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Hydrosilylation of Carbonyl Compounds Using a $PhSeSiMe_3/Bu_3SnH/AIBN$ System

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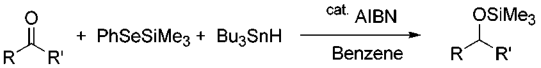
ABSTRACT



When carbonyl compounds were allowed to react with phenyl trimethylsilyl selenide and tributylstannyl hydride in the presence of a catalytic amount of AIBN as a radical initiator, the hydrosilylation of the carbonyl compounds efficiently proceeded to give the corresponding silyl ethers in moderate to good yields.

The development of new methods for the generation of organosilyl radicals such as the trialkylsilyl radical ($R_3Si^\bullet$) and the utilization of these radicals in organic synthesis is one of challenging problems in organic chemistry.[1] Up to now, some generation methods for the organosilyl radical have been reported. However, the efficient utilization of these silicon radicals in organic synthesis is very limited, because the recombination to the disilane or the disproportionation to the trialkylsilane of the silyl radicals by side reactions easily occurred during these preparation methods.[2] New efficient and convenient generation methods for the trialkylsilyl radical are desired.

Clive has reported a method for the efficient generation of carbon centered radicals by using the reaction of organoselenide (RSePh) with tributylstannyl hydride under radical conditions.[8] Since then carbon centered radicals thus generated have been widely used in various transformations.[9] When organoselenium compounds having the selenium−heteroatom bond are reacted with tributylstannyl hydride in the presence of a radical initiater, it is expected that the organoselenium compounds would become excellent precursors for the various heteroatom radical species. We then examined the preparation of the trialkylsilyl radical by the reaction of a small excess of $PhSeSiMe_3$ with tributylstannyl hydride under radical conditions, in the presence of carbonyl

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[1] For recent reviews of the silyl radical: (a) Jackson, R. A. *Adv. Free Radical Chem.* **1969**, *3*, 231. (b) Jackson, R. A. *Spec. Publ. R. Chem. Soc.* **1970**. 295. (c) Sakurai, H. In *Free Radical*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II. (d) Arthur, N. L.; Bell, T. N. *Rev. Chem. Intermed.* **1978**, *1*, 37. (e) Dohmaru, T. Reactions of Special Radicals. In *Chemical Kinetics of Small Organic Radicals*; Alfassic, Z. B., Ed.; CRC Press: Boca Raton, 1988; Vol. III. (f) Chatgilialoglu, C. *Chem. Rev.* **1995**, *95*, 1229.

[2] Substitution of silyl radicals by the introduction of bulky substituents such as *tert*-butyl[3], mesityl,[4] 3,5-di-*tert*-butylphenyl,[5] trimethylsilyl,[6] and other groups[7] has been attempted.

[3] Jackson, R. A.; Weston, H. *J. Organomet. Chem.* **1984**, *277*, 13.

[4] Gynane, M. J. S.; Lappert, M. F.; Riley, P. I.; Rievière-Baudet, M. *J. Organomet. Chem.* **1980**, *202*, 5.

[5] Sakurai, H.; Umino, H.; Sugiyama, H. *J. Am. Chem Soc.* **1980**, *102*, 6837.

[6] (a) Bennett, S. W.; Eaborn, C.; Hudson, A.; Jackson, R. A.; Root, K. D. *J. Chem. Soc. A* **1970**, 348. (b) Cooper, J.; Hudson, A.; Jackson, R. A. *Mol. Phys.* **1972**, *23*, 209. (c) Chatgilialoglu, C.; Rossini, S. *Bull. Soc. Chim. Fr.* **1988**, 298.

[7] (a) Stanislawski, D. A.; Buchanan, A. C., III; West, R. *J. Am. Chem Soc.* **1978**, *100*, 7791. (b) Cotton, J. D.; Cundy, C. S.; Harris, D. H.; Hudson, A.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Chem. Commun.* **1974**, 651. (c) Hudson, A.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Dalton Trans.* **1976**, 2369. (d) McKinley, A. J.; Karatsu, T.; Wallraff, G. M.; Miller, R. D.; Sooriyakumaran, R.; Michl, J. *Organometallics* **1988**, *7*, 2567. (e) McKinley, A. J.; Karatsu, T.; Wallraff, G. M.; Thompson, D. P.; Miller, R. D.; Michl, J. *J. Am. Chem. Soc.* **1991**, *113*, 2003. (f) Kyushin, S.; Sakurai, H.; Betsuyaku, T.; Matsumoto, H. *Organometallics* **1997**, *16*, 5386.

[8] (a) Clive, D. L. J.; Chittattu, G.; Wong, G. K. *J. Chem. Soc., Chem. Commun.* **1978**, 41. (b) Nicolaou, K. C.; Gasic, G. P.; Barnette, W. E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 293. (c) Corey, E. J.; Pearce, H. L.; Szekely, I.; Ishiguro, M. *Tetrahedron Lett.* **1978**, 1023.

