

## Two types of intramolecular homolytic substitution reactions at group XIV atoms: unusual radical 1,4-Sn shifts from Si to C and carbonylative S<sub>H</sub>i reaction at Si†

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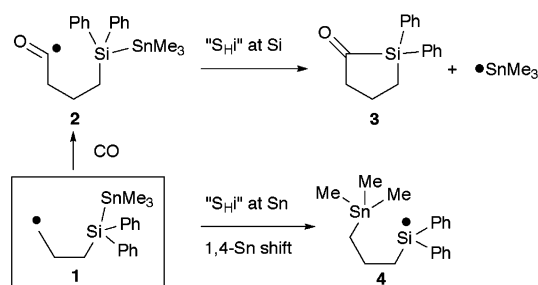
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4-[(Trimethylstannyl)diphenylsilyl]butanoyl radical, arising from the corresponding 3-(stannylsilyl)propyl radical and CO, undergoes an S<sub>H</sub>i reaction at Si with extrusion of trimethyltin radical to give silacyclopentanone. The parent 3-(stannylsilyl)propyl radical was also found to isomerize to (3-stannylpropyl)silyl radical *via* a 1,4-Sn shift from Si to C with a rate constant of  $9.3 \times 10^4 \text{ s}^{-1}$  at 80 °C. *Ab initio* and DFT MO calculations support a front-side attack mechanism.

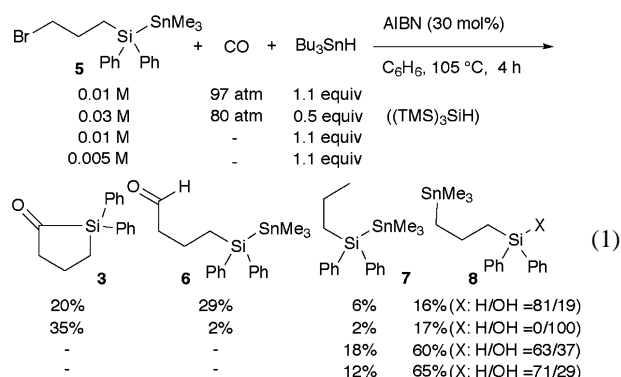
Despite the tremendous achievements in free radical chemistry during the last two decades,<sup>1</sup> many basic transformations still remain to be discovered in this field. Certainly, S<sub>H</sub>2 reactions at hetero-atoms belong to this category.<sup>2</sup> Intramolecular homolytic substitution reactions at group XVI elements have been introduced for the formation of heterocyclic rings.<sup>3</sup> In addition, we have previously reported that radical carbonylation with subsequent intramolecular substitution of acyl radicals at sulfur provides a useful method for the preparation of  $\gamma$ -thiolactones.<sup>4</sup> Encouraged by the recent work of the Studer group, who reported on S<sub>H</sub>i reactions of alkyl and aryl radicals at silicon,<sup>5</sup> we became curious about the similar S<sub>H</sub>i reaction behavior of acyl radicals. Here we present two types of novel S<sub>H</sub>i reactions at Si and Sn, both of which were discovered in the reaction system of carbonylation of 3-(stannylsilyl)propyl radical **1** (Scheme 1). Thus, we report on the intramolecular homolytic substitution reaction of acyl radical **2** at Si, which leads to the formation of silacyclopentanone **3** and an unusual radical 1,4-Sn migration from Si to C in the parent radical **1**. We also report on the rate constant of the 1,4-Sn migration and the results of *ab initio* and density functional (DFT) MO calculations, which predict a front-side attack of carbon radical at the tin group with retention of configuration.



Scheme 1 Two types of S<sub>H</sub>i reactions starting from radical **1**.

† Electronic supplementary information (ESI) available: Experimental procedure, spectral data for all compounds, and kinetic data. See <http://www.rsc.org/suppdata/cc/b3/b301755a/>

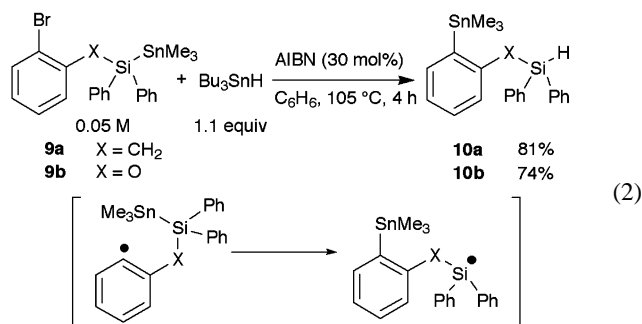
Thus, when 0.01 M of a benzene solution containing 3-[(trimethylstannyl)diphenylsilyl]propyl bromide (**5**) was treated with pressurized carbon monoxide (97 atm) and tributyltin hydride (1.1 equiv) in the presence of AIBN (2,2'-azobisisobutyronitrile), two types of carbonylated product were obtained after isolation by silica gel chromatography (eqn. 1):



one was the envisaged S<sub>H</sub>i product silacyclopentanone **3**<sup>6</sup> and the other was uncyclized aldehyde **6**. The non-polar fraction contained an unexpected product, 1-silyl-3-stannylpropane **8** (X: H/OH = 81/19), which is supposed to be a rearranged product from the parent radical **1**. The use of a slower mediator, (TMS)<sub>3</sub>SiH, suppressed the competitive formation of aldehyde **6** and reduced product **7**, however, the formation of unusual product **8** always competed with the initially planned carbonylation/S<sub>H</sub>i sequence.

