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# A Stannylene/Aryl Iodide Reagent for Allylic CH Activation and Double Bond Addition Chemistry

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*Summary: Allylic CH bond activation and addition across the C═C double bond are both observed in the reactions of alkenes with a stannylene/phenyl iodide reagent. The relative amounts of each of these products are sensitive to the steric bulk of the alkene and of the aryl halide.*

CH activation of hydrocarbons and ethers to form Sn−C and Ge−C bonds can be accomplished under mild conditions using $EY_2$/PhX reagents (E = Ge, Sn; Y = $N(SiMe_3)_2$, $CH(SiMe_3)_2$; X = I, Br).[1,2] The direct reaction of germylenes and stannylenes with functional groups, particularly double bonds,[3,4] represents a major limitation of the chemistry developed to date. When the products of the CH activation contain a primary Sn−C bond, they can be directly employed for Stille cross-coupling chemistry[2,5,6] using the conditions reported by Fouquet.[7] However, these cross-coupling conditions only work with primary alkyl groups and attempts at other types of coupling reactions have often failed in our hands because the $-N(SiMe_3)_2$ substituent on tin transfers instead of the desired −R group.

The stannylene synthesized in 1991 by Kira et al., $\underbracket{SnC(SiMe_3)_2CH_2CH_2C}(SiMe_3)_2$ (**1**),[8,9] provides a possible solution to both of these limitations. **1** has been shown not to react with alkenes, including ethylene, although it does readily undergo 4 + 2 cycloaddition with 1,3-butadiene.[10] Furthermore, the ligand contains a chelated ring with Sn−C bonds which should be much less susceptible to transfer under coupling conditions. When stannylene **1** has been employed, allylic CH activation chemistry has been successfully achieved. Surprisingly, the **1**/PhI reagent is also observed to add across C═C double bonds. The regiochemistry of the reaction is anti-Markovnikov, consistent with an initial attack by a phenyl radical and subsequent trapping by the iodostannyl radical. Replacing PhI with the more bulky mesityl iodide (MesI) reagent has a dramatic impact on the distribution of products formed. The amount of oxidative addition product $ArISn[C_2(SiMe_3)_4C_2H_4]$ and double bond addition products formed is dramatically reduced.

**Activation of Allylic CH Bonds.** Activation of the allylic CH bond was achieved when a 1:1 mixture of **1** and PhI was added to tetramethylethylene, cyclohexene, cyclopentene, 1-pentene, 1-hexene, or 3,4-dihydro-2*H*-pyran (Scheme 1, Table 1). Formation of the CH activation products ranged from 5 to 80% when employing ~0.05 M solutions and slow addition of reagents using a syringe pump. The other major species produced in the reaction were those of the oxidative addition of PhI to **1** to form $PhISn[C_2(SiMe_3)_4C_2H_4]$ (**2**) and of the unexpected addition of **1**/PhI across the double bond (vide infra) to form **6**, **8**, and **10**. Separation of the CH activation, double bond addition, and oxidative addition products could be achieved by fractional crystallization or column chromatography. Column chromatography on silica gel was typically the most convenient and gave the highest yields. The structures of all compounds were assigned via a combination of $^1H$, $^{13}C$, and $^{119}Sn$ NMR spectroscopy, elemental analysis, infrared spectroscopy, and, in the case of **3**, **6**, **10**, and **11**, single-crystal X-ray diffraction (Figure 1). In addition, the bromine derivative of the cyclohexene product **4**, $[C_2H_4(SiMe_3)_4C_2]SnBr(C_6H_9)$ (**4′**), was synthesized independently by the reaction of **1** with 3-bromocyclohexene and fully characterized.

In previous studies employing germylenes, varying the steric bulk of the aryl iodide did not have a large impact on the ratio of CH activation/oxidative addition product formed.[11] However, for the chemistry employing stannylene **1**, increasing the steric bulk of the aryl halide had a major impact on the product distributions. Employing mesityl iodide (MesI) in reactions with tetramethylethylene, cyclohexene, and cyclopentene resulted in a dramatic reduction in the formation of oxidative addition product. Furthermore, the use of MesI also reduced the amount of double bond addition product observed with cyclopentene and 1-hexene. The use of PhBr dramatically reduced the rate of both the CH activation and double bond addition reactions.

