

Reaction of Carbonyl Compounds with Trialkylsilyl Phenylselenide and Tributylstannyl Hydride under Radical Conditions

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A novel method for the hydrosilylation of carbonyl compounds has been developed. When carbonyl compounds were allowed to react with trimethylsilyl phenylselenide and tributylstannyl hydride in the presence of a catalytic amount of AIBN as the radical initiator, hydrosilylation of the carbonyl compounds efficiently proceeded to give the corresponding silyl ethers in moderate to good yields. In the absence of carbonyl compounds, the triethylsilyl hydride was obtained by the reaction of PhSeSiEt_3 with Bu_3SnH . Although the tributylgermyl phenylselenide instead of PhSeSiMe_3 was treated with tributylstannyl hydride in the presence of a benzaldehyde under radical conditions, hydrogermylated product was not obtained and tributylgermyl hydride was mainly formed.

Clive first reported that the reaction of an organoselenide (RSePh) with tributylstannyl hydride under radical conditions was an efficient generation method of carbon radicals.¹ Since then, such generated carbon radicals have found widespread use in various transformations.² For the generation method using organoselenium compounds as a radical precursor, the reaction pathway involved the $\text{S}_\text{H}2$ reaction of tributylstannyl radical with organoselenium compounds on the selenium atom was proposed.³ From this background, it is expected that the reaction of organoselenium compounds having the selenium–heteroatom bond with tributylstannyl hydride in the presence of a radical initiator such as AIBN would become an excellent generation method for the various heteroatom radical species.

The development of new methods for the generation of organosilicon radicals such as the trialkylsilyl radical ($\text{R}_3\text{Si}^\bullet$) and the utilization of these radicals in organic synthesis is one of challenging problems in organic chemistry.⁴ Up to now, some organosilicon radical generation methods have been reported.^{5,6} 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 easily occurred during these preparation methods for the silyl radicals.¹² Therefore, new efficient and convenient generation methods for the trialkylsilyl radical are desired.

We then examined the preparation of the trialkyl silyl radical by the reaction of a small excess amount of

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(3) On the reaction of selenol with tributylstannyl radical, Crich et al. have proposed a stepwise process involving reversible formation of a T-shaped intermediate selenanyl radical. See: Crich, D.; Hwang, J.-T.; Racupero, F.; Wink, D. J. *J. Org. Chem.* **1999**, 64, 2877.

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(5) Sekiguchi et al. reported the first isolation of the stable silyl radical. See: Sekiguchi, A.; Matsuno, T.; Ichinohe, M. *J. Am. Chem. Soc.* **2001**, 123, 12436.

(6) Substitution of silyl radicals by the introduction of bulky substituents such as *tert*-butyl,⁷ mesityl,⁸ 3,5-di-*tert*-butylphenyl,⁹ trimethylsilyl,¹⁰ and other groups¹¹ has been attempted.

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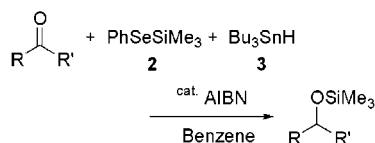
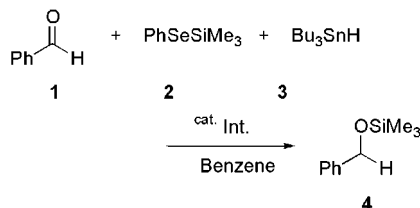
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SCHEME 1

TABLE 1. Reaction of Benzaldehyde (1) with PhSeSiMe₃ (2) and Bu₃SnH (3) under Various Reaction Conditions^a

entry	1/2/3 (mmol/mmol/mmol)	time, h	yield, % ^b
1	1.3/1.3/1.3	8	48
2	1.3/1.3/1.3	18	62
3 ^c	1.3/1.3/1.3	18	trace
4	1.3/1.7/1.7	18	78
5 ^d	1.3/1.7/1.7	18	70
6 ^e	1.3/1.7/1.7	18	65 ^f

^a Reaction conditions: in benzene (5 mL) at 80 °C. ^b GC yield.^c In the absence of AIBN. ^d AMVN (bisdiazoisovaleronitrile) instead of AIBN was used as a radical initiator at 60 °C. ^e PhSeSiEt₃ instead of PhSeSiMe₃ was used as organoselenium compound.^f The yield of triethylsilyl benzyl ether.

