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Protic Solvent-Promoted Neutral Allylation of Aldehydes and Ketones with 1,8-Bis(allylstannyl)naphthalenes

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Abstract: The allylation reactions of carbonyl compounds using 1,8bis(dibutylstannyl)naphthalene **1** (R = Bu) were dramatically promoted by using a mixture of THF and CF₃CH₂OH (5 : 1) as solvent. The rate acceleration was due to the enhancement of the Brønsted acidity of CF₃CH₂OH by the formation of the chelate complex **6** ($R = CH_2CF_3$) resulting from the chelation effect of two neighboring tin atoms.

Recently we reported that 1,8-bis(allylstannyl)naphthalenes **1** are extremely effective allylation agents for aldehydes and ketones under neutral conditions without any catalyst since they take advantage of the chelation-induced Lewis acidity of bidentate bis(stannyl) compounds as shown in **2**.¹ This neutral allylation can be executed even in aqueous media for highly reactive aldehydes such as α -keto and α -halo aldehydes, which usually exist as hydrates, hemiacetals or as an aqueous solution.² This observation prompted us to examine the solvent effect on the rate acceleration of the neutral allylation with 1,8-bis(allylstannyl)naphthalenes **1**. Here we wish to report a new, protic solvent-promoted neutral allylation of carbonyl compounds.³



Allylation of benzaldehyde 4 ($R^1 = Ph$, $R^2 = H$) with 1,8bis(allyldibutylstannyl)naphthalene 1 (R = Bu) was carried out at 60 °C for 3.5 h in various solvents (eq 1) and selected results are summarized in Table 1. Since one of two allyl groups of 1 was transferred to carbonyl compounds, the chemical yields of allylation products were calculated based on the amount of 1. In THF solvent, allylation is very sluggish and furnishes homoallylic alcohol 5 ($R^1 = Ph$, $R^2 = H$) in only 10% yield (entry 1). Addition of DMSO to THF slightly increased the rate of allylation (entry 2). Use of the protic solvents MeOH and H₂O gave better results (entries 3 and 4), and in particular, addition of 17% CF₃CH₂OH in THF (vol ratio, 1:5) markedly enhanced the rate of allylation (entry 6). It should be noted that attempted allylation of benzaldehyde with monoallylic stannane 3 under these reaction conditions resulted in total recovery of benzaldehyde.⁴ However, increasing the volume ratio of CF3CH2OH in THF further enhanced the yield of homoallylic alcohol 5 ($R^1 = Ph$, $R^2 = H$) (entries 7 and 8), thereby providing a synthetically useful allylation procedure, though the corresponding monostannane **3** also gave the allylated product **5** (\mathbf{R}^1 = Ph, $R^2 = H$) in 1~37% yield.



Table 1. Allylation of benzaldehyde with bis(allylstannane) 1 (R = Bu) in various solvents a

| entry | solvent | % yield of 5 b | |
|-------|--|------------------------|--|
| 1 | THF | 10 | |
| 2 | THF/DMSO (5:1) | 24 | |
| 3 | THF/MeOH (5:1) | 24 (71) ^c | |
| 4 | THF/H ₂ O (5:1) | 34 (74) <i>d</i> | |
| 5 | THF/(CF3)2CHOH (5:1) | 30 | |
| 6 | THF/CF ₃ CH ₂ OH (5:1) | 82 | |
| 7 e | THF/CF ₃ CH ₂ OH (2:1) | 79 (1) <i>f</i> | |
| 8 e | CF ₃ CH ₂ OH | 98 (37) <i>f</i> | |

^{*a*} The reaction was carried out using bis(allylstannyl)naphthalene 1 (R = Bu; 1 equiv) and benzaldehyde (5 equiv) at 60 °C for 3.5 h unless otherwise noted. ^{*b*} Isolated yield of 5 (R¹ = Ph, R² = H). ^{*c*} Yield at 60 °C for 9 h. ^{*d*} Yield at 60 °C for 5 h. ^{*e*} The reaction was conducted at 60 °C for 2 h. ^{*f*} Yield with monostannane 3

