Chlorotrimethylsilane-Acetonitrile System as a New Promoter for Carbonyl Allylation by Diallyldibutyltin

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(Received October 12, 1994)

Chlorotrimethylsilane combined with acetonitrile has characteristically promoted allylation of carbonyl compounds by diallyldibutyltin to produce a variety of homoallyl silyl ether in good yields, while the addition of HMPA or LiCl disturbed the allylation.

The addition of allylic tins to carbonyl compounds is a potentially useful tool for stereocontrolled carbon-carbon bond formation, when carbonyl moieties are generally activated by metallic Lewis acids like $TiCl_4$ and BF_3, but transmetallations of allylic tins are often accompanied.[2,3] Therefore, the reaction conditions such as addition orders of reagents must be controlled carefully. The development of new activation method is still a significant target. Chlorotrimethylsilane has recently received attention as a mild and unique activator in Michael type addition using such metallic reagents as cuprates,[4] zincates,[5] silyl enolates[6] and tin (II) enolates.[7]

We now report an alternative promising system in which a good enhancement of the allylation by diallyldibutyltin was obtained with chlorotrimethylsilane in acetonitrile. Of particular note is the sufficient use of an equimolar amount of acetonitrile to chlorotrimethylsilane. In addition, the isolation procedure of the produced silyl ethers is often tedious under considerably acidic conditions, where careful work-up using an amine at low temperature is required for preventing desilylation.[8] On the contrary, our procedure required only simple treatment washing with NH_4F aq to obtain the silylating product without desilylation.

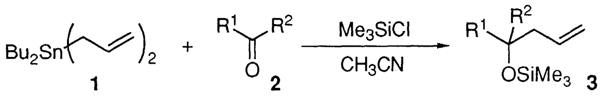
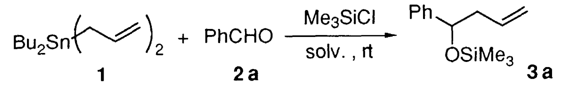


Table 1 shows the effect of solvents examined for the reaction of diallyldibutyltin (**1**) with benzaldehyde (**2a**) in the presence of Me_3SiCl.[9] The choice of solvents was definitively important. The use of benzene completely depressed the allylation. Either THF or dichloromethane, representative solvents for Lewis acid-promoted allylation, gave **3a** in only 5% and 8% yields, respectively, and the allylic tin remained unreactive. Among many solvents examined the most effective one was acetonitrile, affording the silylating product **3a** quantitatively in a short time at ambient temperature. Even adding equimolar acetonitrile in THF solution dramatically accelerated the allylation (Entry 7). Using an equimolar amount of benzonitrile also caused effective carbonyl addition though silylation was insufficient (Entry 8). The addition of either HMPA or LiCl depressed the yield of **3a** (entries 9 and 10).[10] The formation of a complex between iodotrimethylsilane and acetonitrile has been reported by Olah and coworkers.[11] These facts suggest that an appropriate interaction between chlorotrimethylsilane and acetonitrile is crucial for the allylation, and HMPA perhaps disturbed the interaction. This is in an interesting contrast to the effective support of Me_3SiCl-HMPA system in 1,4-addition of organocuprates to enones, where effective silylation has been reported.[4b,12]

No reaction of diallyldimethylsilane with benzaldehyde in the presence of Me_3SiCl took place at room temperature.

Table 1. Solvent Effect in the Reaction of Diallyldibutyltin (**1**) with Benzaldehyde (**2a**)[a]



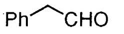
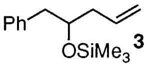
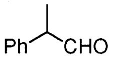
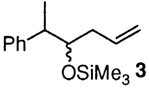
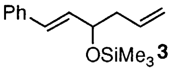
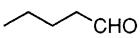
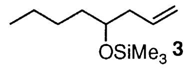
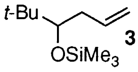
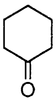
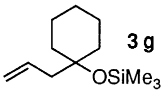
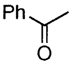
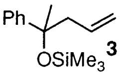
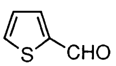
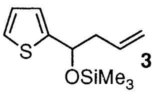
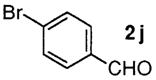
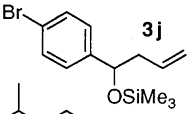
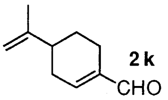
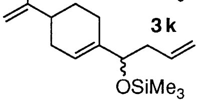
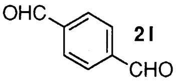
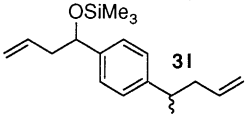
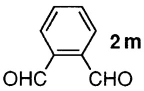
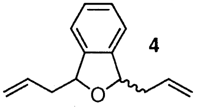
Entry	Solv.	Time /h	Yield /%
1	benzene	5	trace
2	THF	1	5
3	dichloromethane	2	8
4	1,2-dichloroethane	1	trace
5	CH_3CH_2CN	1	95
6	CH_3CN	1	>99
7	THF (CH_3CN[b])	1.5	83
8	THF (PhCN[b])	1	53(35)[c]
9	CH_3CN (HMPA[b])	1	40
10	CH_3CN (LiCl[b])	1	75

[a] All reactions were carried out in solvent (2 mL) using allyltin **1** (1 mmol), aldehyde **2a** (2 mmol) and Me_3SiCl (2 mmol) at room temperature.
[b] 2 mmol. [c] Corresponding homoallylalcohol was obtained.