PhSeSiMe₃ with tributylstannyl hydride under radical conditions in the presence of carbonyl compounds as a trapping agent of the silyl radical and found that the hydrosilylation of the carbonyl compounds efficiently proceeded to give the corresponding trimethylsilyl ethers in moderate to good yields (Scheme 1).¹³ The full results of the reaction of trialkylsilyl or trialkylgermyl phenylselenide with tributylstannyl hydride in the presence of carbonyl compounds under radical conditions are disclosed in this paper.

The treatment of benzaldehyde (1) with trimethylsilyl phenylselenide (PhSeSiMe₃) (2) and tributylstannyl hydride (3) was carried out in the presence of a radical initiator, and the results are shown in Table 1. When 1 was allowed to react with 2 and 3 in the presence of a catalytic amount of AIBN at 80 °C for 8 h, the hydrosilylation of 1 efficiently proceeded to give the trimethylsilylbenzyl ether (4) in 48% yield (entry 1). The extended reaction time (18 h) caused an increase in the yield of silyl ether (entry 2). The yield of 4 was improved by using a small excess amount of 2 (1.3 equiv) and 3 (1.3 equiv), and 4 was obtained in 78% yield (entry 3). In the absence of AIBN, the reaction did not proceed at all (entry 3). When AMVN (azobisisovaleronitrile) instead of AIBN was used as the radical initiator, the hydrosilylation of 1 smoothly proceeded at a lower reaction temperature (entry 5). The hydrosilylation of 1 with triethylsilylphenylselenide and 3 in the presence of AIBN also proceeded to give the triethylsilylbenzyl ether in 65% yield (entry 6).

To know the scope and limitations of the hydrosilylation method of carbonyl compounds with 2 and 3, various

TABLE 2. Hydrosilylation of Aromatic Aldehydes with PhSeSiMe₃ and Bu₃SnH in the Presence of a Catalytic Amount of AIBN^a

entry	carbonyl Compound	yield/% ^b
1	X = H	78
2	= 2-Me	65
3	= 3-Me	77
4	= 4-Me	80
5	= 4-MeO	85
6 ^c	= 4-NO ₂	12
7 ^c	= 4-Cl	74
8 ^c	= 4-Br	45
9 ^c		81
10 ^c		86

^a Reaction conditions: carbonyl compound (1.3 mmol), PhSeSiMe₃ (1.7 mmol), Bu₃SnH (1.7 mmol), AIBN (0.13 mmol), and benzene (5 mL) at 80 °C for 18 h. ^b GC yield. ^c For 48 h.

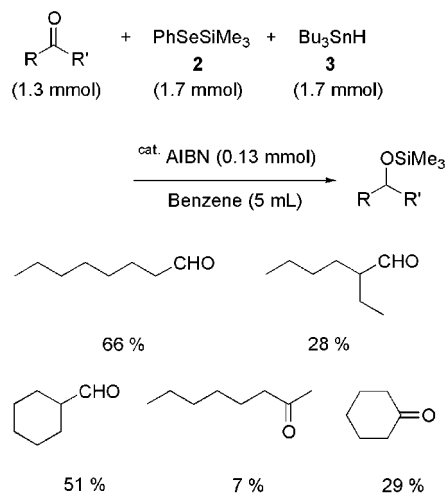
aromatic aldehydes were first allowed to react with a small excess amount of 2 and 3 in the presence of a catalytic of AIBN at 80 °C (Table 2). For the 3- and 4-methylbenzaldehydes, the corresponding silyl ethers were obtained in 77 and 80% yields, respectively (entries 3 and 4). In the case of 2-methylbenzaldehyde, the yield of the silyl ether was slightly decreased (entry 2). Similarly, 4-methoxybenzaldehyde was hydrosilylated by the PhSeSiMe₃/Bu₃SnH/AIBN system giving 4-methoxybenzyltrimethylsilyl ether in 85% yield (entry 5). For the reaction of 4-nitrobenzaldehyde, the yield of the silyl ether was markedly decreased due to the formation of complex byproducts (entry 6). When 4-chlorobenzaldehyde was reacted with PhSeSiMe₃ and Bu₃SnH under the same reaction conditions as for the benzaldehyde, the yield of the product was moderate (48%); however, the product yield was improved by extending the reaction time (48 h) (entry 7). For the 4-bromobenzaldehyde, benzyl trimethylsilyl ether (35%), which is the debromination product, was formed as a byproduct (entry 8). The hydrosilylation of the 1- and 2-naphthylaldehydes also smoothly proceeded to afford the corresponding silyl ethers in good yields (entries 9 and 10). Table 3 shows the results of the treatment of aromatic ketones with PhSeSiMe₃ and Bu₃SnH. Similarly, various silyl ethers were synthesized by the reaction of aromatic ketones with PhSeSiMe₃ and Bu₃SnH in the presence of a catalytic amount of AIBN in moderate yields. Aliphatic aldehydes or ketones were treated with PhSeSiMe₃ and Bu₃SnH under radical conditions, and the results are shown in Scheme 2. For the reaction of octanal, 2-ethylhexanal, and cyclohexanecarbaldehyde, trimethylsilyl ethers were

