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

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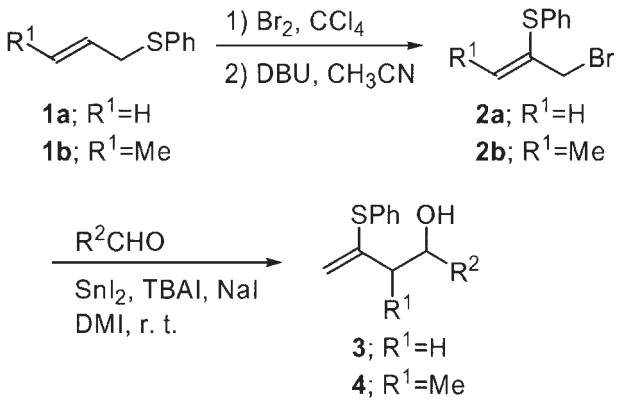
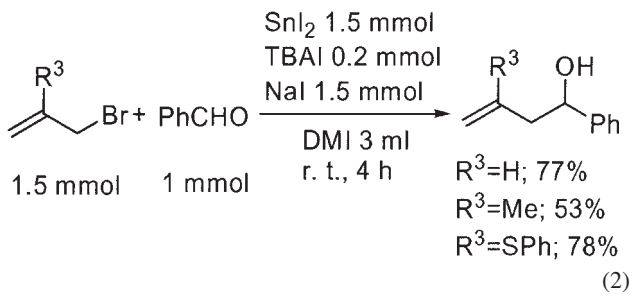
2-Phenylthioallyl bromides, derived from allyl phenyl sulfides via dibromination, followed by dehydrobromination, cause the 2-phenylthioallylation of aldehydes with tin(II) iodide, tetrabutylammonium iodide and sodium iodide in 1,3-dimethylimidazolidin-2-one to produce the corresponding 1-substituted 3-phenylthiohomoallyl 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 SnI_2–TBAI/NaI in DMI–H_2O, 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 SnI_2–TBAI (Eq. 1).



(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 SnI_2, 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.



(2)

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 SnI_2, TBAI, and NaI[a)]

R^2	Time/h	Product	Yield/%[b)]
Ph	4	**3a**	79
4-MeC_6H_4	13	**3b**	67
4-ClC_6H_4	11	**3c**	83
2-Furyl	16	**3d**	86
PhCH=CH	13	**3e**	64
$PhCH_2CH_2$	24	**3f**	60
n-C_6H_{13}	16	**3g**	53
c-C_6H_{11}	46	**3h**	33

a) The allylation of aldehydes (1.0 mmol) by **2a** (1.5 mmol) was carried out with SnI_2 (1.5 mmol), TBAI (0.2 mmol), and NaI (1.5 mmol) at room temperature in DMI (3 mL). b) Isolated yields.

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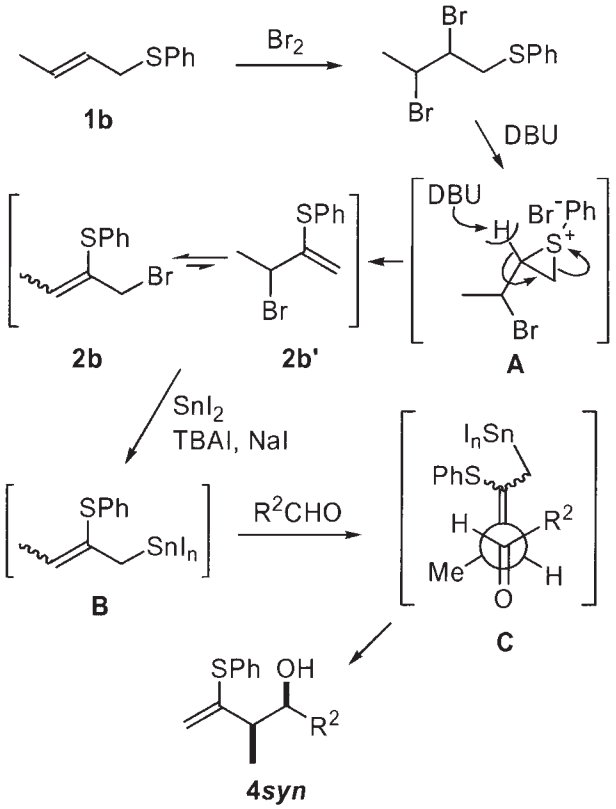
Table 2. *syn*-Diastereoselective Carbonyl Allylation by **2b**[a)]

R^2	Time/h	Product	Yield/%[b)]	*syn*:*anti*[c)]
Ph	11	**4a**	43	93:7
4-MeC_6H_4	20	**4b**	42	95:5
4-ClC_6H_4	19	**4c**	60	93:7
PhCH=CH	21	**4d**	46	94:6
$PhCH_2CH_2$	46	**4e**	46	99:1
n-C_6H_{13}	20	**4f**	31	82:18
$H_2C{=}CH(CH_2)_8$	20	**4g**	32	93:7
c-C_6H_{11}	39	**4h**	43	91:9

a) The allylation of aldehydes (1.0 mmol) by **2b** (2.0 mmol) was carried out with SnI_2 (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 ^{1}H NMR (JEOL Λ-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*-diastereoselectivity[6] (γ-*syn*-selection), which is higher than that in carbonyl allylation by 1-chloro-2-butene or 2-buten-1-ol with SnI_2 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 SnI_2, 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**).



Scheme 1. A plausible mechanism.

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 CCl_4, 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 ^{1}H NMR ($CDCl_3$): 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), SnI_2 (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}. ^{1}H NMR (500 MHz, $CDCl_3$) 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 $C_{16}H_{16}OS$: C, 74.96; H, 6.29%.

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

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5 *E*:*Z* = ca. 1:1, 500 MHz ^{1}H NMR ($CDCl_3$): 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 ^{1}H NMR (JEOL Λ-500). The *syn* structure of **4a** was confirmed by the transformation into *syn*-2-methyl-1-phenyl-3-buten-1-ol; its ^{1}H 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 SnI_2–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 $NiCl_2(PPh_3)_2$ in THF/Et_2O 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.