494 *J. Org. Chem.* **2000,** *65,* 494−498

Regio- and Diastereocontrol in Carbonyl Allylation by 1-Halobut-2-enes with Tin(II) Halides

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Received September 7, 1999

Regio- and diastereoselective carbonyl allylations of 1-halobut-2-enes with tin(II) halides are described. Tin(II) bromide in a dichloromethane−water biphasic system is an effective reagent for unusual α-regioselective carbonyl allylation of 1-bromobut-2-ene to produce 1-substituted pent-3-en-1-ols. The addition of tetrabutylammonium bromide (TBABr) to the biphasic system produces 1-substituted 2-methylbut-3-en-1-ols via usual γ-addition which is opposite to the α-addition without TBABr. The γ-addition to aromatic aldehydes exhibits *anti*-diastereoselectivity, while that to aliphatic aldehydes is not diastereoselective. The allylation of benzaldehyde by 1-chlorobut-2-ene in 1,3-dimethylimidazolidin-2-one (DMI) does not occur with tin(II) chloride or bromide but does proceed with tin(II) iodide and exhibits γ-*syn* selectivity which is unusual for a Barbier-type carbonyl allylation. In the carbonyl allylation by 1-chlorobut-2-ene with any tin(II) halide, the addition of tetrabutylammonium iodide (TBAI) accelerates the reaction and enhances γ-*syn* selectivity. The use of tin(II) iodide and TBAI produces 2-methyl-1-phenylbut-3-en-1-ol with high yield and high *syn*-diastereoselectivity. The *syn*-diastereoselective carbonyl allylation of 1-chlorobut-2-ene using tin(II) iodide, a catalytic amount of TBAI, and NaI in DMI−H_2O is applied to various aldehydes.

Introduction

The addition of γ-substituted allylmetal reagents to carbonyl compounds (carbonyl allylation) has been widely developed with regio- and stereocontrol in a conformationally nonrigid acyclic system.[1] Barbier-type carbonyl allylation is particularly useful due to ease of operation and the availability and tractability of allylic substrates, such as allylic halides,[1] esters,[2,3] and alcohols.[2,4] Carbonyl allylation via (*E*)-γ-substituted allylmetal reagents usually proceeds with γ-*anti* selectivity. Thus, it is important to develop conditions for carbonyl allylation which exhibits either α-regioselectivity or γ-*syn* selectivity, using (*E*)-γ-substituted allylmetal reagents. α-Regioselective carbonyl allylation has been achieved either with γ-substituted allylic halides−Mg/$AlCl_3$[5] or Ba[6] or with α- or γ-substituted allylic alcohols−Me_3SiCl/NaI/Sn.[7] γ-*Syn* selection has been attained by use of either γ-substituted allylic trialkylsilanes[8] and stannanes[9] in the presence of Lewis acids or (*Z*)-γ-substituted allylic metal reagents which are troublesome to prepare.[10] Neither α-regioselection nor γ-*syn* selection has been described for a Barbier-type carbonyl allylation system. In the course of the development of our γ-*anti*-selective palladium-catalyzed carbonyl allylation of allylic alcohols with tin(II) chloride under Barbier-type conditions,[2,4] we have found that nonpolar solvents lead to α-regioselection,[11] and a solvent such as DMSO which is strongly coordinating to the tin of an allylic tin leads to γ-*syn* selection.[12] However, in those reactions the rates are slow and the yields are low. Here, we report that a but-2-enyltin intermediate, prepared from 1-bromobut-2-ene with $SnBr_2$ at the interface of a nonpolar solvent such as CH_2Cl_2 and water, causes α-regioselective carbonyl allylation, while that prepared from 1-chlorobut-2-ene with tin(II) iodide, tetrabutylammonium iodide, and sodium iodide in polar solvents causes γ-*syn*- selective carbonyl allylation (Scheme 1).[13,14]

Results and Discussion

α-Regioselective Carbonyl Allylation on Dichloromethane−Water Biphasic System. The regioselectivity (α and γ) for producing homoallylic alcohols in palladium-catalyzed carbonyl allylation of but-2-en-1-ol with tin(II) chloride correlates with the dielectric constant of solvents; the lower the polarity of the solvents, the higher is the α-regioselectivity.[11,12] However, no allylations with tin(II) chloride occur in nonpolar solvents such as CH_2Cl_2 and $CHCl_3$. The results are probably attribut-

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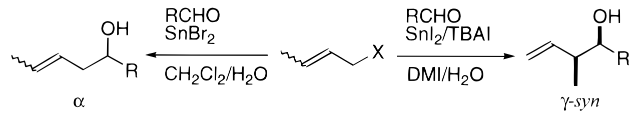
[12] Takahara, J. P.; Masuyama, Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2577.

