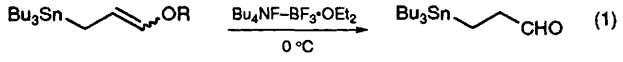
Bu_4NF–BF_3·Et_2O as a New Reagent for the Selective Deprotection of the Enol Ethers of γ-Alkoxyallylstannanes

Vladimir Gevorgyan and Yoshinori Yamamoto*

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

The combination of Bu_4NF–BF_3·OEt_2 deprotects selectively the enol ether protecting group of γ-alkoxy- and benzyloxy-allyltributylstannanes, without destannylating the tributylstannyl group, affording the corresponding γ-tributylstannyl aldehyde in high yield.

Conversion of enol ethers to aldehydes is carried out normally in the presence of mineral acids such as aqueous HCl, H_2SO_4 and $HClO_4$.[1] If another acid labile group exists in the molecule containing an enol ether, the treatment with acids may also remove such an acid-sensitive group. We report an unprecedented facile conversion of γ-alkoxyallylstannanes **1** to γ-stannylpropanal **2** upon treatment with Bu_4NF–BF_3·OEt_2 (1.0 : 1.1–1.5) (eqn. (1)].

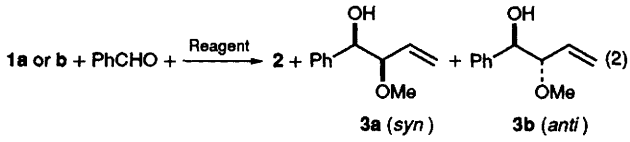


(1)

1a; R = Me, *Z*
b; R = Me, *E*
c; R = CH_2Ph, *Z*
d; R = CHMeOEt, *Z*

2

We have recently reported that the intramolecular allylstannane-aldehyde condensation mediated by Bu_4NF–Lewis acid combination proceeds through a cyclic transition state and the stereochemical outcome is strongly dependent upon the double bond geometry of the allystannane moiety.[2] To clarify whether the cyclic transition state model is applicable to an intermolecular process or not, we examined the γ-methoxyallylstannane (**1a**,**b**)-benzaldehyde condensation in the presence of Bu_4NF–BF_3·OEt_2 [eqn. (2)].



(2)

3a (*syn*) **3b** (*anti*)

The results are summarized in Table 1. Unexpectedly, the reaction using a 1.0 : 1.1 mixture of Bu_4NF and BF_3·OEt_2 produced **2** in very high yields along with trace amounts of **3a** and **3b** (entries 1 and 2). Very surprisingly, the use of a 1.0 : 1.0 mixture of Bu_4NF and BF_3·OEt_2 did not cause any reactions, resulting in complete recovery of **1** (entries 3 and 4). The reaction in the presence of BF_3·OEt_2 gave a mixture of **3a** and **3b**, as observed previously,[3] without being accompanied by **2** (entries 5 and 6); the *syn*-isomer was formed predominantly, as usual, irrespective of the geometry of the allylic double bond.

This unprecedented selective deprotection of the methoxy group in the presence of tributyltin group prompted us to investigate the combination system more precisely and deeply. The results are summarized in Table 2. Treatment of **1a** with 0.1 equiv. BF_3·OEt_2 in CH_2Cl_2 at −78 °C resulted in decomposition of the tin reagent (entry 1). The starting material was recovered completely upon treatment with 1.0 equiv. Bu_4NF [1 mol dm^{-3} solution in tetrahydrofuran (THF)]

Table 1 Intermolecular condensation of **1a, b** with benzaldehyde[a]

