Triarylcarbenium Chlorides as Catalysts in Allylation Reaction: A Unique Type of Reaction with Negligible Intervention of Silyl Catalysis

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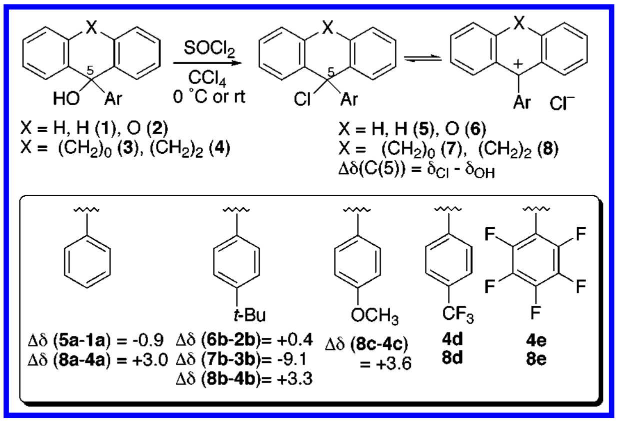
Received October 30, 1998

The addition reaction of allylstannanes to carbonyl-containing compounds by the action of promoters or catalysts has been recognized as an indispensable tactic for the synthesis of homoallylic alcohols.[1] Despite recent efforts along this line, few catalytic allylation systems of this category have been documented.[2] It has been more than 10 years since the seminal description of trityl ions as catalysts in a myriad array of enol silane derivative-mediated addition reactions.[3] However, their actual catalytic roles in such reactions have not yet been substantiated in view of the facile, intervening silyl catalysis vividly described in the literature.[4] Recently, we were engaged in clarifying this issue by directly observing the catalytic behavior of chiral triarylcarbenium ions in asymmetric Mukaiyama aldol additions and have identified the possible cause of competing silyl catalysis as the direct attack of a nucleophile (e.g., silyl ketene acetal) to the carbenium center of the catalyst with concomitant release of silyl-X species.[5] An intrinsically viable solution to this dilemma is by stereoelectronic modification of the trityl ions to increase their reactivity and compatibility and, in the meantime, to judiciously choose a counterion for the minimization of silyl catalysis.[6] On the basis of these two considerations, we sought the possible utility of trityl-type chlorides in catalytic reactions in view of their well-documented partially ionic characters[7] and the extremely weak Lewis acidic character of TMS-Cl in most solvent systems.[8] We herein describe our preliminary studies toward their catalytic uses in allylation reactions, which were not explored previously, and aim at providing more unambiguous evidence as to the role of trityl catalysis.

To find out the best combination of a diarylmethyl template and a pendant aryl group to reach a maximal reactivity of the corresponding trityl-type chloride, we have prepared various trityl-type alcohols by independent treatment of xanthone, fluorenone, benzophenone, and dibenzosuberone with five different aryllithiums of varying electron demands.[6,9] The resulting alcohols can be readily converted to the corresponding chlorides by treatment with $SOCl_2$ (5 equiv) in anhydrous CCl_4 at 0 °C or at ambient temperature, Scheme 1.[10] In the cases with the parent (Ar = C_6H_5) and electron-releasing (Ar = 4-*t*-BuC_6H_4, 4-MeOC_6H_4) aryl appendages, the trityl chlorides are stable enough to allow for full spectroscopic characterizations.[11] Their relative ionic characters were evaluated by the changes in the chemical shifts of the carbenium carbon (C(5)) between the alcohols and the corresponding chorides in ^{13}C NMR. With the same pendant aryl group (i.e., Ar = 4-*t*-BuC_6H_4), the C(5) in the dibenzosuberane(DBS)-based chloride (X = $(CH_2)_2$) shows the largest downfield change ($\Delta\delta = +3.3$ ppm). On the contrary, in the fluorene-based chloride (X= $(CH_2)_0$) it shows the largest upfield shift ($\Delta\delta = -9.1$ ppm). The template effect arranged with a decreasing order of $\Delta\delta(\delta_{Cl} - \delta_{OH})$ is as follows: DBS > xanthene (X = O) > diphenylmethyl (X = H, H) > fluorene. On the other hand, the para-substitution pattern of the aryl appendage exerts a minor inductive effect on the chemical shift of C(5). The largest chemical shift changes observed in the DBS-based system suggest that these trityl chlorides may display better carbenium chloride attributes and may thus be more Lewis acidic.

Scheme 1



Initial attempts in the allylations of benzaldehyde with allyltri-*n*-butyltin (1.2 equiv) catalyzed by the DBS-based trityl chloride **8b** (20 mol %) were disappointing. The addition product was isolated in 34−37% yields when the allylations were conducted in CH_2Cl_2 at ambient temperature for 48 h (entry 4), Table 1. Longer reaction time only slightly improved the chemical conversion. On the basis of a mechanistic consideration, we surmised that the poor conversion may have to do with a sluggish turn-over between Bu_3SnCl and the intermediate tritylated homoallylic alcohol (vide infra). As expected, the chemical yields of the allylation products were significantly improved to 87% when either TMS-Cl[12] or TBS-Cl (1.2 equiv) was added to the reaction media (entries 5 and 6).[13] Moreover, the catalyst **8b** was recovered quantitatively as its corresponding alcohol **4b** after hydrolytic workup.