[13] Preliminary report: Masuyama, Y.; Kishida, M.; Kurusu, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 1405.

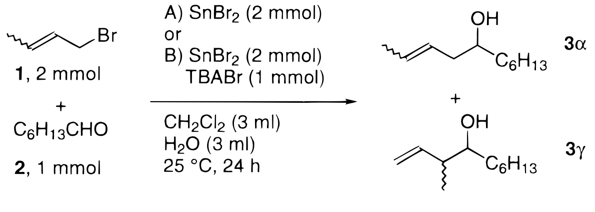
[14] Preliminary report: Masuyama, Y.; Kishida, M.; Kurusu, Y. *Tetrahedron Lett.* **1996**, *37*, 7103.

10.1021/jo991403o CCC: $19.00 © 2000 American Chemical Society
Published on Web 12/31/1999

Scheme 1



Scheme 2



	yield (%)	3α	:	3γ
method A	48	91		9
method B	83	9		91

able to the insolubility of tin(II) chloride in CH_2Cl_2 or $CHCl_3$. Tin(II) halides are soluble in water. Thus, we aimed at carbonyl allylation on biphasic system; the preparation of but-2-enyltin intermediate from 1-halobut-2-ene **1** and tin(II) halide at the interface of a nonpolar solvent, such as CH_2Cl_2, and water followed by the carbonyl allylation by the but-2-enyltin intermediate in CH_2Cl_2. The results of the allylation of heptanal on the biphasic system are illustrated with Scheme 2. No allylation of heptanal by 1-bromobut-2-ene (**1**; X = Br) with tin(II) bromide was observed at 25 °C in CH_2Cl_2. A dichloromethane–water biphasic system allowed the allylation by **1** (X = Br) with tin(II) bromide to proceed with high α-regioselectivity (method A), in contrast to the γ-regioselectivity in polar solvents such as DMF and 1,3-dimethylimidazolidin-2-one (DMI). Addition of tetrabutylammonium bromide (TBABr) promoted the biphasic allylation and reversed the regioselection (method B). The use of either tin(II) chloride instead of tin(II) bromide (25%, **3**α:**3**γ = 81:19) or the use of 1-chlorobut-2-ene (**1**; X = Cl) instead of 1-bromobut-2-ene (**1**; X = Br) (28%, **3**α:**3**γ = 65:35) depressed the reactivity and the α-regioselectivity in the biphasic allylation. The allylation also occurred in only water without a cosolvent and was α-regioselective (36%, **3**α:**3**γ = 77:23). The use of chloroform (78%, **3**α:**3**γ = 56:44) or ether (73%, **3**α:**3**γ = 13:87) instead of dichloromethane in the biphasic system enhanced the yield and lowered the α-regioselectivity.

The regioselective allylation of various aldehydes **2** by **1** (X = Br) with tin(II) bromide was carried out at 25 °C in dichloromethane–water either in the absence of TBABr (method A) or in the presence of TBABr (method B), as shown in Table 1. Most of the aldehydes, such as benzaldehyde, aromatic aldehydes bearing an electron-donating group, and aliphatic aldehydes can be used for both α- and γ-regioselective allylations (entries 1–14). This biphasic system is a method of greater utility for achieving α-regioselection since it is rarer than γ-regioselection. The allylation of benzaldehydes bearing electron-withdrawing groups such as chloro, methoxycarbonyl, and cyano groups exhibited no α-regioselection even in the absence of TBABr (entries 15, 17, and 19). 4-Chlorobenzaldehyde completely underwent γ-regioselective allylation without TBABr at 10 °C. On the other hand, the allylation of 4-chlorobenzaldehyde at 32–35 °C exhibited α-regioselectivity (entry 16). Strongly electron-withdrawing groups such as methoxycarbonyl and cyano did not lead to a remarkable inversion in regioselection (entries 18 and 20). The dependence of α-regioselection upon reaction temperature (10–35 °C) was thus investigated in the allylation of benzaldehyde by **1** (X = Br) on a dichloromethane–water biphasic system; as the reaction temperature rose, the α-regioselectivity was enhanced (10 °C, α:γ = 35:65; 23 °C, α:γ = 68:32; 35 °C, α:γ = 92:8). The α-regioselection using an aliphatic aldehyde, heptanal, was not influenced by reaction temperature over the range studied.

