absence of a catalytic amount of $\text{PdCl}_2(\text{PhCN})_2$ (0.02 mmol) was added **1** (2.0 mmol), and the solution was stirred at room temperature for 24 h. Benzaldehyde (1.0 mmol) was added to the solution, which was then stirred at room temperature. After the usual work-up, 2-chloro-1-phenylbut-3-en-1-ol (**2**, R=Ph) was obtained. The results are summarized in Table 1. The palladium-catalysed carbonyl allylation with SnCl_2 in DMI without H₂O led to usual *anti*-selectivity.³ For addition of TBAX', the carbonyl allylation with SnBr_2 or SnI_2 proceeded without any palladium catalyst. Use of either iodide (SnI_2 or TBAI) enhanced both the yield and the *syn*-selectivity. Addition of a catalytic amount of



Scheme 1

Table 1 Allylation of benzaldehyde by 1,3-dichloropropene (**1**)

X	X'	t/h	Yield ^a of 2 (R = Ph) (%)	2s : 2a ^b
Cl ^c	^d	24	88	41 : 59
Cl ^e	^d	65	70	22 : 78
Br	Br	130	22	46 : 54
Br	I	125	87	85 : 15
I	Br	121	66	90 : 10
I	I	122	63	92 : 8
I ^c	I	70	65	91 : 9
I ^c	I ^f	71	65	92 : 8

^a Isolated yields. ^b The ratio was determined by ¹H NMR spectroscopy (JEOL GX-270). ^c $\text{PdCl}_2(\text{PhCN})_2$ as a catalyst was added. ^d No TBAX' was used. ^e The reaction was carried out without H₂O at 0 °C. ^f TBAI (0.2 mmol) and NaI (2.0 mmol) were used.

$\text{PdCl}_2(\text{PhCN})_2$ accelerated the carbonyl allylation with SnI_2 and TBAI without lowering the *syn*-selectivity. The reaction with NaI accompanied by a catalytic amount of TBAI exhibited the same reactivity and selectivity as those of the reaction with an equimolar amount of TBAI to **1**.

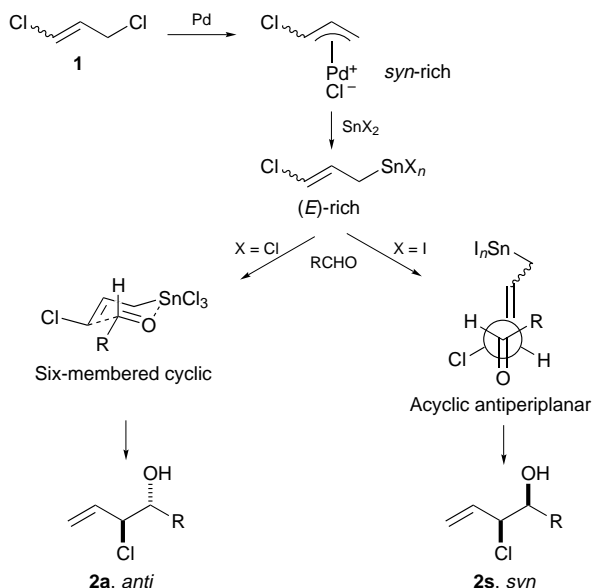
Either *syn*- or *anti*-selective palladium-catalysed allylations of various aldehydes by **1** were carried out with $\text{SnI}_2\text{-TBAI}$ –

Table 2 Diastereoselective carbonyl allylation by **1**^a

Table 2 provides the diastereoselective carbonyl allylation of various aldehydes (**1**) to yield *syn*-2-chlorobut-3-en-1-ol (**2s**) and *anti*-2-chlorobut-3-en-1-ol (**2a**). The reaction conditions are defined as follows:
A: (1) Pd/SnCl_2 , DMI, room temp., 24 h; (2) RCHO, 0 °C
B: (1) Pd/SnI_2 , DMI–H₂O, room temp., 24 h; (2) TBA–NaI, room temp., 3 h; (3) RCHO

R	Method	t/h	Yield ^b of 2 (%)	2s : 2a ^c
4-ClC ₆ H ₄	A	70	74	14 : 86
4-ClC ₆ H ₄	B	71	80	93 : 7
4-NCC ₆ H ₄	A	71	71	15 : 85
4-NCC ₆ H ₄	B	68	72	91 : 9
4-H ₃ CC ₆ H ₄	A	62	58	20 : 80
4-H ₃ CC ₆ H ₄	B	72	49	91 : 9
3,4-(CH ₂ O) ₂ C ₆ H ₃	A	78	56	24 : 76
3,4-(CH ₂ O) ₂ C ₆ H ₃	B	97	24	93 : 7
(<i>E</i>)-C ₆ H ₅ CH=CH	A	72	78	15 : 85 ^a
(<i>E</i>)-C ₆ H ₅ CH=CH	B	96	53	77 : 23 ^d
C ₆ H ₅ CH ₂ CH ₂	A	71	58	32 : 68
C ₆ H ₅ CH ₂ CH ₂	B	96	64	76 : 24
CH ₃ (CH ₂) ₅	A	93	48	36 : 64
CH ₃ (CH ₂) ₅	B	95	48	84 : 16
CH ₂ =CH(CH ₂) ₈	A	70	62	26 : 74
CH ₂ =CH(CH ₂) ₈	B	94	63	78 : 22