[9] See for examples: (a) Krief, A.; Hevesi, L. In *Organoselenium Chemistry*; Springer-Verlag, Berlin, 1988; Vol. 1. (b) Paulmier, C. In *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: Oxford, 1986. (c) Patai, S.; Rappoport, Z. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Wiley: New York, 1986; Vols. 1 and 2. (d) Krief, A. In *Comprehensive Organic Synthesis*; Trost, B. M. Ed., Pergamon Press: Oxford, 1991; Vol. 3, including references therein.

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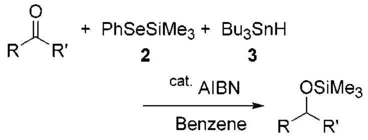
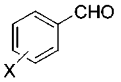
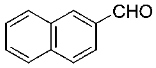
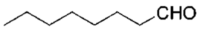
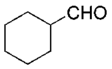
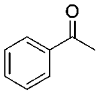
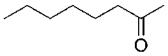
compounds as a trapping agent of the silyl radical, and found that the hydrosilylation of carbonyl compounds efficiently proceeded to give the corresponding trimethylsilyl ethers in moderate to good yields (Scheme 1).[10,11]

Scheme 1



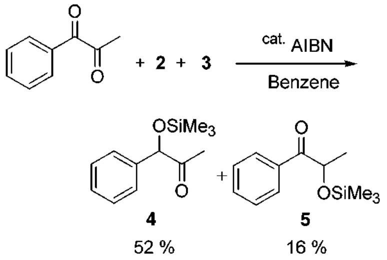
The reaction of benzaldehyde (**1**) with small excess amounts of phenyl trimethylsilyl selenide ($PhSeSiMe_3$) (**2**) (1.3 equiv) and tributylstannyl hydride (**3**) (1.3 equiv) in the presence of a catalytic amount of AIBN at 80 °C for 18 h afforded benzyl trimethylsilyl ether, the hydrosilylated product of **1**, in 78% yield (entry 1, Table 1).[12] When azobisisovaleronitrile (AMVN) instead of AIBN was used as a radical initiator, the hydrosilylation of **1** occurred at a lower reaction temperature (60 °C) (entry 2). To determine the scope and limitation of this hydrosilylation method, various carbonyl compounds were reacted with a small excess of **2** and **3** (1.3 equiv) in the presence of a catalytic amount of AIBN at 80 °C; the results are shown in Table 1. Methyl-substituted benzaldehydes gave the corresponding silyl ethers in 65−80% yields (entries 3−5). 4-Methoxy benzaldehyde was also hydrosilylated by the $PhSeSiMe_3$/Bu_3SnH/AIBN system to afford 4-methoxy benzyl trimethylsilyl ether in 85% yield (entry 6). For the nitro-substituted benzaldehyde, the yield of the silyl ether was markedly decreased as a result of various side reactions (entry 7). When 4-chlorobenzaldehyde was reacted with $PhSeSiMe_3$ and Bu_3SnH under the same conditions as for benzaldehyde, the yield of the silyl ether was moderate (48%); however, the yield of product was improved by extending the reaction time (48 h) (entry 8). Similarly, the hydrosilylation of the 2-naphthylaldehyde efficiently proceeded to afford the corresponding silyl ether in 81% yield (entry 9). For the reaction of octanal and cyclohexanecarboxaldehyde, trimethylsilyl ethers were isolated in 66% and 51% yields, respectively (entries 10 and 11). Aromatic and aliphatic ketones also formed the corresponding trimethylsilyl ethers; however, these yields were lower than those of aldehydes (entries 12 and 13). Upon the hydrosilylation of 1-phenyl-1,2-propanedione using the $PhSeSiMe_3$/Bu_3SnH/AIBN system, the hydrosilylation of the carbonyl group adjacent to the aromatic ring predominantly proceeded to give **4** in 52% yield with the formation of **5** (16%) (Scheme 2).[14]

Table 1. Hydrosilylation of Carbonyl Compounds Using $PhSeSiMe_3$ and Bu_3SnH in the Presence of a Catalytic Amount of AIBN

Entry	Carbonyl Compound	Yield/%[a]
		
1	X = H	78
2[b]		70
3	= 2-Me	65
4	= 3-Me	77
5	= 4-Me	80
6	= 4-MeO	85
7[c]	= 4-NO_2	12
8[c]	= 4-Cl	74
9[c]		81
10		66
11		51
12		56
13[d]		7

[a] Reaction conditions: carbonyl compound (1.3 mmol), $PhSeSiMe_3$ (1.7 mmol), Bu_3SnH (1.7 mmol), AIBN (0.13 mmol), and benzene (5 mL) at 80 °C for 18 h. [b] AMVN (azobisisovaleronitrile) instead of AIBN was used as a radical initiater at 60 °C. [c] For 48 h. [d] For 72 h.