Entry	Substrate	Reagent (equiv.)	React. cond. *t*/h *T*/°C	Total yield[b] (recovery of **1**) (%)	Products distribution (%)[b] **3a** (*syn*)	**3b** (*anti*)	**2**
1	**1a** (*Z*)	Bu_4NF–BF_3·OEt_2 (1.0 : 1.1)	12/0	60(—)	1	1	98
2	**1b** (*E*)	Bu_4NF–BF_3·OEt_2 (1.0 : 1.1)	12/0	85(—)	4	—	96
3	**1a** (*Z*)	Bu_4NF–BF_3·OEt_2 (1.0 : 1.0)	24/25	—(100)	—	—	—
4	**1b** (*E*)	Bu_4NF–BF_3·OEt_2 (1.0 : 1.0)	24/25	—(100)	—	—	—
5	**1a** (*Z*)	BF_3·OEt_2 (2.0)	1/ − 78	>95(—)	89	11	—
6	**1b** (*E*)	BF_3·OEt_2 (2.0)	1/ − 78	93(—)	94	6	—

[a] All reactions were carried out in CH_2Cl_2 with 0.1 mol dm^{-3} concentration of substrate. [b] By GLC, using hexadecane as an internal standard.

Table 2 Deprotection of the enol ether of γ-alkoxystannanes[a]

Entry	Substrate	Reagent (equiv.)	*t*/h	*T*/°C	Yield of **2** (%)[c]	Recovery (%)
1	**1a**	BF_3·OEt_2 (0.1)	1	−78	Decomposition	
2	**1a**	Bu_4NF (1.0)	24	25[b]	0	100
3	**1a**	Bu_4NF–BF_3·OEt_2 (1.0 : 1.0)	24	25[b]	0	100
4	**1a**	Bu_4NF–BF_3·OEt_2 (1.0 : 1.2)	24	0	>95	—
5	**1a**	$Bu_4N^+BF_4^-$ (1.0)	24	0	0	100
6	**1a**	$Bu_4N^+BF_4^-$–BF_3·OEt_2 (1.0 : 0.1)	3	0	Decomposition	
7	**1c**	BF_3·OEt_2 (1.0)	1	−78	Decomposition	
8	**1c**	Bu_4NF–BF_3·OEt_2 (1.0 : 1.5)	18	0	80	—
9	**1c**	$Bu_4N^+BF_4^-$–BF_3·OEt_2 (1.0 : 1.5)	18	0	21	—
10	**1d**	BF_3·OEt_2 (1.0)	1	−78	Decomposition	
11	**1d**	Bu_4NF–BF_3·OEt_2 (1.0 : 1.5)	18	0	86	—
12	**1d**	$Bu_4N^+BF_4^-$–BF_3·OEt_2 (1.0 : 0.4)	18	0	35	—

[a] All reactions were carried out in CH_2Cl_2 with 0.1 mol dm^{-3} concentration of substrate. Substrate was added first. [b] The reactants were mixed at 0 °C, then reactions were carried out at 25 °C. [c] GLC analysis, using hexadecane as an internal standard.

or with a 1.0:1.0 mixture of Bu_4NF and $BF_3{\cdot}OEt_2$ (entries 2 and 3). The use of a 1.0:1.2 mixture of Bu_4NF and $BF_3{\cdot}OEt_2$ produced **2** in essentially quantitative yield (entry 4). The allyltin reagent was decomposed by the use of a 1.0:2.0 mixture of Bu_4NF and $BF_3{\cdot}OEt_2$. It was thought that the combination of Bu_4NF and $BF_3{\cdot}OEt_2$ would result in the formation of Bu_4NBF_4,[4] which might be responsible for the selective deprotection. Accordingly, we examined the reaction of **1a** with 1.0 equiv. Bu_4NBF_4 dissolved in CH_2Cl_2. However, **1a** was recovered completely (entry 5). A 1.0:0.1 mixture of Bu_4NBF_4 and $BF_3{\cdot}OEt_2$ caused the decomposition of **1a** (entry 6), and thus this combination system provides essentially the same effects as the single use of $BF_3{\cdot}OEt_2$ (entry 1). The combination system, Bu_4NF–$BF_3{\cdot}OEt_2$ (1.0:1.5), was also effective for the selective deprotection of **1c** and **1d** (entries 8 and 11), although a 1.0:0.4 mixture of Bu_4NBF_4 and $BF_3{\cdot}OEt_2$ was less effective (entries 9 and 12). Here also, the use of $BF_3{\cdot}OEt_2$ resulted in decomposition of the allylic stannanes even at −78 °C (entries 7 and 10).