Tin compounds derived from stannylenes containing primary and aromatic Sn−C bonds have previously been employed for Stille-type cross-coupling reactions using chemistry developed by Fouquet et al.[2,7,12] In order to assess the utility of secondary allylic Sn−C bonds derived from the CH activation chemistry for Stille-type cross-coupling, compound **4** was mixed with 1.5 equiv of PhI, 3 equiv of $Me_4NF$, and 10 mol % of $Pd(PPh_3)_4$ in 10 mL of dioxane with a 1,3,5-trimethoxybenzene integration standard. After heating at 77 °C for 16 h, 3-phenylcyclohexene was obtained in 70% yield.

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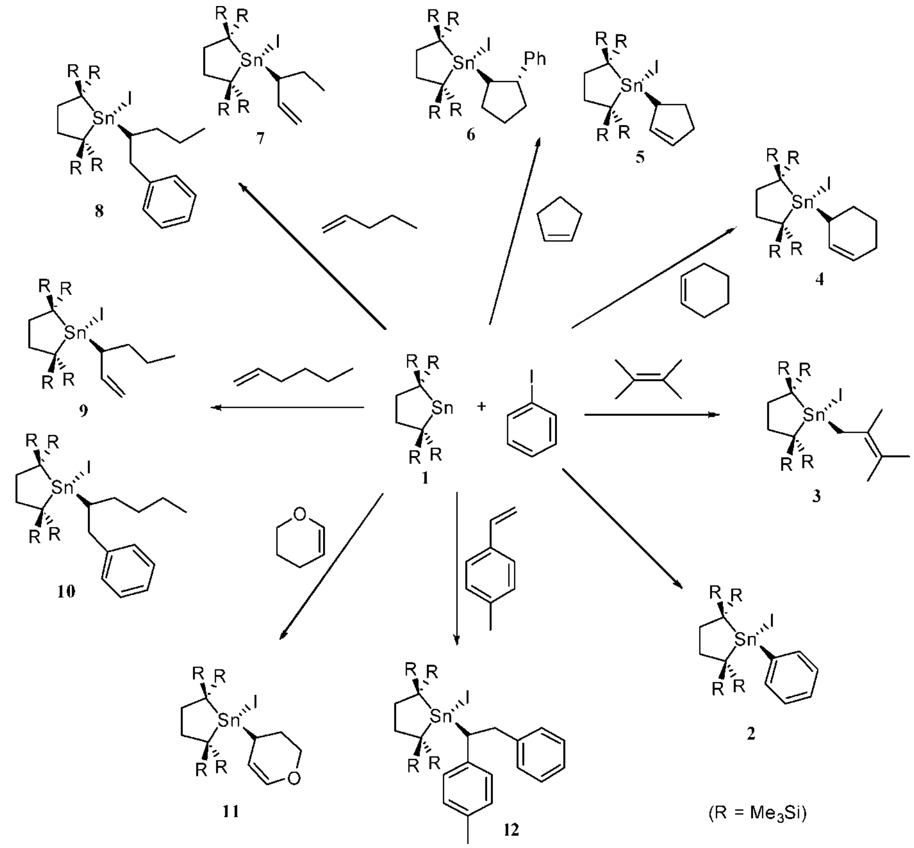
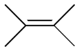
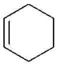
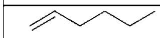
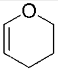
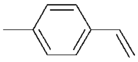
10.1021/om8000108 CCC: \$40.75

**Scheme 1**



(R = $Me_3Si$)

**Table 1. Product Distributions As Measured by $^1$H NMR Spectroscopy**[a]

| Alkene Substrate | % CH-Activation | | % Oxidative-addition | | % Double-Bond Addition | |
|---|---|---|---|---|---|---|
| | PhI | MesI | PhI | MesI | PhI | MesI |
|  | 67 | 100 | 33 | 0 | 0 | 0 |
|  | 74 | 100 | 20 | 0 | 6 | 0 |
|  | 67 | 100 | 1 | 0 | 32 | 0 |
|  | 20 | 40 | 7 | 15 | 67 | 40 |
|  | 5 | 30 | 0 | 15 | 60 | 50 |
|  | 80 | 90 | 0 | 1 | 0 | 0 |
|  | 0 | 0 | 0 | 5 | 90 | 50 |

[a] All reactions were performed using syringe pump techniques. Other unidentified products were also present for cases where the total sums to less than 100%.

