Thermal and Photoinduced Silylallylation Reactions of Organic Halides with 3-Stannyl-2-(silylmethyl)propene

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Thermal and photoinduced silylallylation reactions of organic halides with 3-stannyl-2-(silylmethyl)propene are explored. Silylallylations occur in moderate to high yields, producing various functionalized allylsilane products in which halide carbon is bonded to the terminal alkenic carbon of allylsilane with the removal of tributyltin group. The reactions, which tolerate functional groups such as carboxyl, ester, nitrile, acetal, and ketone, hold synthetic potential for the construction of functionalized allylsilanes.

Introduction

 Allylsilanes have been used extensively for inter- and intramolecular carbon-carbon bond formations. Although various processes for allylsilane synthesis have been explored, simpler and more direct synthetic methods for allylsilanes carrying reactive functionalities are still in demand. One of the most promising methods is to introduce a new substituent or to manipulate substituents on an allylsilane system. We have found that organostannanes having an allylsilane group 2-stannyl-3-silylpropene 1 and 3-stannyl-2-(silylmethyl)propene 2 are very useful for the synthesis of variously functionalized allylsilanes. Palladium catalyzed cross-coupling reactions of 1 with acid chlorides and aryl halides afforded variously substituted allylsilanes, such as α-(silylmethyl)divinyl ketones 3 in good yields. The obtained allylsilanes 3 were observed to undergo selective silicon-directed Nazarov reactions to afford α-methylenecyclopentanones 4.

We also found that reactions of the bismetallic reagent 2 with organic halides proceed smoothly without any catalytic activation to afford ketoallylsilanes 5 or hydroxyallylsilanes 6. Such a high reactivity of reagent 2 is ascribed to the increased activation provided by β-effect of allylic silyl substituent.

Recently we observed that the reactions of 2 with Lewis acid activated aldimines and then with aldehydes afforded various 2,6-disubstituted 4-methylenepiperidines 7 in one-pot procedure.

The radical chain allylation of organic halides by allylstannane reagents is well known as a powerful and selective method to introduce allyl groups into organic molecules. As part of our continuing efforts to develop new synthetically useful reactions utilizing the bismetallic reagent 2, we investigated the thermal and photochemical reactions of 2 with organic halides, finding that the reactions afford an efficient and facile method for the synthesis of functionalized allylsilanes through radical processes. The following is a detailed description of the results obtained from the investigations.

Results and discussion

Preparation of the bismetallic reagent, 3-stannyl-2-(silylmethyl)propene 2. Reagent 2 was prepared in large scale from the reaction of 3-chloro-2-[(trimethylsilyl)methyl]-1-propene (8) with (tributylstannyl)lithium (9).

The chloride 8 could be obtained in large scale from a mixture of the chlorination products 11 and 12 of methallyl chloride 10 as shown in Scheme 1. When the mixture of 11 and 12 was treated with trichlorosilane and triethylamine in the presence of a catalytic amount of cuprous chloride, 11
gave monosilyl product 13 while 12 remained intact under the reaction condition. For the large scale preparation of the chloride 8 this method is proven to be more convenient than using 2-(trimethylsilylmethyl)prop-2-en-1-ol.\textsuperscript{9b,11}

Thermal and photochemical allylation reactions of organic halides with bismetallic reagent 2. Thermal reaction of the bismetallic reagent 2 (2.0 molar equiv.) with 1.0 equiv. of bromoacetonitrile 14a in degassed benzene solution containing catalytic amount of azobis(isobutyronitrile) (AIBN) affords allylsilane 15a in 90% yield. In addition thermal reactions of 2 with the bromides such as \(\alpha\)-bromoester (14b), \(\alpha\)-bromolactone (14c), \(\alpha\)-bromoketone (14d), alkyl bromide (14e), bromoacetals (14f-14h), \(\beta\)-bromoketone (14i), and \(\gamma\)-chloroketone (14j) resulted in the production of the corresponding allylsilanes 15 in good to moderate yields (see Table 1, Method A).