We would like to suggest the following mechanism for selective deprotection with Bu_4NF–$BF_3{\cdot}Et_2O$ (1.0:1.1–1.5), although it is highly speculative.† The acid–base complex $Bu_4NF{\cdot}BF_3$ is formed by treatment of Bu_4NF in THF with $BF_3{\cdot}Et_2O$ in CH_2Cl_2 [eqn. (3)]. The complex is different from $Bu_4N^+BF_4^-$ salt. Small amounts of $BF_3{\cdot}THF$‡ coordinate the enol oxygen to produce **5** [eqn. (4)]. Cleavage of the Me–O bond affords **6** [eqn. (5)], which forms an acid–base complex **7** along with free BF_3 [eqn. (6)]. Hydrolysis of **7** with moisture or small amounts of water present in the reaction medium gives **2**. The regenerated free BF_3 coordinates **1a** to produce **5** [eqn. (4)] and thus a catalytic cycle continues to produce 7.§

$$Bu_4NF + BF_3{\cdot}OEt_2 \rightleftharpoons Bu_4NF{\cdot}BF_3 + OEt_2 \quad (3)$$

$$\mathbf{1a} + BF_3{\cdot}THF \rightleftharpoons \underset{\mathbf{5}}{Bu_3Sn\text{-}CH_2\text{-}CH{=}CH\text{-}CH(OMe)\text{-}BF_3} + Et_2O \quad (4)$$

$$\mathbf{5} \longrightarrow \underset{\mathbf{6}}{Bu_3Sn\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}OBF_2} + MeF \quad (5)$$

$$\mathbf{6} + Bu_4NF{\cdot}BF_3 \rightleftharpoons \underset{\mathbf{7}}{Bu_3Sn\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}OBF_2{\cdot}FNBu_4} + BF_3 \quad (6)$$

Taken together, the above processes seem to be controlled by a 'Lewis acid buffer' system. The Lewis acidity of $BF_3{\cdot}OEt_2$ is diminished or suppressed completely by conjugation with the Lewis base Bu_4NF. The catalytic cycle is made by the regeneration of BF_3 owing to convertion of the acidic **6** to the neutral adduct **7** [eqn. (6)].

The present development not only provides a synthetically useful method for the selective deprotection of γ-alkoxystannanes, but also poses a mechanistically interesting proposal. Studies on a variety of Lewis acid–Lewis base combinations are in progress. Vladimir Gevorgyan gratefully acknowledge the Ciba-Geigy Foundation for financial support.

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Footnotes

† As another reasonable explanation of the results observed one may propose a mechanism involving the formation of the hypervalent tin species **4** at the initial stage of reaction. However, ^{119}Sn NMR spectroscopy investigation revealed that there is no interaction between the Sn atom of **1a** and Bu_4NF; addition of 1 equiv. Bu_4NF in THF to 0.1 mol dm^{-3} solution of **1a** in CD_2Cl_2 (δ ^{119}Sn = −16 *vs.* external standard of Me_4Sn) did not indicate any noticeable up-field shift of the Sn nucleus in the temperature range from +25 to −95 °C. Accordingly, the mechanism *via* **4** is not responsible for the present deprotection.

$$\left[Bu_3Sn(F)\text{-}CH_2\text{-}CH{=}CH\text{-}CH(OR)^{\delta-}\right]^-Bu_4N^+$$

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‡ The $BF_3{\cdot}THF$ donor–acceptor complex obviously formed by the reaction of $BF_3{\cdot}OEt_2$ and Bu_4NF–THF in CH_2Cl_2 because of higher stability of $BF_3{\cdot}THF$ than $BF_3{\cdot}OEt_2$.[5]

§ Eqns. (4) and (5) are consistent with the generally accepted mechanism of alkoxy-deprotection reactions.[6]

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