

2-Phenylthioallylation of Aldehydes with Allyl Phenyl Sulfides via Dibromination, Followed by Dehydrobromination

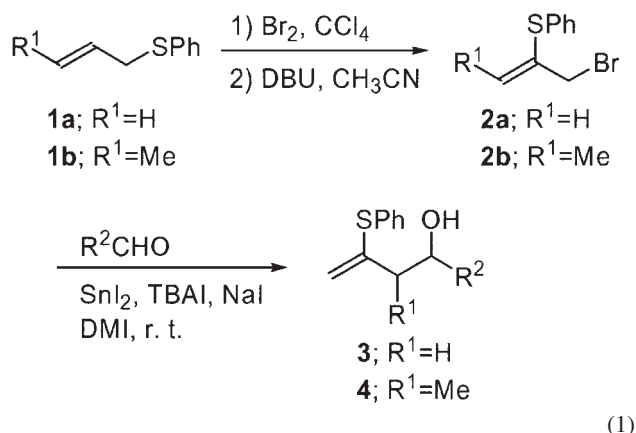
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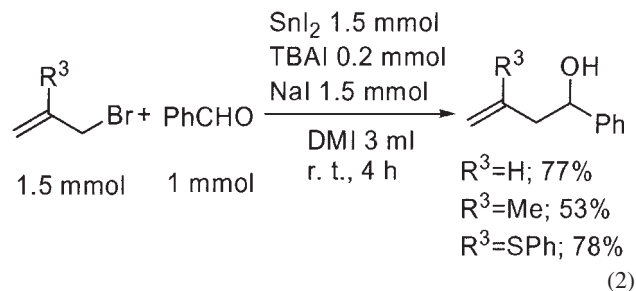
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2-Phenylthioallyl bromides, derived from allyl phenyl sulfides via dibromination, followed by dehydrobromination, cause the 2-phenylthioallylation of aldehydes with tin(II) iodide, tetrabutylammonium iodide and sodium iodide in 1,3-dimethylimidazolidin-2-one to produce the corresponding 1-substituted 3-phenylthiohomomallyl alcohols.

Barbier-type carbonyl allylation is one of the most convenient methods for introducing allylic functions.¹ (*E*)-2-Butenylmetals, prepared from (*E*)-1-halo-2-butene under Barbier conditions, usually cause γ -*anti*-selective addition to aldehydes. Our (*E*)-2-butenyltrichlorotin, derived from (*E*)-2-buten-1-ol with palladium catalysts and tin(II) chloride in 1,3-dimethylimidazolidin-2-one (DMI), also exhibits γ -*anti*-selectivity.² We recently found that tin(II) iodide–tetrabutylammonium iodide (TBAI) combo-reagent functions effectively without palladium catalysts for Barbier-type carbonyl allylations by allyl alcohols or chlorides.^{3,4} Carbonyl allylation by (*E*)-2-butenylpolyiodotin, derived from either (*E*)-2-buten-1-ol or (*E*)-1-chloro-2-butene with SnI₂–TBAI/NaI in DMI–H₂O, leads to γ -*syn*-selection, which is unprecedented under Barbier conditions. The difference of diastereoselection between (*E*)-2-butenyltrichlorotin and (*E*)-2-butenylpolyiodotin can be explained by the Lewis acidity of tin in these 2-butenyltins. The Lewis acidity of tin in (*E*)-2-butenylpolyiodotin is probably low because of the low electronegativity value of the iodide ligand. Therefore, (*E*)-2-butenylpolyiodotin may disfavor the formation of a usual six-membered cyclic transition state with aldehyde, and may slowly make a nucleophilic attack on aldehyde via an acyclic antiperiplanar transition state without Lewis acids, to exhibit γ -*syn*-selectivity. We hoped that an enhancement of the electron density on the γ -carbon of allyltins would promote carbonyl allylation via the acyclic antiperiplanar transition state. We report on the influence of the 2-phenylthio group on the reactivity and diastereoselectivity for carbonyl allylation by 2-phenylthioallyl bromides **2**, derived from allyl phenyl sulfides **1** via dibromination, followed by dehydrobromination, under Barbier conditions using SnI₂–TBAI (Eq. 1).



Carbonyl allylation by 3-bromo-2-phenylthio-1-propene (**2a**), derived from allyl phenyl sulfide (**1a**) via dibromination, followed by dehydrobromination, was investigated with SnI₂, TBAI, and NaI under the same conditions as those for the usual allylic halides.⁴ The reactivity of the carbonyl allylations by allylic trihalotins is usually affected by the bulkiness of β -substituents of the allylic trihalotins.² The reactivity of **2a** in the allylation of benzaldehyde is almost the same as that of 3-bromo-1-propene, in contrast to the low reactivity of 3-bromo-2-methyl-1-propene (Eq. 2). The results of carbonyl allylations with **2a** are summarized in Table 1. Aromatic aldehydes bearing an electron-donating or electron-withdrawing group, α , β -unsaturated aldehydes, and aliphatic aldehydes can be employed for carbonyl allylations.