Quite similar results were obtained from irradiations of 2 and organic bromides in benzene with Pyrex glass filtered light (\(\lambda > 290\) nm) (Table 1, Method B). Dependence of yields on the structure of bromides roughly resembled those in the AIBN induced thermal reactions. Electrophilic radicals derived from the bromides 14a-14d gave allylsilanes 15a-15d in good yields in both the thermal and photoinduced reactions.

When the photochemical reaction of bromoacetophenone (14d) with 2 was performed in the presence of AIBN (Table 1, Method C), yield of allylsilane 15d increased by up to 74% compared with the yield (46%) without AIBN. However, the yield of 15h in the photochemical reaction of 14h with 2 did not improved, even in the presence of AIBN.

The photochemical reactions of 2 with \(\beta\)-bromoketone 14i and with \(\gamma\)-chloroketone 14j in a Pyrex tube did not occur at all even after prolonged irradiations and the starting materials were recovered essentially unchanged. However, when the photochemical reactions of 2 with 14i and 14j were performed using Vycor filtered light (>220 nm), 15i and 15j were obtained, though the yields were low (Table 1, Method D). We found that the photochemical method is not always more efficient than thermal reaction, and this contrasts with the result by Clive.\textsuperscript{9}

The observed reactivity of 14i-j yielding products 15i-j in the irradiation with Vycor-filtered light instead of Pyrex-filtered light seems to be related to their increased light absorptions. It is worthy to note that the photochemical reactions of \(\alpha\)-bromo compounds 14a-d and 14f-g provided high yielding silylallylation products with Pyrex-filtered light.

The above results may be accommodated by a free radical chain mechanism (Scheme 2). The stannyl radical formed by the AIBN-initiated or photolytic reactions abstracts bromine atom from the bromide to afford a carbon centered radical, which adds to the allylstannane moiety of 2. Followed by \(\beta\)-scission of the tributylstannyl radical, it gives the observed allylsilanes 15.

Fleming showed that allylsilane with an acetal terminator 15cyclized to give the methylenecyclohexane 16 as an exclusive product when treated with SnCl\(_4\), and that the site of the double bond is determined by the allylsilane moiety. Although the Lewis acid-catalyzed cyclization reactions of allylsilane-acetals hold synthetic potential for the construction of methylenecycloalkanes, the starting allylsilane-acetal

\textbf{Table 1. Thermal and Photochemical Reactions of 2 with Organic Halides}

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Method\textsuperscript{a} (Reaction Time)</th>
<th>Products</th>
<th>Yields (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>14a</td>
<td>A (15 h)</td>
<td>15a</td>
<td>85</td>
</tr>
<tr>
<td>14b</td>
<td>B (10 min)</td>
<td>15b</td>
<td>80</td>
</tr>
<tr>
<td>14c</td>
<td>A (12 h)</td>
<td>15c</td>
<td>70</td>
</tr>
<tr>
<td>14d</td>
<td>C (2.5 h)</td>
<td>15d</td>
<td>46</td>
</tr>
<tr>
<td>14e</td>
<td>A (12 h)</td>
<td>15e</td>
<td>49</td>
</tr>
<tr>
<td>14f</td>
<td>B (1 h)</td>
<td>15f</td>
<td>56</td>
</tr>
<tr>
<td>14g</td>
<td>A (12 h)</td>
<td>15g</td>
<td>52</td>
</tr>
<tr>
<td>14h</td>
<td>B (2.5 h)</td>
<td>15h</td>
<td>58</td>
</tr>
<tr>
<td>14i</td>
<td>A (12 h)</td>
<td>15i</td>
<td>61</td>
</tr>
<tr>
<td>14j</td>
<td>D (2.5 h)</td>
<td>15j</td>
<td>26</td>
</tr>
<tr>
<td>14k</td>
<td>C (2.5 h)</td>
<td>15k</td>
<td>42</td>
</tr>
<tr>
<td>14l</td>
<td>D (2.5 h)</td>
<td>15l</td>
<td>46</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reactions were performed along the procedures A-D described in the experimental sections unless otherwise stated. \textsuperscript{b}Isolated yields. \textsuperscript{c}Reaction was carried out at room temperature.
compounds have been difficult to prepare and then only via very tedious routes.\textsuperscript{12,13} In light of the difficulty obtaining such acetal-allylsilane, it is observed that thermal and photochemical reactions of bromoacetone acetals 14f-14h with the bimetallic reagent 2 provide the acetal-allylsilane products 15f-h in good to moderate yields.