The effects of templates and pendant aryl groups on the reactivity and compatibility of trityl-type chlorides under

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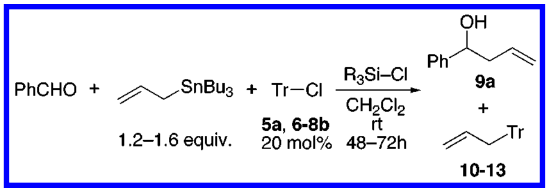
[12] For the uses of TMS-X to assist in turnover of metal-catalyzed reactions, see: (a) Gong, L.; Streitwieser, A. *J. Org. Chem.* **1990**, *55*, 6235. (b) Yu, C.-M.; Choi, H.-S.; Tung, W.-H.; Lee, S.-S. *Tetrahedron Lett.* **1996**, *37*, 7095. (c) Whitesell, J. K.; Apodaca, R. *Tetrahedron Lett.* **1996**, *37*, 3955.

[13] Acetyl chloride and TMS-Br can also promote the turnover of Tr-Cl, albeit with poorer efficiency.

10.1021/jo9821832 CCC: $18.00

Table 1. Effects of Silyl Promoters and Templates on the Trityl Chloride-Catalyzed Allylations of Benzaldehyde with Allytri-*n*-butyltin



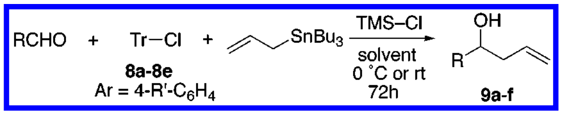
entry	TrCl (X)	promoter[a]	yield[b] (**9a**), %	yield,[b] %
1	**5a** (H, H)	TMSCl	65	quant (**10**)
2	**6b** (O)	TMSCl	56	quant (**11**)
3	**7b** ($(CH_2)_0$)	TMSCl	58	quant (**12**)
4	**8b** ($(CH_2)_2$)		37	0 (**13**)
5	**8b** ($(CH_2)_2$)	TMSCl	87	0 (**13**)
6	**8b** ($(CH_2)_2$)	TBSCl	85	0 (**13**)

[a] In all cases, 1.2 equiv of R_3SiX was added. [b] Isolated yields.

this allylation protocol was next examined. The triphenylmethyl-, fluorene-, and xanthene-derived chlorides, **5a** and **6**–**7b**, were also found to be capable of mediating the catalytic allylations. The homoallylic alcohol **9a** was produced in moderate (56–65%) yields. However, these catalysts were all completely consumed by direct nucleophilic allylation of allylstannane to their respective carbenium centers, Table 1. Presumably, the compatibility of **8b** with the nucleophilic allylstannane arises from the steric encumbrance of the carbenium center imposed by the pseudoaxial hydrogens of the two-carbon linkage in the DBS backbone.[14]

The reactivity of the DBS-based trityl chlorides was governed by the inductive, electronic stabilization of the incipient carbenium ions. The chlorides bearing the electron-withdrawing 4-trifluoromethyl- (R′ = CF_3) and pentafluorophenyl (R′ = F_5) groups led to the least productive allylations (<10 and 46%, respectively), entries 4 and 5 in Table 2. The chlorides bearing electron-releasing aryl groups (i.e., R′ = OCH_3 and *t*-Bu) behave slightly more efficient than the parent chloride (R′ = H) in the allylation (entries 1–3). It is important to note that the allylations in these three cases (entries 1–3) can even be completed at 0 °C in 72 h with equal performances (79–93%).[15] Among seven different solvents examined, the allylation utilizing the best DBS-based trityl chloride **8b** (R′ = *t*-Bu) proceeds most smoothly in CH_2Cl_2 (87%). The chemical yields of the homoallylic alcohol **9a** fell within a range of 20–47% when reactions were run in other solvent systems. More importantly, control experiments in the absence of trityl chloride **8b** revealed that TMS-Cl-mediated allylations were negligible in most solvents under similar reaction conditions except in $C_2H_5NO_2$ (22%) and CH_3CN (34%).[16] The optimal allylation procedure was applicable to both aromatic and aliphatic aldehydes. With the six representative aldehydes examined, the homoallylic alcohols were all furnished in good (77%, R = Ph-$(CH_2)_2$) to excellent yields (97%, R = 2-Naph).