The unusual formation of **8** led us to examine the similar reaction in the absence of carbon monoxide. As expected, this reaction gave the migration product **8** as the major product together with a small amount of simple reduction product **7**. The intramolecularity of the migration reaction was supported by the fact that the reaction at lower concentration ([**5**] = 0.005 M) resulted in a significant increase of the **8**/**7** ratio. The large amount of hydrosilane type product **8** (X = H) indicates that the silyl radical formed after 1,4-Sn migration is mainly reduced by tin hydride under the applied conditions.<sup>7</sup> As a minor reaction pathway, the isomerized silyl radical undergoes bromine abstraction from the starting bromide to provide the corresponding bromosilane, which is eventually converted to silanol **8** (X = OH) during chromatographic separation on silica gel.

When aromatic bromide **9a** was exposed to the tin hydride/AIBN conditions with or without CO, 1,4-Sn migration proceeded very smoothly to give the corresponding phenylstannane **10a** as a sole product (eqn. 2). Similarly, efficient 1,4-Sn migration was observed, when silyl phenyl ether **9b** was used as a substrate. Thus, the 1,4-Sn migration from Si to C is a general process also applicable to aryl radicals.

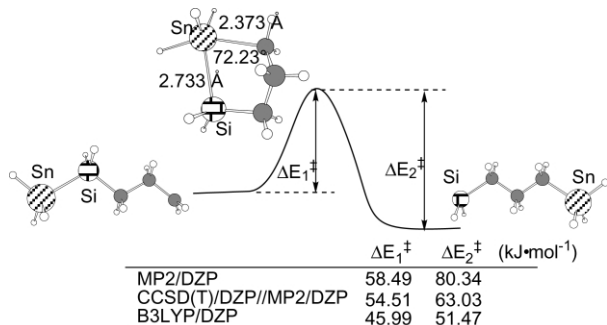


Radical 1,4-migration is very rare,<sup>8,9</sup> and to learn more about the efficiency of the present 1,4-Sn migration, kinetic competition experiments of radical **1** using tributyltin hydride in a classical radical clock experiment<sup>10</sup> were performed (Scheme 2). These investigations provided a rate constant for the 1,4-Sn migration in **1** of  $9.3 \times 10^4 \text{ s}^{-1}$  at 80 °C.



**Scheme 2** Rate constant for 1,4-Sn shift in the isomerization of **1** to **4**.

It is generally understood that transition states involved in S<sub>HI</sub>2 reactions require a collinear (or nearly so) arrangement of both attacking and leaving radicals.<sup>2</sup> Indeed this has been demonstrated clearly for reactions involving radical attack at the halogens as well as sulfur and selenium.<sup>11</sup> There is growing evidence, however, that analogous reactions involving group XIV elements can involve backside or front-side transition mechanisms,<sup>12</sup> and the present 1,4-Sn migration would appear to fall in the latter category. *Ab initio* and DFT MO calculations<sup>13</sup> indicate that the front-side attack of an alkyl radical at tin *via* a five-membered ring transition state is a reasonably favorable reaction pathway. Indeed, energy barriers between about 45 and 60 kJ mol<sup>-1</sup> are calculated at correlated and DFT levels of theory for the rearrangement of the closely related 3-(stannasilyl)propyl radical (Scheme 3).<sup>14</sup>



**Scheme 3** MP2/DZP optimized structure and activation energy (kJ mol<sup>-1</sup>) for 1,4-radical migration of Sn from Si to C.

In summary, we present two types of novel homolytic substitution reactions at group XIV atoms: (i) an S<sub>HI</sub>-type reaction of acyl radical at silicon and (ii) a 1,4-Sn migration from silicon to alkyl and aryl radicals, comprising an unusual S<sub>HI</sub>-type reaction at tin. A kinetic study indicates that the isomerization of **1** to **4** in benzene *via* 1,4-Sn migration takes place with a rate constant of  $9.3 \times 10^4 \text{ s}^{-1}$  at 80 °C. Furthermore, *ab initio* and DFT MO calculations for the tin migration reaction reasonably predict a transition state involving front-side attack at tin. We are currently looking at other substrates and conditions for efficient carbonylative S<sub>HI</sub> cyclization reactions as well as further examples of radical 1,4-migration reactions.

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