Regioselection and diastereoselection in carbonyl allylation by 1-bromo-2-phenylthio-2-butene (**2b**),⁵ derived from 2-butenyl phenyl sulfide (**1b**) via dibromination, followed by dehydrobromination, were investigated under the same conditions

Table 1. Carbonyl Allylation by **2a** with SnI₂, TBAI, and NaI^{a)}

R ²	Time/h	Product	Yield/% ^{b)}
Ph	4	3a	79
4-MeC ₆ H ₄	13	3b	67
4-ClC ₆ H ₄	11	3c	83
2-Furyl	16	3d	86
PhCH=CH	13	3e	64
PhCH ₂ CH ₂	24	3f	60
<i>n</i> -C ₆ H ₁₃	16	3g	53
<i>c</i> -C ₆ H ₁₁	46	3h	33

a) The allylation of aldehydes (1.0 mmol) by **2a** (1.5 mmol) was carried out with SnI₂ (1.5 mmol), TBAI (0.2 mmol), and NaI (1.5 mmol) at room temperature in DMI (3 mL). b) Isolated yields.

Table 2. *syn*-Diastereoselective Carbonyl Allylation by **2b**^{a)}

R ²	Time/h	Product	Yield/% ^{b)}	<i>syn:anti</i> ^{c)}
Ph	11	4a	43	93:7
4-MeC ₆ H ₄	20	4b	42	95:5
4-ClC ₆ H ₄	19	4c	60	93:7
PhCH=CH	21	4d	46	94:6
PhCH ₂ CH ₂	46	4e	46	99:1
<i>n</i> -C ₆ H ₁₃	20	4f	31	82:18
H ₂ C=CH(CH ₂) ₈	20	4g	32	93:7
<i>c</i> -C ₆ H ₁₁	39	4h	43	91:9

a) The allylation of aldehydes (1.0 mmol) by **2b** (2.0 mmol) was carried out with SnI₂ (2.0 mmol), TBAI (0.25 mmol), and NaI (2.0 mmol) at room temperature in DMI (3 mL).

b) Isolated yields. c) The ratio was determined by 500 MHz ¹H NMR (JEOL A-500). See Ref. 6.

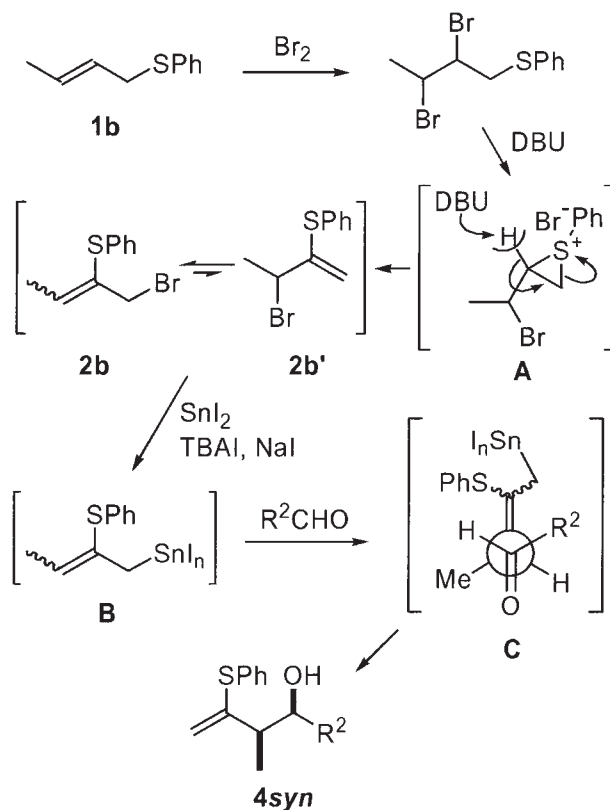
as those of **2a** (Eq. 1). The results are summarized in Table 2. The allylation of any used aldehyde occurred at the γ -position to the bromo group of **2b** accompanying *syn*-diastereoselectivity⁶ (γ -*syn*-selection), which is higher than that in carbonyl allylation by 1-chloro-2-butene or 2-buten-1-ol with SnI₂ and TBAI.^{3,4}

A plausible mechanism that explains the γ -*syn*-selection in the carbonyl allylation by **2b** derived from **1b** is shown in Scheme 1. 1-Bromo-2-phenylthio-2-butene (**2b**) may be formed via the formation of episulfonium bromide (A) after the bromination of **1b**, followed by the isomerization of **2b'** after the dehydrobromination of A. The allylic bromide **2b** may react with SnI₂, TBAI and NaI to produce 2-phenylthio-2-butenylpolyiodotin (B), which may cause γ -*syn*-addition to aldehyde via an acyclic antiperiplanar transition state (C).