Allylation of various carbonyl compounds was investigated and the results are shown in Table 2. It is noteworthy that both of the two allyl groups of **1** participated in this allylation reaction. Acetonitrile could be conveniently used as solvent although an equimolar addition of acetonitrile in THF effected the allylation (**2b**, **e**, **g**, and **h**). Almost all the reactions with aldehydes proceeded exothermically and completed within 1 h. The reaction with branched aldehyde **2c** proceeded to form corresponding homoallyl silyl ether in a high yield. Only 1,2-adduct **3d** was obtained in the reaction with α,β-unsaturated aldehyde **2d**. The aldehyde bearing a bulky substituent **2f** gave a moderate yield. The cyclic ketone **2g** afforded **3g** in high yield, although acetophenone (**2h**) gave a low yield even after a prolonged reaction period at 55 °C. The functional groups in the aldehydes **2i, 2j, 2k** tolerated the carbonyl allylation. Both the carbonyl groups of terephthalaldehyde (**2l**) were allylated to produce the corresponding homoallyl silyl ether **3l**. The phthalan derivative **4** from **2m** seemed to be produced *via* trimethylsilylation because no formation of **4** was detected in the absence of chlorotrimethylsilane.

As to the mechanistic aspect, chlorotrimethylsilane combined with acetonitrile[11] may coordinates the carbonyl oxygen or promote the silylation of the resulting homoallyl stannyl ether into the silyl ether **3**. Although no confirmed evidence has been

Table 2. Allylation of Carbonyl Compounds[a]

Entry	Carbonyl	Product[b]	Yield /%
1	 **2b**	 **3b**	>99 >99[c]
2	 **2c**	 **3c**	>99 (68/32)[d]
3	 **2d**	 **3d**	91
4	 **2e**	 **3e**	72, 81[c]
5	t-BuCHO **2f**	 **3f**	63
6[e]	 **2g**	 **3g**	90, 61[c]
7[f]	 **2h**	 **3h**	32, 57[c]
8	 **2i**	 **3i**	95
9	 **2j**	 **3j**	84
10	 **2k**	 **3k**	47 (50/50)[d] 92[g](50/50)[d]
11[h]	 **2l**	 **3l**	72 (50/50)[d]
12[h]	 **2m**	 **4**	97 (77/23)[i]

[a] Unless otherwise noted, reactions were carried out in CH_3CN (2 mL) using allyltin **1** (1 mmol), carbonyl **2** (2 mmol) and Me_3SiCl (2 mmol) at room temperature for 1 h. [b] All compounds showed characteristic spectral data and exact mass spectroscopic data. [c] CH_3CN (2 mmol), THF (2 mL). [d] Ratio of diastereomers determined by GLC. [e] 24 h. [f] 55 °C, 30 h. [g] 6 h. [h] Allyltin **1**, 2 mmol. [i] Ratio of diastereomers was obtained after column chromatography by GLC.

obtained, the activation of carbonyl moieties seems to be a significant step because no addition to aldehydes was detected in the absence of Me_3SiCl.[13] A possibility of the interaction between acetonitrile and tin reagent can not be excluded in this stage.

The combination of chlorotrimethylsilane and acetonitrile is now a new promoter for carbonyl allylation by diallyldibutyltin and a new approach in the syntheses of homoallyl silyl ethers.

This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236102 and on Japanese Junior Scientists from the Ministry of Education, Science and Culture, Japan.

References and Notes

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9 Typical procedure: Chlorotrimethylsilane (2.0 mmol) was added to a stirred solution of **1** (1.0 mmol) and **2a** (2.0 mmol) in dry acetonitrile (2 mL) and the mixture was stirred at ambient temperature for 1 h. Diethyl ether and aqueous NH_4F (15%) were added, and the organic layer was separated and washed with water, dried ($MgSO_4$) and evaporated. The crude product was purified by distillation to give the homoallyl silyl ether **3a** (bp 55 °C/0.1 mmHg).

10 5 mL of solvent was used because of low solubility of LiCl although it did not dissolve completely.

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13 The trapping by Me_3SiCl in a conjugate alkylation has been reported,[4] where an addition could take place even in the absence of it.