Plausible mechanisms, which explain the α-regioselection observed without TBABr and the γ-regioselection observed with TBABr are shown in Scheme 3. In the presence of more than one equimolar amount of TBABr, $SnBr_2$ is transformed into nucleophilic tetrabutylammonium tribromostannate (Bu_4N^+ $SnBr_3^-$) in H_2O. The tribromostannate probably reacts with 1-bromobut-2-ene in CH_2Cl_2 to produce but-2-enyltribromotin, which causes γ-addition to aldehyde via a six-membered cyclic chair transition state (**B**). On the other hand, in the absence of TBABr, slightly nucleophilic μ-bromoditin $[Br_2Sn-Br-SnBr_2]^-$ may be derived from $3SnBr_2$.[15] The reaction of the μ-bromoditin with 1-bromobut-2-ene at the CH_2Cl_2–H_2O interface may form a but-2-enyl(μ-bromo)ditin intermediate which causes α-regioselective carbonyl allylation via a chair-formed six-membered cyclic transition state (**A**) containing μ-bromoditin.

Influence of Halogens of But-2-enyltrihalotins upon Diastereoselection. The γ-regioselective carbonyl allylation by **1** (X = Br) with $SnBr_2$ and TBABr led to modest *syn*-diastereoselection, in contrast to usual *anti*-diastereoselection in the carbonyl allylation with $SnCl_2$,[12] as shown in Table 1. The influence of halogens on the tin of actual allylic reagents, but-2-enylpolyhalotins, upon the diastereoselection of the γ-regioselective allylation of benzaldehyde (**2**, R = Ph) by 1-halobut-2-enes **1** with tin(II) halides (SnX'_2) and tetrabutylammonium halides (TBAX″) was thus investigated.[16] The results are summarized in Table 2. The carbonyl allylation by **1** (X = Br, *E*:*Z* = 85:15) with $SnCl_2$ led to usual *anti*-selection (entry 1), and that with SnI_2 led to unusual *syn*-selection (entry 5). By adding the result of the carbonyl allylation with $SnBr_2$ (entry 3), the diastereoselection was presumed to be dependent upon the electronegativity of halogens of but-2-enyltrihalotins. Addition of TBABr enhanced the *syn*-selectivity in the carbonyl allylation with any SnX'_2 (entries 1–6). These results suggest that but-2-enyltin intermediates in the presence of TBABr are different from usual but-2-enyltrihalotins in the absence of TBABr; but-2-enyltin intermediates in the presence of TBABr may be pentacoordinated anionic but-2-enyltetrahalostannates. The use of TBAI instead of TBABr moreover enhanced the *syn*-selectivity (entries 7 and 8). Plausible mechanisms for either γ-*syn*- or γ-*anti*-selective carbonyl allylation by **1** (X = Br) are illustrated in Scheme 4.[17] The γ-*anti*-selective carbonyl allylation with $SnCl_2$ likely proceeds via the usual six-membered cyclic chair transition state (**C**) between (*E*)-but-2-enylbromodichlorotin and benzaldehyde (R = Ph), because the tin

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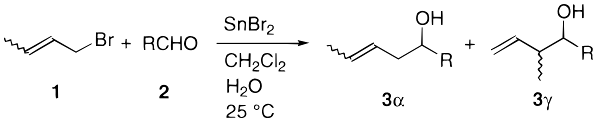
(16) For the γ-*syn*-selective carbonyl allylation by **1** (X = Br), see ref 14.

(17) For reaction mechanisms in γ-*syn*- or γ-*anti*-selective carbonyl allylations by but-2-enyltins, see reviews: Nishigaichi, Y.; Takuwa, A.; Naruta, Y.; Maruyama, K. *Tetrahedron* **1993**, *49*, 7395; Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31.