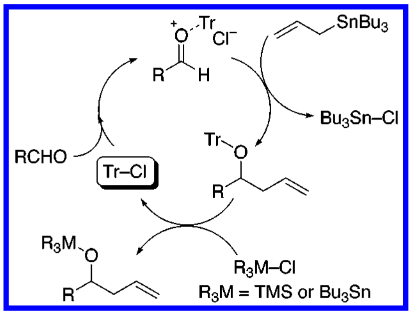
Table 2. Effects of Pendant Aryl Groups and Solvents on the Allylations of Aldehydes with Allytri-*n*-butyltin Catalyzed by 8



entry	R	TrCl (R′)	solvent	yield,[a] %
1	Ph	**8a** (H)	CH_2Cl_2	74/84[b]
2	Ph	**8b** (*t*-Bu)	CH_2Cl_2	87 (18)[c]/93[b]
3	Ph	**8c** (OCH_3)	CH_2Cl_2	77/79[b]
4	Ph	**8d** (CF_3)	CH_2Cl_2	<10
5	Ph	**8e** (F_5)[d]	CH_2Cl_2	46
6	Ph	**8b** (*t*-Bu)	CCl_4	47 (0)[c]
7	Ph	**8b** (*t*-Bu)	toluene	20 (0)[c]
8	Ph	**8b** (*t*-Bu)	Et_2O	41 (5)[c]
9	Ph	**8b** (*t*-Bu)	THF	26 (4)[c]
10	Ph	**8b** (*t*-Bu)	$EtNO_2$	33 (22)[c]
11	Ph	**8b** (*t*-Bu)	CH_3CN	39 (34)[c]
12	2-Naph	**8b** (*t*-Bu)	CH_2Cl_2	97 (**9b**)
13	4-$MeOC_6H_4$	**8b** (*t*-Bu)	CH_2Cl_2	91 (**9c**)
14	4-$NO_2C_6H_4$	**8b** (*t*-Bu)	CH_2Cl_2	87 (**9d**)
15	4-HC(O)C_6H_4	**8b** (*t*-Bu)	CH_2Cl_2	85 (**9e**)[e]
16	Ph$(CH_2)_2$	**8b** (*t*-Bu)	CH_2Cl_2	77 (**9f**)

[a] Isolated yields. [b] The isolated yieds for the reactions performed at 0 °C. [c] The values in parentheses correspond to allyaltions without **8b**. [d] The pending aryl group is C_6F_5. [e] Bis(homoallylic alcohol) was obtained.

Scheme 2



A mechanistic picture converged from the studies is delineated in Scheme 2. Initial attack of allyltri-*n*-butyltin to the trityl chloride-activated aldehyde with extrusion of tri-*n*-butyltin chloride generates the tritylated homoallylic alcohol **14**. Metathesis of the trityl ether with Bu_3SnCl would generate the corresponding stannylated ether with release of the trityl chloride. Since this exchange process is hampered by the steric bulk of Bu_3SnCl, the use of TMS-Cl or TBS-Cl can facilitate this turnover process, thus completing the catalytic cycle. We have further confirmed the feasibility of this exchange process by treatment of an independently prepared tritylated homoallylic alcohol **14a** (Tr = Ph_3C) with TMS-Cl (1.2 equiv) in CD_2Cl_2. The exchange occurs readily with a half-life ($t_{1/2}$) of 30 min as monitored by ^1H NMR.

In conclusion, we have developed a new type of nucleophile-tolerant triarylcarbeium chlorides based on the dibenzosuberane scaffold. *We have provided the first unambiguous evidence claiming their catalytic roles in the allylation reactions with minimal intervention of silyl catalysis.* Efforts aimed at the development of an asymmetric variant of this new catalytic system are currently underway.

Acknowledgment. We are grateful to the National Science Council of the Republic of China for generous support of this research.

Supporting Information Available: Preparation and full spectroscopic characterization of **1a**, **2b**, **3b**, **4a**–**e**, **5a**, **6b**, **7b**, **8a**–**c**, **9a**–**f**, **10**–**13**, and **14a** as well as the optimal procedures for the allylations catalyzed by **5**–**8** are provided.

JO9821832

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(14) A control experiment by direct equimolar mixing of catalyst-**8b** with allyltributyltin in CH_2Cl_2 at ambient temperature for 3 days led to the formation of **13** in <5% yield.

(15) For the allylations catalyzed by **5a**, **6b**, and **7b** at 0 °C, the product yield can be improved from 56% to 83% only in the case of **6b** (X = O) although these catalysts were all still gradually consumed at this temperature. Apparently, the direct nucleophilic allylation of **6b** was effectively slowed down at 0 °C.

(16) Increased Lewic acidity of TMSCl in CH_3CN has been documented; see: (a) Wang, D.-K.; Dai, L.-X.; Hou, X.–L. *Tetrahedron Lett.* **1995**, *36*, 8649. (b) Yasuda, M.; Fujibayashi, T.; Shibata, I.; Baba, A.; Matsuda, H.; Sonoda, N. *Chem. Lett.* **1995**, 167.