ChemComm
www.rsc.org/chemcomm

Two types of intramolecular homolytic substitution reactions at group XIV atoms: unusual radical 1,4-Sn shifts from Si to C and carbonylative S_Hi reaction at Si†

Armido Studer,*[a] Stephan Amrein,[a] Hiroshi Matsubara,[b] Carl H. Schiesser,*[b] Takashi Doi,[c] Tomonori Kawamura,[c] Takahide Fukuyama[c] and Ilhyong Ryu*[c]

[a] *Fachbereich Chemie der Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany. E-mail: studer@Mailer.Uni-Marburg.de*

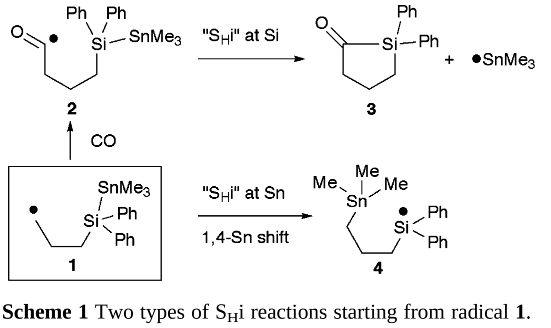
[b] *School of Chemistry, Bio21 Institute of Molecular Science and Biotechnology, The University of Melbourne, Victoria, Australia 3010. E-mail: carlhs@unimelb.edu.au*

[c] *Department of Chemistry, Faculty of Arts and Sciences, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan. E-mail: ryu@ms.cias.osakafu-u.ac.jp*

Received (in Cambridge, UK) 14th February 2003, Accepted 28th March 2003
First published as an Advance Article on the web 17th April 2003

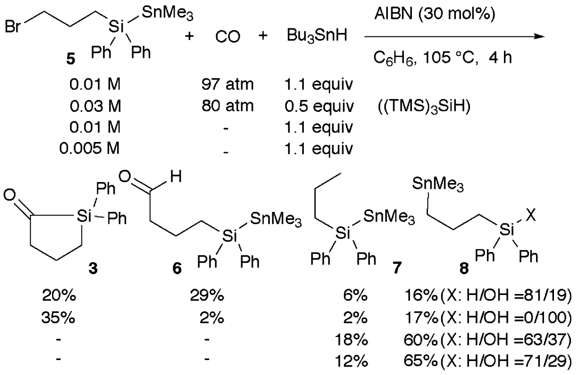
4-[(Trimethylstannyl)diphenylsilyl]butanoyl radical, arising from the corresponding 3-(stannylsilyl)propyl radical and CO, undergoes an S_Hi reaction at Si with extrusion of trimethyltin radical to give silacyclopentanone. The parent 3-(stannylsilyl)propyl radical was also found to isomerize to (3-stannylpropyl)silyl radical *via* a 1,4-Sn shift from Si to C with a rate constant of 9.3×10^4 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,[1] many basic transformations still remain to be discovered in this field. Certainly, S_H2 reactions at hetero-atoms belong to this category.[2] Intramolecular homolytic substitution reactions at group XVI elements have been introduced for the formation of heterocyclic rings.[3] 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 γ-thiolactones.[4] Encouraged by the recent work of the Studer group, who reported on S_Hi reactions of alkyl and aryl radicals at silicon,[5] we became curious about the similar S_Hi reaction behavior of acyl radicals. Here we present two types of novel S_Hi 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_Hi reactions starting from radical **1**.

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):



(1)

one was the envisaged S_Hi product silacyclopentanone **3**[6] 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, $(TMS)_3SiH$, 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_Hi sequence.

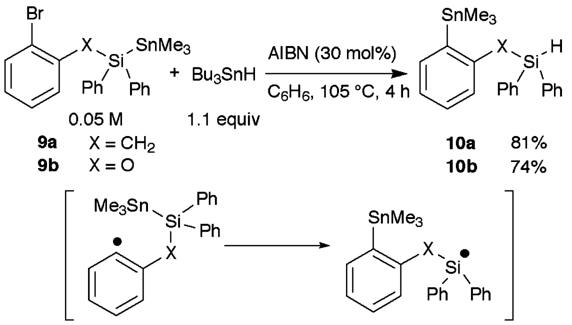
The unusual formation of **8** led us to examine the similar reaction in the absence of carbon monoxide. As expected, this reaction gave the migration product **8** as the major product together with a small amount of simple reduction product **7**. The intramolecularity of the migration reaction was 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.[7] 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.