(13) For recent reviews of the radical-mediated reduction of carbonyl compounds by using silicon reagents. See ref 4f.

TABLE 3. Hydrosilylation of Aromatic Ketones Using PhSeSiMe_3 and Bu_3SnH in the Presence of a Catalytic Amount of AIBN^a

entry	carbonyl Compound	yield/% ^b
1	R = H	56
2	R = Me	60
3 ^c		71
4 ^c		46
5 ^c		56
6 ^c		48
7		64

^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 GC yield. ^c For 48 h.

SCHEME 2

obtained in 66, 28, and 51% yields, respectively. For the aliphatic ketones, the yields of the silyl ethers were lower than those of the aromatic ketones.¹⁴

Next, α -dicarbonyl compounds were treated with a small excess amount of PhSeSiMe_3 and Bu_3SnH in the presence of a catalytic amount of AIBN (Table 4). The

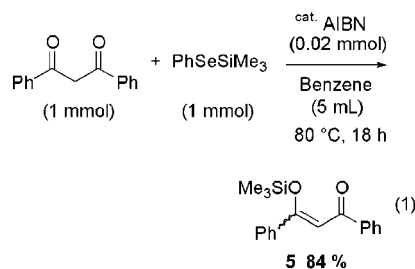
(14) The absolute rate constants for the reaction of triethylsilyl radical with some carbonyl compounds are reported. The ease of addition of Et_3Si radical was found to decrease in order benzaldehyde > alkyl aryl ketone > alkyl aldehyde > acyclic dialkyl ketone; see: (a) Chatgililoglu, C.; Irgol, K. 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.

TABLE 4. Hydrosilylation of Dicarbonyl Compounds Using PhSeSiMe_3 and Bu_3SnH in the Presence of a Catalytic Amount of AIBN^a

entry	α -dicarbonyl compound	products (yield/%) ^b
1		(73)
2 ^c		(52)
3		(20) (3)
4 ^d		(52) (16%)

^a Reaction conditions: carbonyl compound (0.5 mmol), PhSeSiMe_3 (1.2 mmol), Bu_3SnH (1.2 mmol), AIBN (0.05 mmol), and benzene (5 mL) at 80 °C for 18 h. ^b GC yield. ^c For 24 h. ^d Phenyl(1-trimethylsiloxy)ethyl ketone was formed in 16% yield.

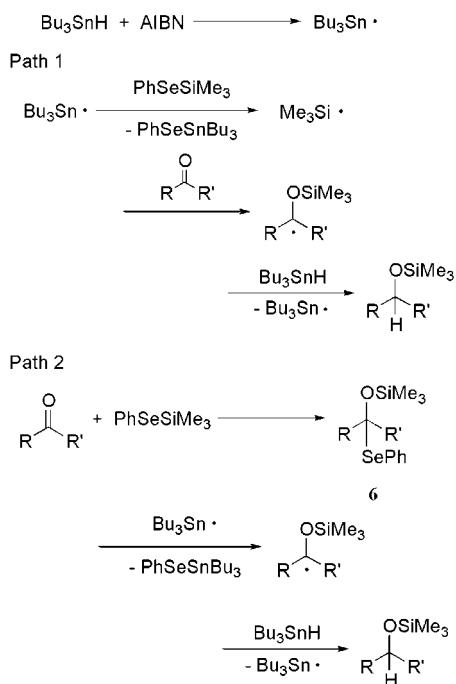
monohydrosilylation of benzil and acenaphthenequinone smoothly proceeded to give the corresponding monohydrosilylated products in moderate yield (entries 1 and 2). Although the reaction of benzil with an excess amount of PhSeSiMe_3 and Bu_3SnH (5/5 equiv) was carried out, the dihydrosilylated product was not formed. In contrast to the reaction of diaryl ketone, for the reaction of 2,3-butanedione, a mixture of mono- and dihydrosilylated products was formed (entry 3). Upon hydrosilylation of 1-phenyl-1,2-propanedione using this system, the hydrosilylation of the carbonyl group adjacent to the aromatic ring predominantly proceeded to give the methyl(trimethylsiloxy)benzyl ketone in 52% yield with the formation of phenyl(1-trimethylsiloxy)ethyl ketone (16%) (entry 4). On the other hand, for the β -dicarbonyl compound, the β -siloxy- α,β -unsaturated ketone derivative (**5**) was formed in 84% yield (eq 1).¹⁵