With this information at hand, the allylations of 1 (R = Bu) in the mixture of CF₃CH₂OH and THF (volume ratio = 1:5) were carried out with several carbonyl substrates and the results are recorded in Table 2.⁵

| Table | 2. | Allylation | of | several | carbonyl | substrates | with |
|----------|------|----------------------|------|------------|----------|------------|------|
| bis(ally | lsta | nnane) 1 (R = | : Bu |) <i>a</i> | | | |

| entry | carbonyl substrate | solvent | condition (°C, h) | % yield ^l |
|-------|------------------------------------|----------------|----------------------|----------------------|
| 1 | PhCHO | THF/CF3CH2OH c | 60, 3.5 | 82 |
| 2 | PhCHO | THF | 60, 3.5 | 10 |
| 3 | C ₆ H ₁₁ CHO | THF/CF3CH2OH c | 60, 4.5 | 70 |
| 4 | C ₆ H ₁₁ CHO | THF | 60, 4.5 | 15 |
| 5 | cyclohexanone | THF/CF3CH2OH c | 60, 24 | 67 |
| 6 | cyclohexanone | THF | 60, 24 | trace |

^a The reaction was carried out using bis(allylstannyl)naphthalene 1 (R = Bu; 1 equiv) and carbonyl substrate (5 equiv). ^b Isolated yield. ^c Volume ratio of THF/CF₃CH₂OH = 5:1

Since the present allylation can be accelerated in protic solvents to a greater extent than in the polar, aprotic DMSO, the polarity of solvents is apparently not an important factor. Assuming that the chelate complex **6** (R = CH₂CF₃) between **1** (R = Bu) and CF₃CH₂OH would be formed by the latent Lewis acidity of bis(stannyl) group of **1** (R = Bu), this chelation should induce the activation of carbonyl substrates greatly via the effective hydrogen bonding between the carbonyl group and the coordinated solvent, thereby promoting the allylation reaction through the eight-membered transition state as depicted in **7** (R = CH₂CF₃).⁶



References and Notes

- Asao, N.; Liu, P.; Maruoka, K. Angew. Chem., Int. Ed. Engl. 1997, 36, 2507.
- (2) Reviews on the reactivity of allylstannane: a) Yamamoto, Y. *Aldrichim. Acta* 1987, 20, 45; b) Yamamoto, Y. *Acc. Chem. Res.* 1987, 20, 243; c) Hull, C.; Mortlock, S. V.; Thomas, E. J. *Tetrahedron* 1989, 45, 1007; d) Nishigaichi, Y.; Takuwa, A.; Naruta, Y.; Maruyama, K. *ibid.* 1993, 49, 7395.
- (3) a) Cokley, T. M.; Marshall, R. L.; McCluskey, A.; Young, D. J. *Tetrahedron Lett.* 1996, *37*, 1905; b) Cokley, T. M.; Harvey, P. J.; Marshall, R. L.; McCluskey, A.; Young, D. J. *J. Org. Chem.* 1997, 62, 1961.

- (4) Attempted allylation of benzaldehyde with 1-(allyldibutyl-stannyl)naphthalene in place of **3** gave similar results.
- (5) The allylation of benzaldehyde is representative (entry 1 in Table 2): To a solution of $\mathbf{1}$ (R = Bu) (337 mg, 0.50 mmol) in 1.2 mL of THF/CF₃CH₂OH (vol. ratio = 5:1) was added benzaldehyde (0.25 mL, 2.5 mmol) at room temperature under Ar. The mixture was allowed to warm to 60 °C, and stirred for 3.5 h at this temperature. After cooling to room temperature, the mixture was directly applied to column chromatography on basic silica gel using a mixture of hexane and EtOAc (5:1) as eluent to give 1-phenyl-3-buten-1-ol, $\mathbf{5}$ (R¹ = Ph, R² = H) (61 mg, 82% yield) as a colorless oil.
- (6) The similar eight-membered transition state was suggested in the reaction of tetraallyltin with aldehydes in methanol: See ref. 3.
- (7) Brønsted acid catalyzed allylations: a) Denmark, S. E.; Weber, E. J.; Wilson, T. M.; Willson, T. M. *Tetrahedron* 1989, 45, 1053;
 b) Gevorgyan, V.; Kadota, I.; Yamamoto, Y. *Tetrahedron Lett.* 1993, *34*, 1313.