Experimental

The Carbonyl Allylation by 3-Bromo-2-phenylthio-1-propene (2a), Derived from Allyl Phenyl Sulfide (1a) via Dibromination Followed by Dehydrobromination: 3-Bromo-2-phenylthio-1-propene (**2a**), which was prepared by the dibromination of allyl phenyl sulfide (**1a**) with bromine in CCl₄, followed by dehydrobromination of the resulting dibromide with DBU in acetonitrile, was roughly purified by column chromatography (silica gel, hexane:ethyl acetate = 15:1); 76–78% yields; 500 MHz ¹H NMR (CDCl₃): δ 4.02 (d, J = 0.92 Hz, 2H), 5.26 (s, 1H), 5.65 (t, J = 0.92 Hz, 1H), 7.31–7.39 (m, 3H), 7.45–7.48 (m, 2H). And then to the solution of benzaldehyde (1.0 mmol), SnI₂ (1.5 mmol), TBAI (0.2 mmol), and NaI (1.5 mmol) in DMI (3 mL) was immediately added **2a** (1.5 mmol) in DMI (1 mL). The solution was stirred at room temperature for 4 h. After the mixture had been worked up as usual, purification by column chromatography (Merck silica gel 60, hexane:ethyl acetate = 7:1) afforded 1-phenyl-3-phenylthio-3-buten-1-ol (**3a**, 0.20 g, 78%). IR (neat) 3421, 2924, 1607, 1583, 1475, 1439, 1024, 874, 748, 700 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 2.31 (br, 1H), 2.56–2.64 (m, 2H), 4.98 (dd, 1H, J = 8.0, 5.5 Hz), 5.02 (s, 1H), 5.23 (br, 1H), 7.23–7.26 (m, 1H), 7.28–7.36 (m, 7H), 7.44–7.47 (m, 2H). Anal. Found: C, 74.44; H, 6.31%. Calcd for C₁₆H₁₆OS: C, 74.96; H, 6.29%.

The structure of all other products was determined by IR, ¹H NMR, and elemental analysis (or HRMS for **3d** and **3g**). These materials for characterizations are available.



Scheme 1. A plausible mechanism.

References

- 1 Y. Yamamoto and N. Asao, *Chem. Rev.*, **93**, 2207 (1993).
- 2 Y. Masuyama, *J. Synth. Org. Chem., Jpn.*, **50**, 202 (1992); Y. Masuyama, in "Advances in Metal-Organic Chemistry," ed by L. S. Liebeskind, JAI Press, Greenwich (1994), Vol. 3, p. 255.
- 3 Y. Masuyama, T. Ito, K. Tachi, A. Ito, and Y. Kurusu, *Chem. Commun.*, **1999**, 1261.
- 4 A. Ito, M. Kishida, Y. Kurusu, and Y. Masuyama, *J. Org. Chem.*, **65**, 494 (2000).
- 5 *E:Z* = ca. 1:1, 500 MHz ¹H NMR (CDCl₃): δ 1.68 (2d, J = 6.5 Hz, 3H), 3.83 (2s, 2H), 5.80 (2q, J = 6.5 Hz, 1H). This crude **2b** includes 4.7% of 3-bromo-2-phenylthio-1-butene (**2b'**) [δ 1.91 (d, J = 7.0 Hz, 3H), 4.71 (q, J = 7.0 Hz, 1H), 5.06 (s, 1H), 5.64 (s, 1H)] and 22% of 3-bromo-1-phenylthio-2-butene [δ 2.28 (s, 3H), 3.66 (d, J = 7.0 Hz, 2H), 5.75 (t, J = 7.0 Hz, 1H)].
- 6 The diastereomer ratio of **4** was determined by 500 MHz ¹H NMR (JEOL A-500). The *syn* structure of **4a** was confirmed by the transformation into *syn*-2-methyl-1-phenyl-3-buten-1-ol; its ¹H NMR spectrum was consistent with that of an authentic sample.⁷ See: J. P. Takahara, Y. Masuyama, and Y. Kurusu, *J. Am. Chem. Soc.*, **114**, 2577 (1992). On the basis of the *syn*-diastereoselection for benzaldehyde, other aldehydes are presumed to undergo *syn*-allylation by **2b** with SnI₂–TBAI.
- 7 The transformation (reductive desulfurization) of **4a** into 2-methyl-1-phenyl-3-buten-1-ol was carried out with EtMgBr in the presence of a catalytic amount of NiCl₂(PPh₃)₂ in THF/Et₂O at room temperature. No exchange of phenylthio group with ethyl group occurred, in contrast with PhMgBr and BuMgBr. See: H. Okamura, M. Miura, and H. Takei, *Tetrahedron Lett.*, **1979**, 43.