Carbonyl Allenylations and Propargylations by 3-Chloro-1-propyne or 2-Propynyl Mesylates with Tin(IV) Chloride and Tetrabutylammonium Iodide

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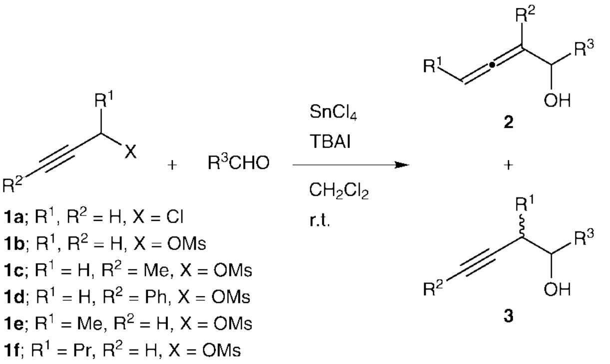
Abstract: By the use of tin(IV) chloride and tetrabutylammonium iodide in dichloromethane, 3-chloro-1-propyne or 2-propynyl mesylate can be applied to allenylation and propargylation of aldehydes (carbonyl allenylation and propargylation) to produce a mixture of 1-substituted 2,3-butadien-1-ols and 1-substituted 3-butyn-1-ols. 1-Substituted 2-propynyl mesylates selectively cause carbonyl propargylation, while 3-substituted 2-propynyl mesylates cause carbonyl allenylation.

Key words: nucleophilic additions, allenylations, propargylations, organometallic reagents, tin(IV) chloride

Alkynes and allenes are attractive synthetic tools for high reactivities to metal complexes or reagents.[1] Thus, the preparation of alkynes and allenes becomes an important theme. Barbier-type carbonyl allenylation or propargylation with propargylic halides is one of the most convenient methods for introduction of allenyl or propargyl function.[2] However, it is not so easy to control the selectivity between the allenylation and the propargylation with propargylic halides. We have established that either Barbier-type carbonyl allenylations or propargylations by 3-halo-1-propynes or 2-propynyl mesylates with tin(II) halides and tetrabutylammonium halides can be controlled by reaction conditions[3] and by varying the bulkiness of substituents.[4] The allenylations or propargylations by 3- or 1-substituted 2-propynyl mesylates need high-boiling polar solvents such as 1,3-dimethylimidazolidin-2-one and DMF to dissolve tin(II) iodide, though the solvents make workup troublesome.[4] We have recently found that tin(II) chloride, in situ prepared by the reduction of tin(IV) chloride with tetrabutylammonium iodide (TBAI), can be applied to carbonyl allylations by 3-halo-1-propenes or 2-propenyl mesylate in low-boiling nonpolar dichloromethane.[5] We here report on the carbonyl allenylations and propargylations by 3-chloro-1-propyne and 2-propynyl mesylate via the in situ preparation of tin(II) species from tin(IV) chloride and TBAI in dichloromethane. We describe some applications to steric factor-mediated selective carbonyl allenylations or propargylations by 3- or 1-substituted 2-propynyl mesylates respectively (Scheme 1).[6]



Scheme 1

The allenylation and propargylation of benzaldehyde by 3-chloro-1-propyne (**1a**) with tin(IV) chloride and TBAI were investigated under various conditions. Some representative results are summarized in Table 1 (entries 1–3). The optimum method proved to be the same as that of the carbonyl allylations by 2-propenyl mesylate with tin(IV) chloride and TBAI (entry 2).[5,7] The reaction at 0 ºC for 46 hours lowered the yield (46%) of products **2** and **3** without enhancing the selectivity of either allenylation or propargylation. No reaction occurred at temperatures below –20 °C. Stirring the solution of 3-chloro-1-propyne (2.0 mmol), tin(IV) chloride (2.0 mmol), and TBAI (6.0 mmol) in CH_2Cl_2 at room temperature for 24 hours, adding benzaldehyde (1.0 mmol) and further stirring the solution for 24 hours afforded a slightly lower yield than that of entry 2 (76%, **2**:**3** = 65:35). Carbonyl allenylations and propargylations using **1a** and 2-propynyl mesylates **1b**–**f** were carried out with various aldehydes under the same conditions as those of entry 2 (entries 4–29 in Table 1). The selectivity between allenylation and propargylation can be controlled by the bulkiness of 1- or 3-substituents of 2-propynyl mesylates **1c**–**f**; 3-substituted 2-propynyl mesylates **1c** and **1d** preferentially cause the allenylation of aldehydes, while 1-substituted 2-propynyl mesylates **1e** and **1f** dominantly cause the propargylation of aldehydes. This carbonyl allenylation and propargylation are outlined in Scheme 2, by reference to the carbonyl allylation by 3-halo-1-propenes or 2-propenyl mesylate with $SnCl_4$-TBAI reagent.[5] Iodide ion probably serves as a reducing agent for preparing trichlorostannate(II) ion ($^{-}SnCl_3$) from $SnCl_4$ via the formation of pentacoordinate stannate(IV) ion ($^{-}SnCl_4I$), followed by the reductive elimination of iodine monochloride (I-Cl). The trichlorostannate(II) ion may cause nucleophilic substitution to propargyl sub-