Scheme 2



Although we cannot explain the reaction pathway of the hydrosilylation of the carbonyl compounds using the $PhSeSiMe_3$/Bu_3SnH/AIBN system in detail, two possible reaction pathways were proposed for this reaction (Scheme 3).

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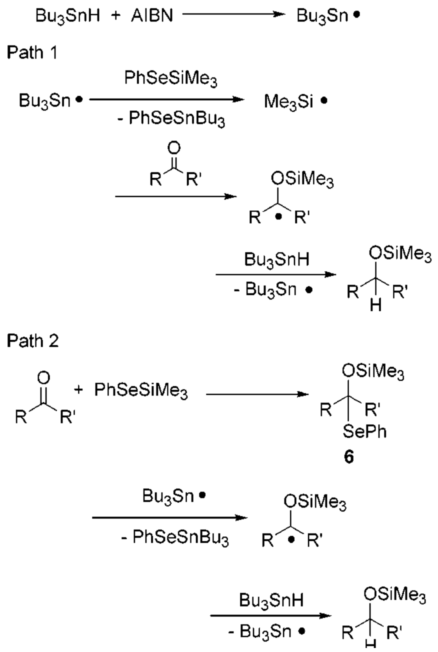
(10) (a) Gilman, H.; Wittenberg, D. *J. Org. Chem*. **1958**, *23*, 501. (b) Sakurai, H.; Hosomi, A.; Kumada, M. *Bull. Chem. Soc. Jpn*. **1967**, *40*, 1551. (c) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc*. **1982**, *104*, 5119.

(11) For recent reviews of the radical-mediated reduction of carbonyl compounds by using silicon reagents, see: Chatgilialoglu, C. *Chem. Rev*. **1995**, *95*, 1229.

(12) A benzene (5 mL) solution of the carbonyl compound (1.3 mmol), $PhSeSiMe_3$[13] (400 mg, 1.7 mmol), Bu_3SnH (510 mg, 1.7 mmol), and AIBN (22 mg, 0.13 mmol) was stirred at 80 °C for 18−72 h under a nitrogen atmosphere. After the reaction was complete, H_2O (10 mL) was added to the reaction mixture, which was extracted with Et_2O (10 mL × 3). The combined organic layer were dried over $MgSO_4$ and removed under reduced pressure. The remaining solution was purified by HPLC to give the corresponding silyl ether.

Scheme 3. Plausible Reaction Pathways



One is the addition of the trimethylsilyl radical, which was generated in situ by the reaction of $PhSeSiMe_3$ with tributylstannyl radical, to the carbonyl compound and subsequent S_H2 reaction with Bu_3SnH to form the silyl ethers (path 1). It was already reported that the silylselenation of carbonyl compounds with $PhSeSiMe_3$ was promoted by a Lewis acid[15] or I_2,[16] giving α-silyloxyphenylselenides (**6**) in good yields. From this result, another reaction pathway included the silylselenation of the carbonyl compounds with **2**; the reductive dephenylselenation by the Bu_3Sn radical followed by the S_H2 reaction with Bu_3SnH was proposed (path 2). To clarify this reaction pathway, although benzaldehyde was allowed to react with $PhSeSiMe_3$ in the absence of Bu_3SnH, the silylselenated product was not formed and the benzaldehyde (97%) was recovered. Furthermore, when $PhSeSiEt_3$ was treated with Bu_3SnH in the absence of a carbonyl compound under the radical conditions, triethylsilyl hydride was formed in 43% yield. From these results, it appears reasonable to assume the generation pathway of the silyl radical as an intermediate (path 1).

In summary, we have successfully explored an efficient synthetic method for silyl ethers by the hydrosilylation of carbonyl compounds using the $PhSeSiMe_3/Bu_3SnH$/AIBN system. Further studies regarding the widespread use of the silyl radical generated in situ by the reaction of organoselenium compounds having Se−Si bonds with the tributylstannyl radical in organic reactions are underway in our laboratory.

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(13) Phenyl trimethylsilyl selenide was prepared by a literature method; see: Miyoshi, N.; Ishii, H.; Kondo, K.; Murai, S.; Sonoda, N. *Synthesis* **1979**, 300

(14) The absolute rate constants for the reaction of triethylsilyl radical with some carbonyl compounds are reported. The ease of addition of the Et_3Si radical was found to decrease in the order benzaldehyde > alkyl aryl ketone > alkyl aldehyde > acyclic dialkyl ketone; see: (a) Chatgilaloglu, C.; Irgolg, K. V.; Scaiano, J. *J. Am. Chem. Soc.* **1982**, *104*, 5119. (b) Cooper, J.; Hudson, A.; Jackson, R. A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1933.

(15) Liotta, D.; Petty, P. B.; Johnston, J.; Zima, G. *Tetrahedron Lett.* **1978**, 5091.

(16) Detty, M. R. *Tetrahedron Lett.* **1979**, 4189.