Bismetallic reagent 2 was shown to be a promising agent for the preparation of variously functionalized allylsilanes through thermal and photoinduced reactions, with the radical process tolerating the presence of various functional groups, such as nitrile, ester, lactone, ketone, acetal, and ketal.\textsuperscript{8a}

**Experimental**

Photochemical initiation was achieved by using a conventional 450 W Hanovia medium-pressure mercury lamp equipped with a Pyrex or Vycor filter. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian Gemini-200 (200 MHz) spectrometer using CDCl$_3$ as solvent and an internal standard. GC-MS were taken on a Kratos Profile HV-3 instrument with a Pyrex or Vycor filter. $^1$H NMR and $^{13}$C NMR were recorded on a V arian Gemini-200 (200 MHz) spectrometer using CDCl$_3$ as solvent and an internal standard.

To a THF (100 mL) solution of diisopropylamine (9.8 g, 97 mmol) n-butylithium (96 mmol, 60 mL of 1.6 M hexane solution) was added at 0 °C. Stirring at 0 °C was continued for 20 min, and Bu$_3$SnH (27.6 g, 95 mmol) was added. After 30 min stirring, the chlorine 8 (15.0 g, 92 mmol) was added to the resulting solution containing (tributylstannyl)lithium at 0 °C, and then stirred at room temperature for 24 h. The reaction mixture was poured into ice water and extracted with ether. The combined organic extracts were dried (Na$_2$SO$_4$), filtered, and concentrated to a residue under reduced pressure. Vacuum distillation of residue (bp 131-135 °C/0.4 mmHg) afforded 33.0 g (86%) of 2.

**Reactions of Bimetallic Reagent 2 with Organic Halides**

_AIBN-Induced Thermal Reactions (Method A)._ The bimetallic reagent 2 (2.0 mmol) and organic halide 14a-k (1.0 mmol) were dissolved in sodium dried benzene (2 mL). The solution was degassed with a vigorous stream of Ar for 15 min. Azobisisobutyronitrile (AIBN, 0.15 mmol) was added and the mixture heated at reflux under Ar for the period shown in Table 1. The mixture was cooled to room temperature and the solvent removed _in vacuo_. The residue was subjected to column chromatography (silica gel, hexane: ether = 5:1) to give allylsilane 15.

15a\textsuperscript{15}: $^1$H NMR $\delta$ 0.03 (s, 9H), 1.53 (s, 2H), 2.32 (t, 2H, $J$ = 6.4 Hz), 2.44 (t, 2H, $J$ = 6.4 Hz), 4.67 (s, 2H); $^{13}$C NMR $\delta$ 1.54, 15.85, 26.52, 33.39, 108.79, 119.36, 143.58; MS m/z 167 (M$^+$, 91), 152 (100), 126 (55), 113 (30), 98 (98), 84 (50), 73 (84%).

15b\textsuperscript{16}: $^1$H NMR $\delta$ 0.02 (s, 9H), 1.25 (t, 3H, $J$ = 7.2 Hz), 1.53 (s, 2H), 2.27 (t, 2H, $J$ = 8.4 Hz), 2.46 (t, 2H, $J$ = 8.4 Hz), 4.13 (q, 2H, $J$ = 7.2 Hz), 4.54 (s, 1H), 4.58 (s, 1H); $^{13}$C NMR $\delta$ -1.39, 14.22, 27.06, 32.85, 33.03, 60.26, 107.11, 145.97, 173.30.