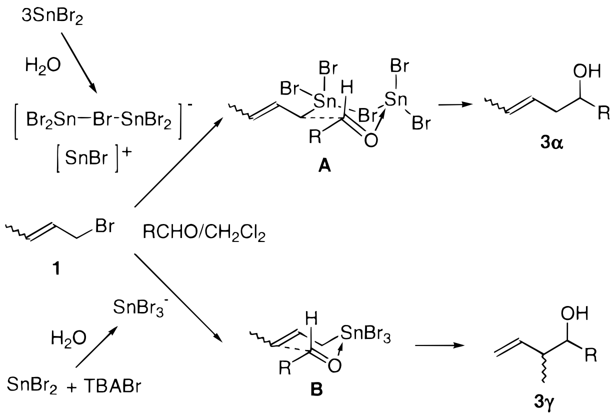
Table 1. Regioselective Allylation of Various Aldehydes by 1 (X = Br) with $SnBr_2$[a]



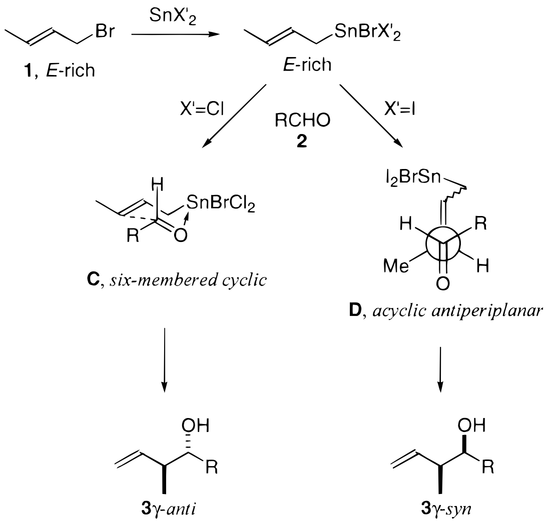
entry	R	method[b]	time (h)	yield[c] (%)	α (*E*:*Z*):γ(*syn*:*anti*)[d]
1	C_6H_5	A	24	60	94 (85:15):6 (90:10)
2	C_6H_5	B[e]	24	83	5 (89:11):95 (33:67)
3	$4\text{-}CH_3C_6H_4$	A	24	66	86 (97:3):14 (36:64)
4	$4\text{-}CH_3C_6H_4$	B[e]	24	70	10 (93:7):90 (31:69)
5	$C_6H_5CH_2CH_2$	A	24	61	92 (58:42):8(79:21)
6	$C_6H_5CH_2CH_2$	B	24	99	7 (62:38):93 (57:43)
7	C_6H_{13}	A	75	98	87 (64:36):13 (62:38)
8	C_6H_{13}	B	24	83	9 (62:38):91 (51:49)
9	$H_2C{=}CH(CH_2)_8$	A	24	68	92 (66:34):8 (79:21)
10	$H_2C{=}CH(CH_2)_8$	B[f]	25	75	1[g]:99 (53:47)
11	*c*-C_6H_{11}	A	50	76	92 (80:20):8 (28:72)
12	*c*-C_6H_{11}	B[f]	26	79	2[g]:98 (30:70)
13	$(CH_3)_3C$	A	31	60	89 (18:82):11[g]
14	$(CH_3)_3C$	B[e]	24	38	31 (37:63):69 (76:24)
15	$4\text{-}ClC_6H_4$	A	68	83	11 (50:50):89 (15:85)
16	$4\text{-}ClC_6H_4$	A[h]	48	38	87 (83:17):13 (37:63)
17	$4\text{-}CH_3OOCC_6H_4$	A	46	75	18 (77:23):82 (8:92)
18	$4\text{-}CH_3OOCC_6H_4$	A[h]	48	33	52 (61:39):48 (74:26)
19	$4\text{-}NCC_6H_4$	A	46	95	0:~100 (11:89)
20	$4\text{-}NCC_6H_4$	A[h]	48	36	25 (81:19):75 (51:49)

[a] The allylation of aldehydes (1 mmol) by 1-bromobut-2-ene (2 mmol) was carried out with $SnBr_2$ (2 mmol) in CH_2Cl_2 (3 mL) and H_2O (3 mL) at 25 °C. [b] A: Without TBABr. B: After the solution of **1** and $SnBr_2$ was stirred with TBABr (1 mmol) for 2 h, **2** was added. [c] Isolated yields. [d] The ratio was determined by ^1H NMR (JEOL GX-270) and by GC (capillary column PEG 20M, 0.25 mm × 30 m). [e] H_2O (6 mL) was used as a solvent. [f] CH_2Cl_2 (1 mL) and H_2O (5 mL) were used as solvents. [g] The ratio (*E*:*Z* or *syn*:*anti*) was not confirmed. [h] The reaction was carried out at 32–35 °C.

