

binding are distinct processes, which are not necessarily related.^{3,5,12}

From correlation analysis of rate data using steric parameters, Matsui et al.³ concluded that the substituents of *p*-X-phenyl acetates are probably not inside the cavity of β -CD during the transition state for acyl transfer. The present results provide direct evidence for this conclusion.

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(12) Schowen, R. L. In *Transition States in Biochemical Processes*; Gaudour, R. D., Schowen, R. L. Eds.; Plenum: New York, 1978; Chapter 2. Tee, O. S. *Carbohydr. Res.* In press.

Chemoselective Synthesis of Allyltrimethylsilanes by Cross-Coupling of Vinyl Triflates with Tris((trimethylsilyl)methyl)aluminum Catalyzed by Palladium(0)[†]

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The palladium(0)-catalyzed cross-coupling of organostannanes with vinyl triflates recently developed by Stille¹ constitutes an especially valuable olefin synthesis, in part due to the easy access of the triflate from carbonyl precursors.² The organostannane, the organometallic component of this reaction, derives its special utility from its stability and chemoselectivity³ vis-à-vis, for example, the more typical Grignard,⁴ organozinc, or alane reagents in this regard.⁵ Using tetrakis((trimethylsilyl)methyl)tin⁶ [Sn(CH₂SiMe₃)₄] in conjunction with a vinyl triflate should then provide an elegant route to allyltrimethylsilanes. However, in our hands, and as noted by Stille in the context of aryl triflates,⁸ this stannane does not function in the cross-coupling reaction with vinyl triflates. In this communication, we now report that tris((trimethylsilyl)methyl)aluminum (**1**),⁹ (Me₃SiCH₂)₃Al, conveniently generated in situ from commercially available ((trimethylsilyl)methyl)lithium and aluminum trichloride, functions as an unusually chemoselective alane reagent in the palladium(0)-catalyzed cross-coupling of vinyl triflates to give allyltrimethylsilanes as shown in Table I.

[†] Dedicated to the memory of Professor J. K. Stille.

(1) (a) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. (b) Scott, W. J.; Stille, J. K. *Ibid.* **1986**, *108*, 3033. (c) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(2) (a) Scott, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47. (b) McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1983**, *24*, 979. (c) Crisp, G. T.; Scott, W. J. *Synthesis* **1985**, 335. (d) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Ibid.* **1982**, 85. (e) Stang, P. J.; Treptow, W. *Ibid.* **1980**, 283.

(3) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 4051.

(4) For example, see: Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M. *Tetrahedron* **1982**, *38*, 3347.

(5) For some leading references, see: (a) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669. (b) Negishi, E. *Acc. Chem. Res.* **1982**, *15*, 340. (c) Trost, B. M.; Verhoeven, T. R. *Compr. Organomet. Chem.* **1982**, *8*, 799.

(6) Kruglaya, O. A.; Kalinina, G. S.; Petrov, B. I.; Vyazankin, N. S. *J. Organomet. Chem.* **1972**, *46*, 51.

(7) For some pertinent references on the utility of allylsilanes, see: (a) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200. (b) Colvin, E. W. *Silicon in Organic Synthesis*; R. E. Krieger Publishing Co.: Malabar, Florida, 1985; Chapter 9. (c) Parnes, Z. N.; Bolestova, G. I. *Synthesis* **1984**, 991.

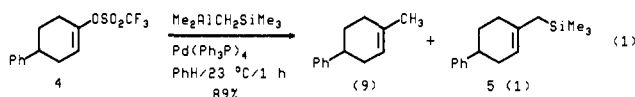
(8) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.

(9) Neat tris((trimethylsilyl)methyl)aluminum is a pyrophoric liquid. See: Tessier-Youngs, C.; Beachley, O. T. *Inorg. Synth.* **1986**, *24*, 92.

We were prompted to undertake this study from a need for substantial quantities of 2-((trimethylsilyl)methyl)-2-cyclohexen-1-one (**2**), previously reported¹⁰ only as a component of a mixture, after five steps and in less than 10% yield. Thus, we reasoned that **2** might be quickly fashioned from triflate **3**, available from 1,2-cyclohexanedione (Tf₂O, Et₃N, CH₂Cl₂, -78 °C, 91%), and Sn(CH₂SiMe₃)₄. However, enone triflate **3**, as well as triflate **4**, derived from 4-phenylcyclohexanone (81%),^{2c} did not react with this stannane when the Stille protocol¹ was used.