15c: $^1$H NMR $\delta$ 0.03 (s, 9H), 1.50 (s, 2H), 1.88-2.08 (m, 2H), 2.34-2.47 (m, 1H), 2.55-2.75 (m, 2H), 4.14-4.31 (m, 1H), 39.06, 46.17, 109.15, 144.20, 179.21; MS m/z 211 (M$^+$, 75), 197 (70), 169 (46), 157 (91), 122 (53), 95 (69), 73 (100%).

15d: $^1$H NMR $\delta$ 0.06 (s, 9H), 1.56 (s, 2H), 2.40 (t, 2H, $J$ = 8.6 Hz), 3.14 (t, 2H, $J$ = 8.6 Hz), 4.58 (s, 1H), 4.63 (s, 1H), 7.43-8.01 (m, 5H); $^{13}$C NMR $\delta$ -1.35, 27.26, 32.37, 37.10, 107.03, 128.02, 128.57, 132.95, 137.01, 145.79, 199.76; MS m/z 246 (M$^+$, 41), 231 (50), 217 (38), 156 (48), 141 (26), 105 (47), 77 (77), 73 (100%).

15e: $^1$H NMR $\delta$ 0.03 (s, 9H), 1.54-1.73 (m, 13H), 1.61 (s, 2H), 4.67 (s, 1H), 4.90 (s, 1H).

15f\textsuperscript{17}: $^1$H NMR $\delta$ 0.02 (s, 9H), 1.53 (s, 2H), 1.76 (m, 2H), 2.01 (t, 2H, $J$ = 7.2 Hz), 3.23 (s, 6H), 4.38 (t, 1H, $J$ = 5.6 Hz), 4.53 (s, 1H), 4.60 (s, 1H); $^{13}$C NMR $\delta$ -1.35, 26.91, 30.63, 32.94, 52.62, 104.10, 106.97, 146.82; MS m/z 216 (M$^+$, 5), 154 (21), 151 (52), 75 (88), 73 (100%).

15g: $^1$H NMR $\delta$ 0.03 (s, 9H), 1.53 (s, 2H), 2.16 (s, 3H), 2.23 (t, 2H, $J$ = 5.4 Hz), 2.58 (t, 2H, $J$ = 5.4 Hz), 3.24 (s, 6H), 4.54 (s, 2H); $^{13}$C NMR $\delta$ -1.38, 20.27, 23.13, 29.91, 31.96, 42.08, 99.86, 106.90, 146.26.

15h: $^1$H NMR $\delta$ 0.01 (s, 9H), 1.52 (s, 2H), 1.50-1.62 (m, 4H), 1.99 (t, 2H, $J$ = 7.2 Hz), 3.93 (s, 4H), 4.51 (s, 1H), 4.59 (s, 1H), 4.86 (s, 1H, $J$ = 4.3 Hz); $^{13}$C NMR $\delta$ -1.34, 22.10, 26.63, 33.51, 37.95, 64.83, 104.56, 107.15, 147.10.

15i: $^1$H NMR $\delta$ 0.01 (s, 9H), 1.50 (s, 2H), 1.61-1.76 (m, 2H), 1.96 (t, 2H, $J$ = 7.7 Hz), 2.14 (t, 3H), 2.43 (t, 2H, $J$ = 7.7 Hz), 4.54 (s, 1H), 4.59 (s, 1H); $^{13}$C NMR $\delta$ -1.36, 26.48, 29.91, 32.14, 34.39, 43.05, 107.56, 146.70, 183.49; MS m/z 198 (M$^+$, 8), 125 (38), 88 (100), 82 (90), 73 (79%).