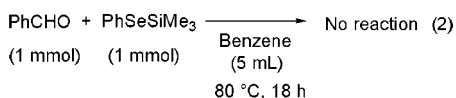
Although we cannot explain the reaction pathway of the hydrosilylation of the carbonyl compounds using the $\text{PhSeSiMe}_3/\text{Bu}_3\text{SnH}/\text{AIBN}$ system in detail, two possible reaction pathways were proposed for the reaction (Scheme 3). One is the addition of the trimethylsilyl radical, which was generated in situ by the reaction of PhSeSiMe_3 with

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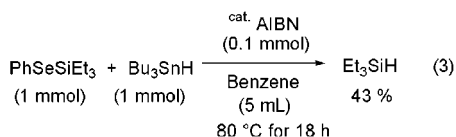
SCHEME 3. Plausible Reaction Pathways



the tributylstannyl radical, to the carbonyl compound and subsequent $\text{S}_{\text{H}}2$ reaction with Bu_3SnH to form the silyl ether (path 1). It was already reported that the silylselenation of carbonyl compounds with PhSeSiMe_3 was promoted by a Lewis¹⁵ acid or I_2 ¹⁶ giving α -siloxyphenylselenides (**6**) in good yields. From this result, another reaction pathway including the silylselenation of the carbonyl compounds with PhSeSiMe_3 and the dephenylselenation by the tributylstannyl radical followed by the $\text{S}_{\text{H}}2$ 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 (eq 2). Further-

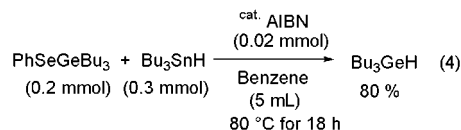


more, when PhSeSiEt_3 was treated with Bu_3SnH in the absence of a carbonyl compound under the radical conditions (in the presence of a catalytic amount of AIBN), the triethylsilyl hydride was obtained in 43% yield (eq 3). From these results, it appears reasonable to assume the generation pathway of the silyl radical as an intermediate (path 1).

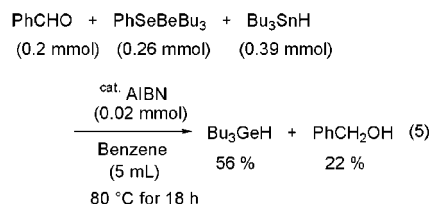


When an organoselenium compound having the selenium–germanium bond is reacted with tributylstannyl hydride in the presence of AIBN as the radical initiator, it is expected that the compound would become an

excellent precursor for the trialkylgermyl radical species. In fact, the treatment of PhSeGeBu_3 with Bu_3SnH in the presence of a catalytic amount of AIBN gave tributylgermyl hydride in 80% yield (eq 4). Although the reaction



was carried out in the presence of benzaldehyde, in contrast to that of the trialkylsilyl phenylselenide, the hydrogermylated product was not formed and the trialkylgermyl hydride was mainly obtained in 56% yield (eq 5).



In summary, we have successfully explored an efficient synthetic method for silyl ethers by the hydrosilylation of carbonyl compounds by the $\text{PhSeSiMe}_3/\text{Bu}_3\text{SnH}/\text{AIBN}$ system. In this reaction, the in situ generation of a silyl radical by the reaction of organoselenium compounds having Se–Si bonds with the tributyl stannyl radical was proposed.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on 400 and 99.5 MHz spectrometers in CDCl_3 as the solvent with tetramethylsilane as the internal standard. FT-IR spectra were recorded using a KBr disk. Mass spectra were measured on a GC mass spectrometer. Gas chromatography was carried out on a Shimadzu GC-14A equipped with a flame-ionization detector using a capillary column (Hicap-CBP-1-S25-025, 0.25 mm \times 25 m). The carbonyl compounds, Bu_3SnH , and benzene, were purified by the usual methods before use. PhSeSiMe_3 was prepared by the literature method.¹⁷ Tributylgermyl phenylselenide was synthesized by the reaction of tributylgermyl chloride with lithium phenylselenoate generated in situ by the treatment of PhLi and elemental selenium. 1-Phenyl-1,2-propanedione was synthesized by the oxidation of propiophenone with SeO_2 .¹⁸