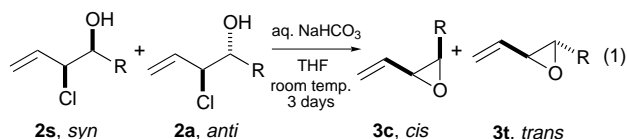
^a The allylation of aldehydes (1.0 mmol) by **1** (2.0 mmol) was carried out with $\text{PdCl}_2(\text{PhCN})_2$ (0.02 mmol), SnX_2 (2.0 mmol), TBAI (0.2 mmol) and NaI (2.0 mmol) in DMI (3 ml) and H₂O (0.1 ml). ^b Isolated yields. ^c The ratio was determined by ¹H NMR spectroscopy (JEOL GX-270). ^d The ratios (*cis* : *trans*) refer to the corresponding vinyl epoxides.



Scheme 2 Plausible mechanism in either γ -*syn*- or γ -*anti*-selective palladium-catalysed carbonyl allylation by mixed (*E*)- and (*Z*)-1,3-dichloropropene (**1**)

NaI and SnCl₂ in DMI–H₂O and DMI, respectively, as shown in Table 2. Any aldehyde, such as aromatic aldehydes bearing either an electron-donating group or an electron-withdrawing group, α,β -unsaturated aldehydes, and aliphatic aldehydes, can be used for the diastereo-defined carbonyl allylation. 1-Substituted 2-chlorobut-3-en-1-ols **2**, which are chlorohydrins, were transformed into the corresponding 1-substituted 2-vinyl epoxides **3** with aqueous NaHCO₃–THF solution in 70–90% yields [reaction (1)]. The *cis*:*trans* ratios of **3** were similar to the *syn*:*anti* ratios of **2**.[§]

The *anti*-selection with SnCl₂ probably occurs *via* the usual six-membered cyclic transition states (coordination) between (*E*)-rich 3-chloroprop-2-enyltrichlorotin, derived from *syn*-rich 1-chloro- π -allylpalladium chloride and tin(II) chloride, and aldehydes.¹ The coordination suggests high Lewis acidity of tin



in (*E*)-3-chloroprop-2-enyltrichlorotin, as shown in Scheme 2. However, *syn*-selectivity with SnI₂–TBAI (–NaI) probably occurs *via* acyclic antiperiplanar transition states between pentacoordinate 3-chloroprop-2-enyltetraiodotin, in which the tin has no Lewis acidity, and aldehydes.² The *syn*-selection *via* the acyclic antiperiplanar transition state is independent of the olefinic geometry of 3-chloroprop-2-enyltin intermediate, in contrast to the *anti*-selection *via* the six-membered cyclic transition state.¹ Thus the *syn*-selectivity with SnI₂–TBAI is probably superior to the *anti*-selectivity with SnCl₂.

Notes and References

* E-mail: y-masuya@hoffman.cc.sophia.ac.jp

† 1,3-Dichloropropene (**1**, *E*:*Z* = 48:52) was purchased from Tokyo Chemical Industry Co.

‡ DMI–H₂O is a most effective solvent in *syn*-selective carbonyl allylation by 1-chlorobut-2-ene with SnI₂–TBAI.

§ The *syn* (**2s**) and *anti* (**2a**) structures were determined by the ratios and structures of the *cis*- (**3c**) and *trans*-epoxides (**3t**). The *cis* (**3c**) and *trans* (**3t**) structures of the epoxides were determined from the coupling constants of vicinal protons of the epoxides in ¹H NMR spectra (JEOL GX-270); $J_{cis} = 4.27$ – 4.28 and $J_{trans} = 2.03$ – 2.45 Hz.⁵

1 For a review, see: Y. Yamamoto and N. Asao, *Chem. Rev.*, 1993, **93**, 2207.

2 Y. Masuyama, M. Kishida and Y. Kurusu, *Tetrahedron Lett.*, 1996, **37**, 7103.

3 For palladium-catalysed carbonyl allylation, 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.

4 For carbonyl allylation by (*Z*)-rich 1-chloro-3-iodoprop-1-ene with tin(II) chloride, see: J. Auge and S. David, *Tetrahedron Lett.*, 1983, **24**, 4009.

5 S. Hu, S. Jayaraman and A. C. Oehlschlager, *J. Org. Chem.*, 1996, **61**, 7513 and references cited therein.

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