Scheme 3



Scheme 4



of but-2-enylbromodichlorotin is Lewis acidic.[12] In contrast, the γ-*syn*-selection with SnI_2 does not suggest a six-membered cyclic transition state, but rather an acyclic antiperiplanar transition state (**D**), because no (*Z*)-but-2-enyltin intermediate has been prepared from (*E*)-rich 1-bromobut-2-ene.[1] That is to say, the weak Lewis acidity of tin in but-2-enylbromodiiodotin, which is based on low electronegativity of iodine, probably disfavors the formation of the six-membered cyclic transition state.[18] The enhancement of the *syn*-selectivity by the addition of TBAI can be explained by non-Lewis acidity of tin in pentacoordinated anionic but-2-enylbromotriiodostannate.[19]

The carbonyl allylation by **1** (X = Cl) did not occur with $SnCl_2$ or $SnBr_2$ but with SnI_2 accompanied by *syn*-selectivity (entries 9, 12, and 15). The addition of TBABr or TBAI to the reaction conditions of entries 9 and 12 enabled the carbonyl allylation by **1** (X = Cl); TBAI particularly accelerated the allylation (entries 10, 11, 13, and 14). The combination of SnI_2 and TBAI led to high reactivity and high *syn*-selectivity in the carbonyl allylation by **1** (X = Cl) (entry 17). The allylation with a catalytic amount of TBAI and an equimolar amount of NaI to **1** (X = Cl) exhibited the same reactivity and *syn*-selectivity as those stoichiometric in TBAI (entry 18). The absence of water decreased both the yield and the *syn*-selectivity (entry 19). The allylation by **1** (X = Cl) with

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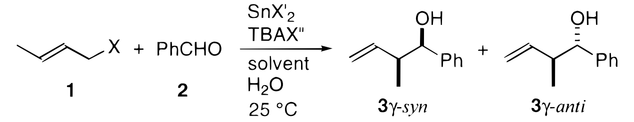
(18) Tin(IV) compounds, prepared in the initial stage by the hydrolysis of products, 2-methyl-1-phenylbut-3-enyloxybromodiiodotin, may function as a Lewis acid in the reaction of but-2-enylbromodiiodotin which is hard to form by the six-membered cyclic transition state.

(19) Pentacoordination of aromatic diolate or fluoride to silicon or tin of allylic silanes and tins usually promotes carbonyl allylations to lead to γ-*anti*-selection via six-membered cyclic transition states: Sakurai, H. *Synlett* **1989**, 1. Denmark, S. E.; Coe, D. M.; Pratt, N. E.; Griedel, B. D. *J. Org. Chem.* **1994**, *59*, 6161.

Table 2. *Syn*-Diastereoselective Allylation of Benzaldehyde by 1 with Tin(II) Halides[a]



entry	X	X′	X″	solvent	time (h)	yield[b] (%)	*syn*:*anti*[c]
1	Br	Cl	none	THF	24	63	16:84
2	Br	Cl	Br	THF	24	58	52:48
3	Br	Br	none	THF	23	75	42:58
4	Br	Br	Br	THF	22	68	77:23
5	Br	I	none	THF	15	55	73:27
6	Br	I	Br	THF	15	78	84:16
7	Br	I	Br	DMI	17	90	81:19
8	Br	I	I	DMI	18	88	87:13
9	Cl	Cl	none	DMI	72	N.R.	–
10	Cl	Cl	Br	DMI	72	14	40:60
11	Cl	Cl	I	DMI	48	80	59:41
12	Cl	Br	none	DMI	72	N.R.	–
13	Cl	Br	Br	DMI	53	39	47:53
14	Cl	Br	I	DMI	45	80	82:18
15	Cl	I	none	DMI	64	53	82:18
16	Cl	I	Br	DMI	48	56	85:15
17	Cl	I	I	DMI	40	80	90:10
18	Cl	I	I[d]	DMI	41	83	89:11
19	Cl	I	I	DMI[e]	91	60	69:31
20	Cl	I	I[d]	Et_2O[e]	94	10	81:19[f]
21	Cl	I	I[d]	CH_2Cl_2[e]	92	70	75:25[g]
22	Cl	I	I[d]	THF	70	84	83:17
23	Cl	I	I[d]	DMF	43	82	87:13
24	Cl	I	I[d]	DMSO	43	85	78:22