General Procedure for the Hydrosilylation of Carbonyl Compounds with PhSeSiMe_3 and Bu_3SnH in the Presence of a Catalytic Amount of AIBN. A benzene (5 mL) solution of the carbonyl compound (1.3 mmol), PhSeSiMe_3 (400 mg, 1.7 mmol), Bu_3SnH (510 mg, 1.7 mmol), and AIBN (22 mg, 0.13 mmol) was stirred at 80 $^\circ\text{C}$ for 18–72 h under a nitrogen atmosphere. After the reaction was completed, H_2O was added to the reaction mixture and extracted with Et_2O ($\times 3$). The combined organic layers were dried over MgSO_4 and removed under reduced pressure. The remaining solution was purified by HPLC to give the corresponding silyl ether. The structures of the products were determined by ^1H and ^{13}C NMR, IR, and MS.

General Procedure for the Hydrosilylation of α -Dicarbonyl Compounds with PhSeSiMe_3 and Bu_3SnH in the Presence of a Catalytic Amount of AIBN. A benzene

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(5 mL) solution of the α -dicarbonyl compound (0.5 mmol), PhSeSiMe₃ (270 mg, 1.2 mmol), Bu₃SnH (350 mg, 1.2 mmol), and AIBN (9 mg, 0.05 mmol) was stirred at 80 °C for 48 h under a nitrogen atmosphere. After the reaction was completed, H₂O was added to the reaction mixture and extracted with Et₂O ($\times 3$). The combined organic layers were dried over MgSO₄ and removed under reduced pressure. The remaining solution was purified by HPLC to give the corresponding silyl ether. The structures of the products were determined by ¹H and ¹³C NMR, IR, and MS.

Reaction of PhSeSiMe₃ with Bu₃SnH in the Presence of a Catalytic Amount of AIBN. A benzene (5 mL) solution of PhSeSiMe₃ (240 mg, 1.0 mmol), Bu₃SnH (291 mg, 1.0 mmol), and AIBN (22 mg, 0.13 mmol) was stirred at 80 °C for 18 h under a nitrogen atmosphere. After the reaction was completed, H₂O was added to the reaction mixture and extracted with Et₂O ($\times 3$). The combined organic layers were dried over MgSO₄ and removed under reduced pressure. The remaining solution was purified by HPLC to give the corresponding silyl ether. The structures of product were determined by ¹H and ¹³C NMR, IR, and MS.

Reaction of PhSeGeBu₃ with Bu₃SnH in the Presence of a Catalytic Amount of AIBN. A benzene (5 mL) solution of PhSeGeBu₃ (104 mg, 0.26 mmol), Bu₃SnH (113 mg, 0.39 mmol), and AIBN (4 mg, 0.02 mmol) was stirred at 80 °C for 18 h under a nitrogen atmosphere. After the reaction was completed, H₂O was added to the reaction mixture and extracted with Et₂O ($\times 3$). The combined organic layers were dried over MgSO₄ and removed under reduced pressure. The

remaining solution was purified by HPLC to give the mixture of benzyl alcohol and tributylgermyl hydride. The structures of the products were determined by ¹H and ¹³C NMR, IR, and MS.

Reaction of Benzaldehyde with PhSeGeBu₃ and Bu₃SnH in the Presence of a Catalytic Amount of AIBN. A benzene (5 mL) solution of benzaldehyde (21 mg, 0.2 mmol), PhSeGeBu₃ (104 mg, 0.26 mmol), Bu₃SnH (113 mg, 0.39 mmol), and AIBN (4 mg, 0.02 mmol) was stirred at 80 °C for 18 h under a nitrogen atmosphere. After the reaction was complete, H₂O was added to the reaction mixture and extracted with Et₂O ($\times 3$). The combined organic layers were dried over MgSO₄ and removed under reduced pressure. The remaining solution was purified by HPLC to give the mixture of benzyl alcohol and tributylgermyl hydride. The structures of the products were determined by ¹H and ¹³C NMR, IR, and MS.

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Supporting Information Available: NMR spectra of obtained compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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