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Carbonyl allylations by allylic chlorides utilizing a reduction of tin(IV) iodide to triiodostannate(II) species with iodide sources

Yoshiro Masuyama,* Kaori Takeuchi and Yasuhiko Kurusu

Department of Chemistry, Sophia University, 7-1 Kioicho, Chiyoda-ku, Tokyo 102-8554, Japan

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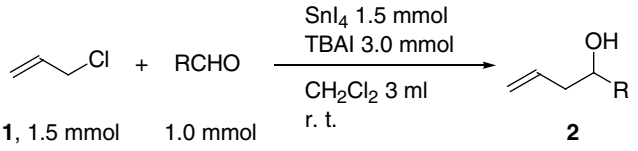
Abstract—Carbonyl allylations by allylic chlorides either with tin(IV) iodide and tetrabutylammonium iodide (TBAI) in dichloromethane or with tin(IV) iodide and sodium iodide in 1,3-dimethylimidazolidin-2-one at room temperature produced the corresponding homoallylic alcohols. The carbonyl allylations probably proceeded via the reduction of tin(IV) iodide to triiodostannate(II) species with iodide sources such as TBAI and NaI, which led to the construction of a tin(IV)-catalytic cycle based on regeneration of tin(IV) iodide via the transmetalation of homoallyloxytriiodotin to homoallyloxytrimethylsilane with iodotrimethylsilane.

Allylic trihalotins, derived from starting allylic compounds, such as allylic halides,[1] alcohols,[2] and esters[2,3] with tin(II) halides, are one of the most convenient allylating agents in Barbier-type carbonyl allylations.[4,5] These need a stoichiometric amount of metals or metal compounds as reducing agents like tin(II) halides to form allylic trihalotins. No Barbier-type carbonyl allylation with a catalytic amount of a metal reducing agent and a stoichiometric amount of non-metal reducing agents has been known. We have found that a combo-reagent of tin(IV) chloride and tetrabutylammonium iodide (TBAI) functions as a reducing agent similar to tin(II) halides for the Barbier-type carbonyl allylations with allylic halides.[6] Tin(IV) chloride is probably reduced to trichlorostannate(II) by TBAI via the formation of iodotetrachlorostannate(IV). This reduction of tin(IV) to stannate(II) with TBAI led us to plan a tin(IV)-catalytic cycle for Barbier-type carbonyl allylation based on regeneration of tin(IV) halide by transmetalation of homoallyloxytrihalotin with halotrimethylsilane.[7] However, no tin(IV) chloride-catalytic cycle with TBAI and chlorotrimethylsilane in dichloromethane could be constructed. We here report that changing tin(IV) chloride into tin(IV) iodide not only has smoothly caused the Barbier-type carbonyl allylation by allylic chlorides with TBAI or NaI, but also has led to the construction of a tin(IV) iodide-catalytic cycle with iodotrimethylsilane in DMI.



(1)

We first found that tin(IV) iodide functioned similar to tin(IV) chloride for Barbier-type carbonyl allylation with a combo-reagent of tin(IV) chloride and TBAI (Eq. 1, Table 1). The balance between the yield and the reaction rate determined optimal conditions; the allylation of benzaldehyde (1.0 mmol) by 3-chloropropene (**1**, 1.5 mmol) was carried out with tin(IV) iodide (1.5 mmol) and TBAI (3.0 mmol) in dichloromethane (3 mL) at room temperature (Eq. 1, R = C_6H_5; entry 3 in Table 1). The amount of TBAI was cut down by the use of tin(IV) iodide instead of tin(IV) chloride.[6] Dichloromethane is superior to other solvents such as THF and DMF. The allylation of various aldehydes with **1** was carried out under the same conditions as the optimal conditions of benzaldehyde (Method A). Some representative results are summarized in Table 2 (entries 1–9). Using 1,3-dimethylimidazolidin-2-one (DMI, 2 mL) as a solvent, which could not be used in the case of tin(IV) chloride, we applied sodium iodide instead of TBAI to the carbonyl allylation by **1** with tin(IV) iodide (Method B, entries 10–18 in Table 2).