Reasoning that a sluggish transmetalation step in the catalytic cycle^{1b} might explain the reluctance of the (trimethylsilyl)methyl (Me₃SiCH₂) group to be delivered via initial Sn → Pd transfer, we considered more reactive metals (MgX, ZnX, AlR₂) in this regard. However, Me₃SiCH₂MgCl¹¹ is not expected to be compatible with the enone function in **2** or **3**, and the corresponding organozinc chloride reagent results in only 25% conversion of **4** to **5** (2 equiv, 5 mol % NiCl₂-dppp, THF, 65 °C, 12 h). Although an aluminum reagent seemed attractive,¹² chemoselectivity vis-à-vis the enone remained in doubt¹³ due to the reactivity of this functionality toward alanes.¹⁴

Nevertheless, we chose ((trimethylsilyl)methyl)dimethylaluminum (Me₂AlCH₂SiMe₃) as our trimethylsilylmethylating reagent, which was prepared in situ from 1 equiv each of Me₃SiCH₂Li and Me₂AlCl.¹⁵ From eq 1, it can be seen that triflate **4** gives a 9:1 mixture of olefins using Me₂AlCH₂SiMe₃ in conjunction with a highly active in situ generated Pd(0) catalyst¹⁶ wherein CH₃ transfers in preference to CH₂SiMe₃.



From Table I it can be seen that (Me₃SiCH₂)₃Al (**1**), generated in situ by addition of 3 equiv of Me₃SiCH₂Li (1 M in pentane) to 1 equiv of AlCl₃ suspended in 1,2-dichloroethane, reacts with a variety of vinyl triflates under mild conditions, catalyzed by in situ formed tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄]¹⁶ in benzene, to give good yields of the corresponding allyltrimethylsilanes. The reaction proceeds with a remarkably high degree of chemoselectivity. As seen in entries 1 and 4–8, enone, enoate, ester, allyl alcohol, and aryl bromide functionalities remain intact even in the presence of excess **1**. That only one of the three Me₃SiCH₂ groups in **1** is transferred is supported by the fact that less than 1 equiv of **1** results in incomplete reaction, and typically 1.2–1.4 equiv gives the best results. Although we did not explore the use of neat **1**,⁹ the hazard of dealing with this reagent coupled with the need for LiCl (typically 3 equiv) in the vinyl triflate/Pd(0) oxidative addition step¹ favors the current protocol.

The expected stereospecificity of the title reaction was addressed and confirmed by using the pure (*E*)-vinyl triflate **6** (52%) derived from ethyl acetoacetate (Tf₂O, Et₃N, CH₂Cl₂, -78 °C; 2.5:1 *E/Z*). Under the typical conditions, only the (*E*)-allylsilane isomer **7** is

(10) Fleming, I.; Goldhill, J.; Perry, D. A. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1563.

(11) For the synthesis of allylsilanes from vinyl phosphonates using this reagent, see: Heptelicidic acid synthesis. Danishefsky S. J.; Mantlo, N. *J. Am. Chem. Soc.* **1988**, *110*, 8129 and ref 15 therein.

(12) For successful cross-coupling of alanes with enol and aryl phosphonates, see: (a) Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1980**, *21*, 2531. (b) Sato, M.; Takai, K.; Oshima, K.; Nozaki, H. *Ibid.* **1981**, *22*, 1609. (c) Hayashi, T.; Katsuro, Y.; Okamoto, Y.; Kumada, M. *Ibid.* **1981**, *22*, 4449.

(13) For a review of the reaction of carbonyl compounds with various alkylaluminum reagents, see: (a) Eisch, J. J. *Compr. Organomet. Chem.* **1982**, *1*, 555. (b) Zietz, J. R.; Robinson, G. C.; Lindsay, K. L. *Ibid.* *7*, 365.

(14) For examples of chemoselectivity observed with alane reagents, see: (a) Et₂AlSnBu₃: Trost, B. M.; Herndon, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 6835. (b) (Me₃Si)₃Al: Trost, B. M.; Yoshida, J.; Lautens, M. *Ibid.* **1983**, *105*, 4494. (c) Reference 15b.

(15) For examples of similar in situ generation of alanes and selective group transfer, see: (a) References 12a and 14a. (b) Trost, B. M.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1986**, *108*, 1098.

(16) Trost, B. M.; Bonk, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 1778.