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Table 1 Carbonyl Allenylations and Propargylations with **1**[a]

Entry	Substrate	R^3	Time (h)	**2**+**3**; Yield (%)[b]	**2**/**3** (**3**; *syn*/*anti*)[c]
1[d]	**1a**	Ph	24	84	60/40
2	**1a**	Ph	24	85	60/40
3[e]	**1a**	Ph	48	35	50/50
4	**1a**	4-ClC_6H_4	23	89	66/34
5	**1a**	4-MeC_6H_4	23	74	59/41
6	**1a**	$PhCH_2CH_2$	45	65	62/38
7	**1a**	C_6H_{13}	42	47	61/39
8	**1a**	$c\text{-}C_6H_{11}$	49	82	70/30
9	**1b**	Ph	44	74	54/46
10	**1b**	4-ClC_6H_4	71	87	57/43
11	**1b**	4-MeC_6H_4	70	68	61/39
12	**1b**	C_6H_{13}	72	70	55/45
13	**1b**	$c\text{-}C_6H_{11}$	73	81	65/35
14	**1c**	Ph	70	48	70/30
15	**1c**	4-ClC_6H_4	69	43	68/32
16	**1c**	$PhCH_2CH_2$	72	34	76/24
17	**1c**	C_6H_{13}	74	50	73/27
18	**1c**	$c\text{-}C_6H_{11}$	72	28	73/27
19	**1d**	Ph	72	33	91/9
20	**1d**	4-ClC_6H_4	72	28	>99/1
21	**1d**	$c\text{-}C_6H_{11}$	73	39	93/7
22	**1e**	Ph	72	70	2/98 (48/52)
23	**1e**	4-ClC_6H_4	68	86	0/100 (47/53)
24	**1e**	PhCH=CH	69	71	2/98 (53/47)
25	**1e**	C_6H_{13}	73	73	2/98 (77/23)
26	**1e**	$c\text{-}C_6H_{11}$	74	41	0/100 (–)[f]
27	**1f**	Ph	71	80	2/98 (46/54)
28	**1f**	4-ClC_6H_4	70	70	0/100 (48/52)
29	**1f**	C_6H_{13}	72	41	1/99 (85/15)

[a] The reaction of **1a–f** (2 mmol) and aldehydes (1 mmol) with TBAI (6 mmol) and a one-molar CH_2Cl_2 solution of $SnCl_4$ (2 mL) was carried out in CH_2Cl_2 (2 mL) at r.t.

[b] Isolated yields.