---

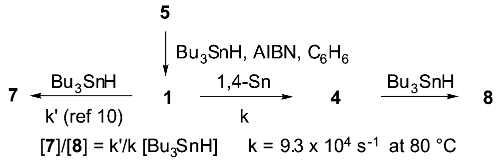
† Electronic supplementary information (ESI) available: Experimental procedure, spectral data for all compounds, and kinetic data. See http://www.rsc.org/suppdata/cc/b3/b301755a/

DOI: 10.1039/b301755a



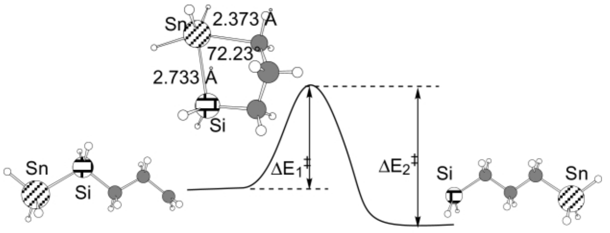
(2)

Radical 1,4-migration is very rare,[8,9] 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[10] were performed (Scheme 2). These investigations provided a rate constant for the 1,4-Sn migration in **1** of 9.3×10^4 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_H2 reactions require a collinear (or nearly so) arrangement of both attacking and leaving radicals.[2] Indeed this has been demonstrated clearly for reactions involving radical attack at the halogens as well as sulfur and selenium.[11] There is growing evidence, however, that analogous reactions involving group XIV elements can involve backside or front-side transition mechanisms,[12] and the present 1,4-Sn migration would appear to fall in the latter category. *Ab initio* and DFT MO calculations[13] 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^{-1} are calculated at correlated and DFT levels of theory for the rearrangement of the closely related 3-(stannasilyl)propyl radical (Scheme 3).[14]



	$\Delta E_1^‡$	$\Delta E_2^‡$ (kJ•mol^{-1})
MP2/DZP	58.49	80.34
CCSD(T)/DZP//MP2/DZP	54.51	63.03
B3LYP/DZP	45.99	51.47

Scheme 3 MP2/DZP optimized structure and activation energy (kJ mol^{-1}) 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_Hi-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_Hi-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 9.3×10^4 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_Hi cyclization reactions as well as further examples of radical 1,4-migration reactions.

IR is grateful for a Grant-in-Aid for Scientific Research on Priority Areas (A) "Exploitation of Multi-Element Cyclic Molecules" from the Ministry of Education, Culture, Sports, Science and Technology, Japan. AS thanks the Fonds der Chemischen Industrie for financial support. CS and HM thank the Melbourne Advanced Research Computing Centre for generous computing support.

Notes and reference

1 *Radicals in Organic Synthesis*, ed. P. Renaud and M. P. Sibi, vols 1 and 2, Wiley-VCH, Weinheim, Germany, 2001.

2 Reviews: (*a*) C. H. Schiesser and L. M. Wild, *Tetrahedron*, 1996, **52**, 13265; (*b*) J. C. Walton, *Acc. Chem. Res.*, 1998, **31**, 99; (*c*) A. L. J. Beckwith, *J. Chem. Soc. Rev.*, 1993, **22**, 143.

3 For recent work, see: (*a*) N. Al-Maharik, L. Engman, J. Malmström and C. H. Schiesser, *J. Org. Chem.*, 2001, **66**, 6286; (*b*) M. W. Carland, R. L. Martin and C. H. Schiesser, *Tetrahedron Lett.*, 2001, **42**, 4737; (*c*) C. L. Winn and J. M. Doodman, *Tetrahedron Lett.*, 2001, **42**, 7091; (*d*) R. Leardini, H. McNab, M. Minozzi and D. Nanni, *J. Chem. Soc., Perkin Trans. 1*, 2001, 1072; (*e*) T. Ooi, M. Furuya, D. Sakai, Y. Hokke and K. Maruoka, *Synlett*, 2001, 541; (*f*) Y. Nishiyama, Y. Hada, M. Anjiki, K. Miyake, S. Hanita and N. Sonoda, *J. Org. Chem.*, 2002, **67**, 1520.