Keywords: Nucleophilic addition; Carbonyl allylation; Tin(IV)-catalytic cycle; Allylic tins; Tin(IV) iodide.
* Corresponding author. Tel.: +81 3 3238 3453; fax: +81 3 3238 3361; e-mail: y-masuya@sophia.ac.jp

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Table 1. Allylation of PhCHO by **1** with SnI_4 and TBAI for 40 h

Entry	TBAI/mmol	Solvent	**2** (R = C_6H_5), Yield/%[a]
1	1.5	CH_2Cl_2	15
2	2.0	CH_2Cl_2	35
3	3.0	CH_2Cl_2	68
4	4.0	CH_2Cl_2	63
5[b]	3.0	CH_2Cl_2	12
6	3.0	THF	53
7	3.0	DMF	30

[a] Isolated yields.[8]
[b] The reaction was carried out at 0 °C.

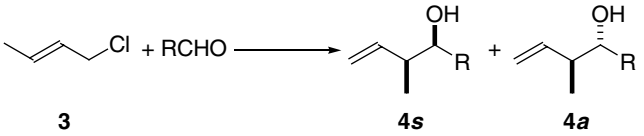
Table 2. Carbonyl allylations by **1** with TBAI or NaI

Entry	R	Method	Time/h	**2**, Yield/%[a]
1	C_6H_5	A	24	68
2	4-ClC_6H_4	A	23	92
3	4-$MeOOCC_6H_4$	A	26	84
4	2-$MeOC_6H_4$	A	24	58
5	$C_6H_5CH{=}CH$	A	25	58
6	$C_6H_5CH_2CH_2$	A	24	64
7	C_6H_{13}	A	45	69
8	*c*-C_6H_{11}	A	48	50
9	$C_6H_5(CH_3)CH$	A	24	75[b]
10	C_6H_5	B	24	90
11	4-ClC_6H_4	B	24	99
12	4-$MeOOCC_6H_4$	B	24	96
13	4-NCC_6H_4	B	24	70
14	4-$MeOC_6H_4$	B	26	71
15	$C_6H_5CH{=}CH$	B	23	74
16	C_6H_{13}	B	50	73
17	*c*-C_6H_{11}	B	52	73
18	$C_6H_5(CH_3)CH$	B	45	82[b]

[a] Isolated yields.[8]
[b] 2(*anti*)-Phenyl-5-hexen-3-ol was preferentially produced (entry 9, *syn*:*anti* = 27:73; entry 18, *syn*:*anti* = 28:72). The ratios were determined by ^1H NMR analysis (JEOL JNM-LA500).[8]

Aromatic aldehydes bearing an electron-withdrawing group or an electron-donating group, α,β-unsaturated aldehyde, and aliphatic aldehydes can be employed in both methods. No allylation with sodium iodide proceeded in either dichloromethane or THF. Method A in dichloromethane is superior to method B in DMI with respect to workup, while method B has the advantages of yield and cost of iodide sources over method A.

Regio- and diastereoselectivity were investigated in the reaction of 1-chloro-2-butene (**3**)[9] and some aldehydes by method B (Eq. 2, Table 3). The reaction led to *syn*-selection accompanied by γ-regioselection.[8] The γ-*syn* selection can be explained by the non-Lewis acidity of the tin in 2-butenylpolyiodotin intermediate that forms unusual Lewis acid-non-participating acyclic antiperiplanar transition states with aldehydes, similar to the carbonyl allylation with tin(II) iodide, TBAI and NaI (Scheme 1).[10,11]



3 **4*s*** **4*a***

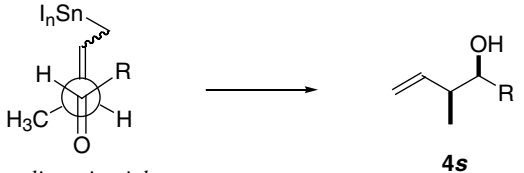
(2)

Table 3. Regioselective carbonyl allylations with **3** by means of method B

Entry	R	Time/h	**4**, Yield/%[a]	**4*s*:4*a***[b]
1	C_6H_5	46	68	88:12
2	4-ClC_6H_4	28	76	90:10
3	4-$MeOC_6H_4$	46	40	87:13
4	$C_6H_5CH{=}CH$	70	45	85:15
5	$C_6H_5CH_2CH_2$	45	55	89:11
6	C_6H_{13}	70	63	81:19
7	*c*-C_6H_{11}	70	47	63:37