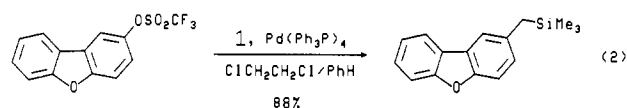
Table I. Conversion of Vinyl Triflates to Allyltrimethylsilanes

entry	vinyl triflate ^a	temp, °C/time, h/ equiv of 1	product	yield, ^b %
1		23/0.6/1.2		60
2		23/2/1.4		81
3		23/1/1.4		75
4 ^c		40/8/1.4		70 (83)
5 ^d		23/0.8/2.0		65
6 ^e		23/2/1.4		81
7		23/0.2/2.2		84
8 ^f		23/2.5/1.2		48 (68)

^a The preparation of the vinyl triflates is described in the supplementary material. ^b Isolated yields of homogeneous material; yields in parentheses are based on recovered vinyl triflate. ^c 60% conversion to the allylsilane after 1 h/23 °C with 1.3 equiv of 1. ^d 50% conversion to the allylsilane after 1 h/23 °C with 1.1 equiv of 1. ^e The allylsilane is known; see ref 21. ^f Decomposition of the catalyst occurred after 2 h.

obtained (entry 8). The structures of 6 and 7 are secured from a strong NOE enhancement of the vinyl proton (δ 5.43) upon irradiation of the CH₂ signal (δ 1.68) in 7 and the lack of any such enhancement upon irradiation of the CH₃ in 6 or 7.

In addition to vinyl triflates, aryl triflates also serve as suitable partners for the Pd(0)-catalyzed reaction with 1 (eq 2).



The utility of these functionally diverse allyltrimethylsilanes is illustrated, for example, by Luche¹⁷ 1,2-reduction of 2 (prepared in ca. 50% yield on a 0.1-mol scale) to 2-((trimethylsilyl)methyl)-2-cyclohexen-1-ol (78%). This bifunctional reagent has been employed by Trost in an approach to taxane¹⁸ and in trimethylenemethane-palladium chemistry.¹⁹

In summary, we have presented a highly chemoselective method for the formation of functionalized allyltrimethylsilanes from an array of vinyl triflates. The ready availability of the triflate from carbonyl precursors,² coupled with the high degree of selectivity exhibited by (Me₃SiCH₂)₃Al (1), now offers a valuable tool for

introduction of the Me₃SiCH₂ moiety²⁰ into organic molecules. A sample experimental procedure is given in ref 22.

Supplementary Material Available: Experimental protocols and characterization data for the compounds from Table I and eq 2 (6 pages). Ordering information is given on any current masthead page.

(20) For recent reports on the synthesis of allyltrimethylsilanes, see: (a) Hwu, J. R.; Lin, L. C.; Liaw, B. R. *J. Am. Chem. Soc.* **1988**, *110*, 7252 and ref 9 therein. (b) Ni, Z.-J.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1011. (c) Wang, K. K.; Yang, K. E. *Tetrahedron Lett.* **1987**, *28*, 1003. (d) Hayashi, T.; Konishi, M.; Okamoto, Y.; Kabeta, K.; Kumada, M. *J. Org. Chem.* **1986**, *51*, 3772.

(21) Hosomi, A.; Iguchi, H.; Sasaki, J.; Sakurai, H. *Tetrahedron Lett.* **1982**, *23*, 551.

(22) To a magnetically stirred suspension of AlCl₃ (8.55 mmol) in dry 1,2-dichloroethane (50 mL) under argon was added, over 10 min, ((trimethylsilyl)methyl)lithium (1.0 M in pentane; 26.0 mmol). The resulting mixture was stirred at room temperature for 30 min and then treated rapidly by cannula transfer with a solution of ethyl 4-(((trifluoromethyl)sulfonyl)oxy)-3-cyclohexene-1-carboxylate and the palladium(0) catalyst, which was prepared in a separate flask as follows: A solution of Pd(OAc)₂ (0.58 mmol) and Ph₃P (2.33 mmol) in dry benzene (25 mL) under argon was treated with *n*-butyllithium (2.5 M in hexane; 1.15 mmol) followed after 5 min by the addition of the vinyl triflate (6.00 mmol) either as a neat liquid or in dry benzene (10 mL). This solution was then immediately transferred via cannula as indicated above, and the reaction mixture was stirred for 2 h at 23 °C (or as indicated in the table). The workup consisted of dilution with CH₂Cl₂ and washing with 0.2 M HCl, H₂O, and brine. Purification by flash chromatography on silica gel using CH₂Cl₂/hexane gave 1.17 g (81%) of the pure product as a colorless liquid.

(17) Gemal, A. L.; Luche, J.-L. *J. Am. Chem. Soc.* **1981**, *103*, 5454.

(18) Trost, B. M.; Hiemstra, H. *Ibid.* **1982**, *104*, 886.

(19) Trost, B. M.; Nanninga, T. N. *Ibid.* **1985**, *107*, 1075.