[a] The allylation of benzaldehyde (1 mmol) by 1-halobut-2-ene (2 mmol) was carried out with SnX'_2 (2 mmol) and TBAX″ (2 mmol) in solvent (3 mL) and H_2O (0.1 mL) at 25 °C. [b] Isolated yield. [c] The ratio was determined by ^1H NMR (JEOL GX-270 or Λ-500) and by GC (capillary column PEG 20M, 0.25 mm × 30 m). [d] The reaction was carried out with TBAI (0.2 mmol) and NaI (2.0 mmol). [e] The reaction was carried out without H_2O. [f] $\gamma:\alpha = 98:2$. [g] $\gamma:\alpha = 95:5$.

SnI_2 and TBAI occurred in nonpolar solvents such as diethyl ether and CH_2Cl_2, despite the low solubility of SnI_2 (entries 20 and 21). Polar solvents such as THF, DMF, and DMSO can be used for the γ-*syn*-selective carbonyl allylation (entries 22–24).

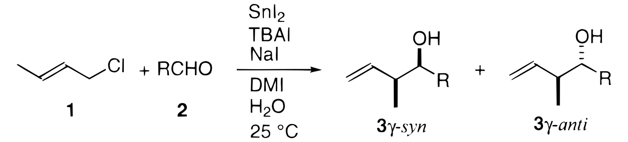
γ-*Syn*-Selective Carbonyl Allylation. As shown in Table 3, the *syn*-selective allylation of various aldehydes **2** was investigated under the same conditions as those which gave highest *syn*-selectivity in the allylation of benzaldehyde by **1** (X = Cl) (entry 17 in Table 2). Aromatic aldehydes, bearing either an electron-donating group or an electron-withdrawing group, and α,β-unsaturated aldehydes can be used in the *syn*-selective allylation. Aliphatic aldehydes, especially 3-phenylpropanal and cyclohexanecarbaldehyde, underwent allylation but *syn*-selectivity was poor (entries 7 and 10).

In summary, the carbonyl allylation by 1-bromobut-2-ene with $SnBr_2$ in CH_2Cl_2–H_2O at 25–32 °C proceeds with α-regioselection to produce 1-substituted pent-3-en-1-ols, while that by 1-chlorobut-2-ene with SnI_2, TBAI, and NaI in DMI–H_2O at 25 °C undergoes γ-*syn*-selection to produce *syn* 1-substituted 2-methylbut-3-en-1-ols.

Experimental Section

General. All solvents had been dried over desiccant and had been distilled before being used. 1-Bromobut-2-ene (**1**, X = Br), which has been purchased from Tokyo Chemical Industry Co., Ltd., contains 14% 3-bromobut-1-ene [(*E*)-**1**:(*Z*)-**1**:3-bromobut-1-ene = ca. 73:13:14]. (*E*)-1-chlorobut-2-ene (**1**, X = Cl) was also purchased from Tokyo Chemical Industry Co., Ltd. The 1-halobut-2-enes and aldehydes used were commercial samples purified by distillation or recrystallization. Diastereomer ratios were determined by ^1H NMR and GC analysis (accuracy ±1%).

Table 3. *Syn*-Diastereoselective Carbonyl Allylation by 1 (X = Cl)[a]



entry	R	time (h)	yield[b] (%)	syn:*anti*[c]
1	4-ClC_6H_4	42	90	91:9
2	4-NCC_6H_4	50	94	91:9
3	4-$CH_3OOCC_6H_4$	72	93	93:7
4	4-$CH_3OC_6H_4$	50	85	85:15
5	4-$CH_3C_6H_4$	42	82	92:8
6	$C_6H_5CH{=}CH$	50	85	83:17
7	$C_6H_5CH_2CH_2$	47	81	68:32
8	$H_2C{=}CH(CH_2)_8$	45	65	77:23
9	C_6H_{13}	40	76	77:23
10	*c*-C_6H_{11}	47	76	60:40

[a] The allylation of aldehydes (1 mmol) by 1-chlorobut-2-ene (2 mmol) was carried out with SnI_2 (2 mmol), TBAI (0.2 mmol), and NaI (2 mmol) in DMI (3 mL) and H_2O (0.1 mL) at 25 °C. [b] Isolated yield. [c] The ratio was determined by ^1H NMR (JEOL Λ-500) and/or GC (capillary column PEG 20M, 0.25 mm × 30 m).