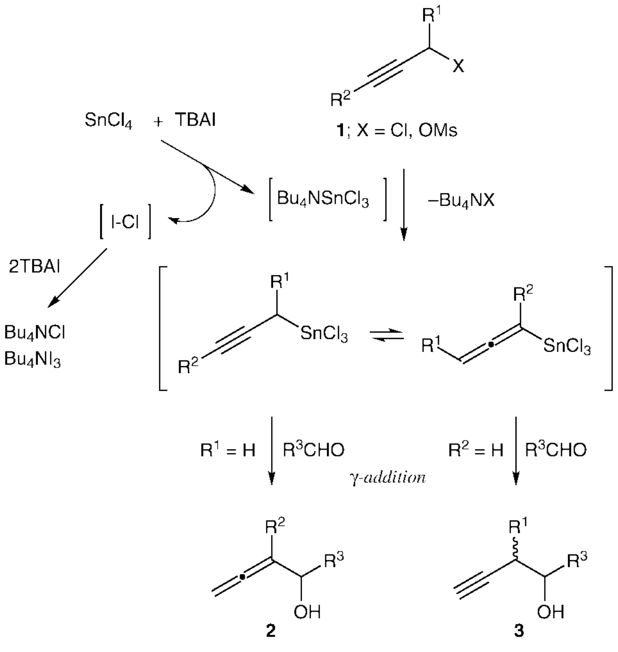
[c] The ratios were determined by ^1H NMR analysis (JEOL Λ-500).

[d] Aldehydes (1 mmol), **1a** (3 mmol), TBAI (9 mmol), and a one-molar CH_2Cl_2 solution of $SnCl_4$ (3 mL) were used.

[e] Aldehydes (1 mmol), **1a** (1.5 mmol), TBAI (4.5 mmol), and a one-molar CH_2Cl_2 solution of $SnCl_4$ (1.5 mL) were used.

[f] The ratio was not confirmed.

strates **1** preferentially to afford sterically unhindered propargyltrichlorotins ($R^1 = H$) or allenyltrichlorotins ($R^2 = H$) that function as nucleophiles for carbonyl allenylations or propargylations respectively. I-Cl may react with two equimolar amounts of TBAI to produce TBACl and tetrabutylammonium triiodide ($TBAI_3$). $SnCl_4$–TBAI is a useful reagent for Barbier-type carbonyl allenylation and propargylation without reducing aldehydes. This $SnCl_4$–TBAI reagent is superior to SnI_2–TBAI reagent for the selective propargylation by 1-substituted 2-propynyl mesylates.[4]



Scheme 2

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(7) A typical procedure is as follows: To the solution of **1a** (2 mmol), benzaldehyde (1 mmol) and TBAI (6 mmol) in CH_2Cl_2 (2 mL) was added drop by drop a one-molar CH_2Cl_2 solution of tin(IV) chloride (2 mL) on an ice-bath for 15 min, and then the solution was stirred at r.t. for 24 h. The solution was diluted with 120 mL of a mixed solvent (Et_2O:CH_2Cl_2 = 2:1) and washed successively with aq 10% HCl solution (20 mL), aq $NaHCO_3$ solution (20 mL), H_2O (20 mL), and brine (20 mL). The extracts were dried over anhyd $MgSO_4$. After evaporation of solvent, purification by column chromatography (silica gel, hexane:EtOAc = 10: 1) and then HPLC (Japan Analytical Industry Co. Ltd., LC-908; JAIGEL-2H; chloroform) afforded 124 mg (85%) of a mixture (**2**:**3** = 60:40) of 1-phenyl-2,3-butadien-1-ol (**2**; R^1, R^2 = H, R^3 = Ph) and 1-phenyl-3-butyn-1-ol (**3**; R^1, R^2 = H, R^3 = Ph) as a colorless oil. R_f = 0.33 (silica gel, hexane:EtOAc = 3: 1). IR(neat): 3300, 3060, 3030, 2910, 2150, 1960, 1600, 1540, 1490, 1450, 1390, 1190, 1160, 1030, 910, 860, 760, 700, 640 cm^{-1}. Compound **2**: ^1H NMR (500 MHz, $CDCl_3$): δ = 2.11 (d, J = 3.5 Hz, 1 H), 4.90–4.98 (m, 2 H), 5.26–5.31 (br, 1 H), 5.45 (q, J = 6.5 Hz, 1 H), 7.27–7.45 (m, 5 H). Compound **3**: ^1H NMR (500 MHz, $CDCl_3$): δ = 2.08 (t, J = 2.5 Hz, 1 H), 2.35 (d, J = 3.0 Hz, 1 H), 2.63 (ddd, J = 11, 2.5, 1.0 Hz, 1 H), 2.67 (dd, J = 11, 2.5 Hz, 1 H), 4.86–4.91 (m, 1 H), 7.27–7.45 (m, 5 H).