**Addition to Double Bonds.** In addition to the anticipated allylic CH activation and oxidative addition products, a third species was also present in the reactions with tetramethylethylene, cyclohexene, cyclopentene, 1-pentene, and 1-hexene. $^1$H NMR spectroscopy indicated that the phenyl group was present but not attached to the tin atom, as could be ascertained by the absence of the characteristic ortho protons at $\delta$ 7.92 with $^3J_{^{119}\mathrm{Sn}-\mathrm{H}} = 16.5$ Hz. In addition, vinylic protons in the region $\delta$ 6.0–5.8 indicative of double bonds were absent. The implication of phenyl and tin addition across the double bond and the

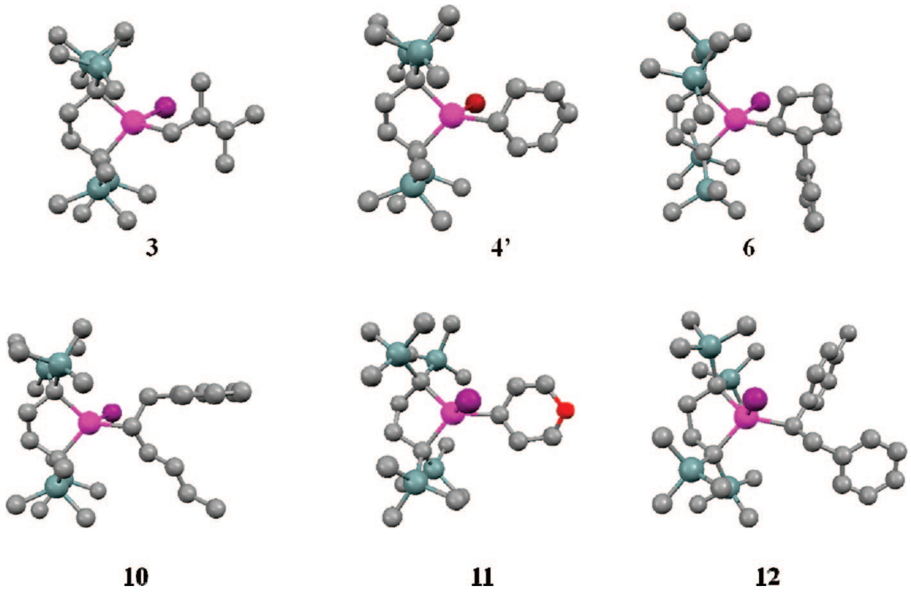


**Figure 1.** Ball and stick plots of $[C_2H_4(SiMe_3)_4C_2]SnI(C_6H_{11})$ (**3**), $[C_2H_4(SiMe_3)_4C_2]SnBr(C_6H_9)$ (**4′**), $[C_2H_4(SiMe_3)_4C_2]SnI(C_{11}H_{13})$ (**6**), $[C_2H_4(SiMe_3)_4C_2]SnI(C_{12}H_{17})$ (**10**), $[C_2H_4(SiMe_3)_4C_2]SnI(C_5OH_7)$ (**11**),and $[C_2H_4(SiMe_3)_4C_2]SnI(C_{14}H_{15})$ (**12**). Full experimental details and ORTEP diagrams are provided in the Supporting Information.

anti-Markovnikov regiochemistry of this addition were confirmed by a single-crystal X-ray diffraction study of products **6** and **10**. In the case of 4-methylstyrene, no CH activation was observed at the methyl group and only double bond addition to give **12** was observed. The reaction is sensitive to the steric constraints of the substrates, as indicated by the formation of both CH activation and double bond addition products for cyclopentene, in 67% and 32% conversion, respectively, as indicated by $^1$H NMR spectroscopy, whereas little to no double bond addition was observed in the reaction with cyclohexene (6%) or 3,4-dihydro-2*H*-pyran (0%). The C═C−C angle in cyclopentene is 112°, as opposed to 123° in cyclohexene and 122 and 124° in 3,4-dihydro-2*H*-pyran, thus substantially reducing the steric restriction around the cyclopentene double bond. 1-Pentene, 1-hexene, and 4-methylstyrene, which contain only one R substituent on the double bond, are substantially less sterically constrained and give double-bond addition in yields of 67, 60, and 90%, respectively (Table 1). The double bond addition chemistry follows the behavior expected for a radical process in terms of the anti-Markovnikov regiochemistry of addition to the terminal olefins and the antiaddition to the cyclopentene.[13]

**Conclusions.** The direct formation of Sn−C bonds from allylic CH bonds has been demonstrated by employing the mixed reagent $Sn[C_2(SiMe_3)_4C_2H_4]/PhI$. The products of these reactions are viable for C−C bond forming reactions under Stille-type cross-coupling conditions. The unexpected addition of phenyl and the tin complex across double bonds was also discovered. We are currently exploring the utility of this chemistry, particularly with respect to the development of novel routes for the synthesis of heterocycles.

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**Supporting Information Available:** Text giving complete experimental preparation details and ORTEP plots for **3**, **4′**, **6**, and **10**−**12** and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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