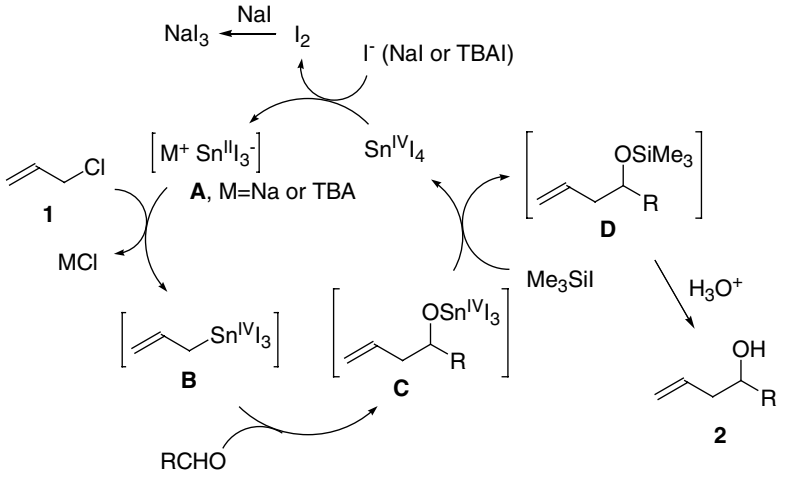
[a] Isolated yields.[8]
[b] The ratios were determined by ^1H NMR analysis (JEOL JNM-LA500).[8]

The tin(IV)-catalytic cycle was constructed by using tin(IV) iodide (0.05 mmol), TBAI (0.10 mmol), sodium iodide (3.0 mmol), iodotrimethylsilane (1.1 mmol), **1** (1.5 mmol), and benzaldehyde (1.0 mmol) in DMI (1 mL) at room temperature (48 h, **2** (R = C_6H_5), 58%). Even if TBAI (3.0 mmol) was used instead of TBAI (0.10 mmol) and sodium iodide (3.0 mmol), no tin(IV)-catalyzed allylation of benzaldehyde occurred in dichloromethane (2 mL). The allylation of benzaldehyde, either with chlorotrimethylsilane instead of iodotrimethylsilane or without iodotrimethylsilane, for 48 h proceeded just stoichiometrically to tin(IV) iodide; using 0.10 mmol of tin(IV) iodide afforded **2** (R = C_6H_5) in about 10% yield. In the case of no TBAI, the yield of the allylation of benzaldehyde for 48 h lowered (35%). Tin(II) iodide functioned as a catalyst similar to tin(IV) iodide in the allylation of benzaldehyde (35%). Some aldehydes can be used in the tin(IV)-catalyzed allylation; 4-ClC_6H_4CHO (30 h, 70%), $C_6H_5CH{=}CHCHO$ (70 h, 38%), $C_6H_5CH_2CH_2CHO$ (66 h, 41%), $C_6H_{13}CHO$ (75 h, 34%). A plausible mechanism for the tin(IV)-catalyzed carbonyl allylation is illustrated in Scheme 2. Tin(IV) iodide is first reduced to triiodostannate(II) ion **A** with iodide sources via the reductive elimination of iodine from pentaiodostannate(IV) ion. Iodine is scavenged by another iodide to produce sodium triiodide.[6,12] The stannate(II) ion **A** causes nucleophilic substitution to **1** to prepare 2-propenyltriiodotin (**B**), which undergoes nucleophilic addition to aldehydes to afford homoallyloxytriiodotin **C**. The homoallyloxytriiodotin **C** transmetalates with iodotrimethylsilane to produce homoallyloxytrimethylsilane **D**, and then tin(IV) iodide is regenerated for the sake of tin(IV)-catalytic cycle.[7] Tin(II) iodide may react with iodide sources to prepare **A**, which starts the same tin(IV)-catalytic cycle as that of tin(IV) iodide.



acyclic antiperiplanar **4*s***

Scheme 1. *syn*-Selection via acyclic antiperiplanar transition state.



Scheme 2. A plausible mechanism for the tin(IV)-catalyzed carbonyl allylation.

In conclusion, we have established a Barbier-type carbonyl allylation by allylic chloride with triiodostannate(II) species derived from SnI_4 and I^- source (TBAI or NaI). Noteworthy features are that (1) SnI_4 can be reduced with I^- to triiodostannate(II) species without reducing aldehydes, (2) SnI_4 can be regenerated by transmetalation of homoallyloxytriiodotin with iodotrimethylsilane; a construction of SnI_4-catalytic cycle, (3) SnI_2 can be also used as a starting tin catalyst similar to SnI_4, and (4) SnI_4 system is superior to $SnCl_4$ system[6] from the viewpoints of resource saving of I^- (TBAI or NaI) and tractability of tin(IV) halides.

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