α-Regioselective Carbonyl Allylation by 1-Bromobut-2-ene with $SnBr_2$. A typical procedure is as follows: To a solution of $SnBr_2$ (0.56 g, 2 mmol) and 1-bromobut-2-ene (0.27 g, 2 mmol) in CH_2Cl_2 (3 mL)-H_2O (3 mL) was added heptanal (0.11 g, 1 mmol) at ambient temperature under a nitrogen atmosphere. After being stirred for 24 h, the mixture was diluted with 120 mL of a mixed solvent (ether:dichloromethane = 2:1) and washed successively with aqueous 10% HCl solution (10 mL), aqueous $NaHCO_3$ solution (10 mL), water (10 mL), and brine (10 mL). The extracts were dried over anhydrous $MgSO_4$. Then evaporation of solvent and purification by column chromatography on silica gel (hexane:ethyl acetate = 7:1) afforded 0.082 g (0.48 mmol, 48%) of undec-2-en-5-ol as a colorless oil.

γ-*syn*-Selective Carbonyl Allylation by 1-Chlorobut-2-ene with SnI_2 and TBAI. A typical procedure is as follows: To a solution of SnI_2 (0.74 g, 2.0 mmol), TBAI (0.074 g, 0.20 mmol), and NaI (0.30 g, 2.0 mmol) in DMI (3 mL)-H_2O (0.1 mL) was added 1-chlorobut-2-ene (0.19 mL, 2.0 mmol) followed by benzaldehyde (0.10 mL, 1.0 mmol) at ambient temperature under a nitrogen atmosphere. After being stirred for 41 h, the mixture was diluted with CH_2Cl_2 (100 mL) and was washed successively with aqueous 10% HCl solution (10 mL), aqueous $NaHCO_3$ solution (10 mL), water (10 mL), and brine (10 mL). The extracts were dried over anhydrous $MgSO_4$. Then evaporation of CH_2Cl_2 and purification by column chromatography on silica gel (hexane:ethyl acetate = 10:1) afforded 0.13 g (0.83 mmol, 83%) of 2-methyl-1-phenylbut-3-en-1-ol as a colorless oil.

The structures of the following alcohols were confirmed by the comparison of spectroscopic values with those of authentic samples in the literature: 1-phenylpent-3-en-1-ol,[20] 2-methyl-

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1-phenylbut-3-en-1-ol,[21] 1-(4-chlorophenyl)-2methylbut-3-en-1-ol,[12] 1-[4-(methoxycarbonyl)phenyl]-2-methylbut-3-en-1-ol,[12] 1-(4-methoxyphenyl)-2-methylbut-3-en-1-ol,[12] 4-methyl-1-phenylhex-1(*E*),5-dien-3-ol,[22] 1-cyclohexyl-2-methylbut-3-en-1-ol,[12] 1-cyclohexylpent-3-en-1-ol,[12] 3-methyldec-1-en4-ol,[23] 2,2-dimethylhept-5-en-3-ol.[24] The characterization data of new compounds are present in the Supporting Information: α and γ mixtures of **3** [R = C_6H_{13}, 4-$CH_3C_6H_4$, $C_6H_5CH_2CH_2$, and $H_2C{=}CH(CH_2)_8$] in Table 1.

Supporting Information Available: Characterization data for compounds **3** [R=C_6H_{13}, 4-$CH_3C_6H_4$, $C_6H_5CH_2CH_2$, and $H_2C{=}CH(CH_2)_8$] in Table 1, and details of α-regioselection depending upon reaction temperature (10−35 °C) in the allylation of benzaldehyde by **1** (X = Br) on a dichloromethane−water biphasic system. This material is available free of charge via the Internet at http://pubs.acs.org.

JO991403O