4 (*a*) I. Ryu, T. Okuda, K. Nagahara, N. Kambe, M. Komatsu and N. Sonoda, *J. Org. Chem.*, 1997, **62**, 7550. For reviews on acyl radicals and radical carbonylations, see (*b*) C. Chatgilialoglu, D. Crich, M. Komatsu and I. Ryu, *Chem. Rev.*, 1999, **99**, 1991; (*c*) I. Ryu and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1050; (*d*) I. Ryu, N. Sonoda and D. P. Curran, *Chem. Rev.*, 1996, **96**, 177.

5 (*a*) A. Studer, *Angew. Chem., Int. Ed.*, 1998, **37**, 462; (*b*) A. Studer and H. Steen, *Chem. Eur. J.*, 1999, **5**, 759; (*c*) S. Amrein, M. Bossart, T. Vasella and A. Studer, *J. Org. Chem.*, 2000, **65**, 4281; (*d*) A. Studer, M. Bossart and T. Vasella, *Org. Lett.*, 2000, **2**, 985. See also (*e*) C. H. Schiesser, M. L. Styles and L. M. Wild, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2257 and references therein.

6 Silacyclopentanones belong to an exotic class of silaheterocycles. For a previous synthesis, see: (*a*) J. A. Soderquist and A. Hassner, *J. Org. Chem.*, 1980, **45**, 541; (*b*) A. Hassner and J. A. Soderquist, *Tetrahedron Lett.*, 1980, **21**, 429.

7 D. Dakternieks, D. J. Henry and C. H. Schiesser, *Organometallics*, 1998, **17**, 1079.

8 For a rare example of 1,4-Si migration, see ref 5*d*.

9 For 1,3-Sn migration, see: (*a*) S.-Y. Chang, Y.-F. Shao, S.-F. Chu, G.-T. Fan and Y.-M. Tsai, *Org. Lett.*, 1999, **1**, 945. For 1,5-Sn migrations (*b*) S. Kim, S. Lee and J. S. Koh, *J. Am. Chem. Soc.*, 1991, **113**, 5106; (*c*) S. Kim and J. S. Koh, *Chem. Commun.*, 1992, 1377; (*d*) E. Hasegawa, K. Ishiyama, T. Kato, T. Horaguchi, T. Shimizu, S. Tanaka and Y. Yamashita, *J. Org. Chem.*, 1992, **57**, 5352; (*e*) S. Kim, K. M. Yeon and K. S. Yoon, *Tetrahedron Lett.*, 1997, **38**, 3919; (*f*) S. Kim, M. S. Jung, C. H. Cho and C. H. Schiesser, *Tetrahedron Lett.*, 2001, **42**, 943; (*g*) H. Sano, D. Asanuma and M. Kosugi, *Chem. Commun.*, 1999, 1559. For 1,6-Sn migration see (*h*) S. Kim and K. M. Lim, *Chem. Commun.*, 1993, 1152.

10 C. Chatgilialoglu, K. U. Ingold and J. C. Scaiano, *J. Am. Chem. Soc.*, 1981, **103**, 7739.

11 (*a*) C. H. Schiesser and L. M. Wild, *J. Org. Chem.*, 1998, **63**, 670; (*b*) C. H. Schiesser and L. M. Wild, *J. Org. Chem.*, 1999, **64**, 1131.

12 (*a*) S. M. Horvat, C. H. Schiesser and L. M. Wild, *Organometallics*, 2000, **19**, 1239; (*b*) S. Kim, S. M. Horvat and C. H. Schiesser, *Aust. J. Chem.*, 2002, **55**, 753.

13 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98*, Revision A.7, Gaussian Inc., Pittsburgh, PA, 1998.

14 Preliminary experiments provide values of 46 kJ mol^{-1} and 11.8 for the energy barrier and log (A/s^{-1}) for the migration in **1**, in good agreement with these caluculated data.