15j: $^1$H NMR $\delta$ 0.01 (s, 9H), 1.51 (s, 2H), 1.34-1.62 (m, 4H), 1.96 (t, 2H, $J$ = 7.2 Hz), 2.14 (t, 3H), 2.44 (t, 2H, $J$ = 7.2 Hz), 4.51 (s, 1H), 4.56 (s, 1H); $^{13}$C NMR $\delta$ -1.34, 14.11,
23.56, 26.70, 27.29, 37.90, 43.66, 107.05, 147.22, 184.35; MS m/z 212 (M^+, 7), 156 (70), 73 (100%).

15k: ^1^H NMR δ 0.5 (s, 9H), 1.57 (s, 2H), 1.61 (t, 2H, J = 4.6 Hz), 2.35 (t, 2H, J = 4.6 Hz), 4.76 (s, 1H), 4.79 (s, 1H), 7.26-7.38 (m, 5H); MS m/z 218 (M^+, 5), 145 (96), 131 (66), 113 (52), 77 (55), 73 (100%).

Photochemical Reactions in a Pyrex Tube (Method B). Organic halide (1.0 mmol) and AIBN (0.15 mmol) in a Pyrex tube was irradiated. All of the other procedures were followed as in Method B.

Photochemical Reactions in a Vycor Tube (Method C). A DME (2 mL) solution of 2 (2.0 mmol) and organic halide (1.0 mmol), and AIBN (0.15 mmol) in a Pyrex tube was irradiated. All of the other procedures were followed as in Method B.

Photochemical Reactions in a Vycor Tube (Method D). A DME (2 mL) solution of 2 (2.0 mmol) and organic halide (1.2 mmol) in a Vycor tube was irradiated. All of the other procedures were followed as in Method B.

2-(4-Trimethylsilylmethyl-4-penteny1)-1,3-dioxolane (15h)
To a THF (3.5 mL) solution of 2 (450 mg, 1.0 mmol) was added 1.0 mL (1.6 mmol) of a 1.6 M solution of methyllithium. After stirring 30 min, 226 mg (1.0 mmol) of 2-(2-iodoethyl)-1,3-dioxolane was added via a microsyringe. The reaction mixture was stirred for 30 min and warmed to room temperature. The mixture was poured into a saturated solution of sodium bicarbonate and extracted with ether (20 mL × 2). The combined organic layers were dried over Na2SO4 and the solvent was removed. The crude product was chromatographed on silica gel (hexane:ether = 1:1) to yield 150 mg (66%) of 15h.

3-(2-Hydroxyethoxy)-1-methylenecyclohexane (16)
Anhydrous tin (IV) chloride (30 µL, 67 mg, 0.23 mmol) and 15h (155 mg, 0.68 mmol) in dry carbon tetrachloride (20 mL) were stirred under Ar at 0 °C for 2h. The reaction mixture was warmed to room temperature and stirred for 24h. The mixture was poured into saturated aqueous sodium bicarbonate and extracted with carbon tetrachloride (10 mL × 2). The combined organic extracts were dried (Na2SO4), filtered, and concentrated. The residue was chromatographed on silica gel (ether) to give 48 mg (44%) of 16.

16: ^1^H NMR δ 1.21-2.22 (8H, m), 2.54 (1H, dd, J = 12.9, 3.7 Hz), 3.31-3.43 (1H, m), 3.56-3.62 (2H, m), 3.68-3.76 (2H, m), 4.68 (1H, s), 4.71 (1H, s); ^13^C NMR δ 23.96, 31.63, 34.35, 40.94, 62.06, 68.97, 78.09, 109.35, 146.26; Ms m/z 156 (M^+, trace), 101 (100), 94 (95), 91 (31), 79 (91), 67 (63), 57 (84), 45 (72), 41 (55%).

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References


9. (a) During the course of the study, we met the report which described the photoinduced radical reactions of 2. (b) Clive, D. L. J.; Paul, C. C.; Wang, Z. J. Org. Chem. 1997, 62, 7028.


14. We observed that allysilane 15h was also produced conveniently from the reaction of 14 with 2-(lithiomethyl)-3-(trimethylsilyl)propane (17) generated by treatment of 2 with methyllithium.

