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Reagents for Diverse Iodosilane-Mediated Transformations

Masatoshi Shibuya,* Masanori Abe, Shoji Fujita and Yoshihiko Yamamoto

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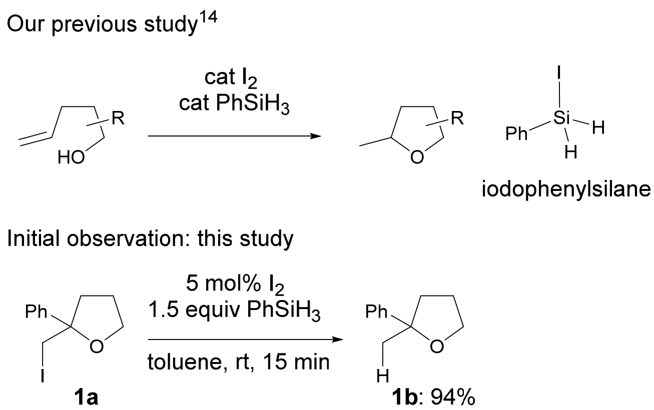
It was observed that a $PhSiH_2I$-mediated protocol using $PhSiH_3$ and cat. I_2 caused the deiodination of 2-iodomethyltetrahydrofuran. Stemming from the investigation of the mechanism, we found that the $PhSiH_3$–I_2 system selectively promotes diverse cascade transformations from cyclic ethers to acyclic alkyl iodides, and the $PhSiH_3$–*N*-iodosuccinimide (NIS) system also promotes cascade transformations from cyclic ethers to acyclic alcohols.

Introduction

Organosilicon reagents enable various indispensable reaction in organic chemistry owing to their unique property.[1-3] Hydrosilanes such as Et_3SiH, Et_2SiH_2, and $PhSiH_3$ are used as a hydride source owing to the lower eletronegativity of silicon (1.7) than that of hydrogen (2.1). These reagents cause the reduction of a carbonyl group, acetal, or benzylic ether in the presence of a Lewis acid or a Brønsted acid,[4] and the hydrosilylation of unsaturated bonds catalyzed by a transition metal.[5] $(Me_3Si)_3SiH$ and $PhSiH_3$ are used as a hydrogen source in radical reactions.[6,7] Recently, hydrosilanes have also been utilized in the catalytic functionalization of unactivated C-H bonds.[8,9] On the other hand, silyl halides such as Me_3SiCl, Et_3SiCl, and *tert*-butyldimethylsilyl chloride (TBDMSCl) are used as silylation reagents for the protection of a hydroxy group and an amino group in the presence of a base.[10] Although silyl halides also have the Lewis acidic property,[11] the typical silyl iodide, trimethylsilyl iodide (TMSI), has a particularly high reactivity owing to its Si-I bond consisting of a hard silicon atom and a soft iodine atom.[12] It is able to cleave inert C-O bonds of ethers, esters, and alcohols with the formation of a C-I bond and a Si-O bond.[13] These properties of TMSI enable a variety of synthetically useful transformations, whereas the storage of TMSI requires special care owing to its lability. Recently, we have developed a silane-iodine catalytic system for the intramolecular hydroalkoxylation reaction of unactivated alkenes.[14] The mechanistic study indicates that iodophenylsilane, $PhSiH_2I$, generated in situ from $PhSiH_3$ and I_2, acts as a possible actual catalytic species. Although the generation of silyl iodides from hydrosilanes such as polymethylhydrosiloxane (PHMS) and Et_3SiH by I_2 has been reported, most of them are trialkylsilanes.[15] Because $PhSiH_2I$ has a distinctive structure possessing a hydrosilane (Si-H) moiety and a silyl iodide (Si-I) moiety in one molecule, we are interested in its reactivity. Although the preparation of $PhSiH_2I$ has been reported, its reactivity remains unreported except in our report.[14,16] During our continuing studies on the $PhSiH_3$–I_2 system, it was found that the deiodination of iodoether **1a** smoothly proceeds to provide cyclic ether **1b** (Scheme 1). To determine the reactivity of $PhSiH_2I$ and explore the mechanism, different iodoethers were subjected to the deiodination reaction.[17] Taking a cue from the mechanistic study, we found that a series of cascade reactions are caused by $PhSiH_3$–I_2 and $PhSiH_3$–NIS. Herein, we report these reactions together with our investigation of the deiodination reaction.



Scheme 1 Intramolecular hydroalkoxylation and deiodination catalysed by silane-iodine system.

Department of Basic Medicinal Sciences, Graduate School of Pharmaceutical Sciences, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8601, Japan. E-mail: m-shibu@ps.nagoya-u.ac.jp

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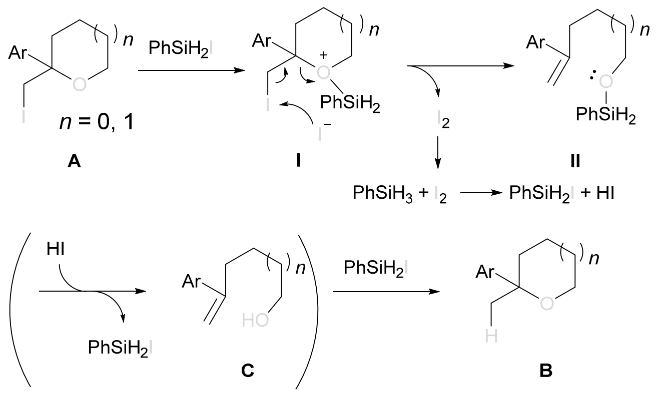
Results and discussion

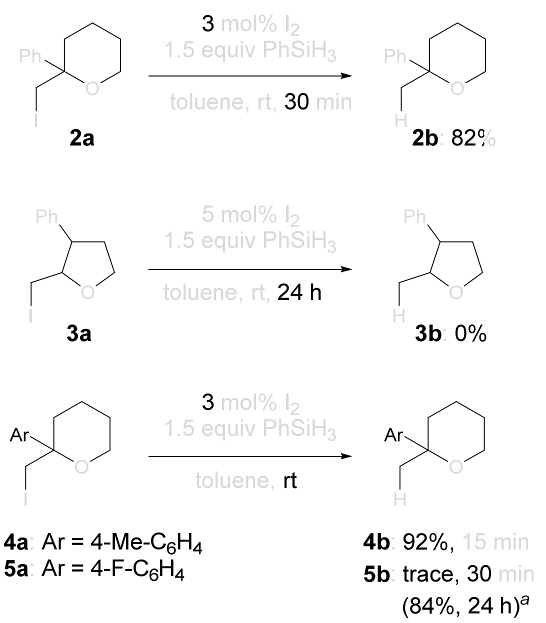
The investigation commenced with the treatment of 6-membered iodoether **2a** and 5-membered iodoether **3a** with a catalytic amount of I_2 and 1.5 equiv of $PhSiH_3$ (Scheme 2). The deiodination of 6-membered iodoether **2a** efficiently proceeded to provide cyclic ether **2b** in high yield, as is the case for **1a**. In contrast, 5-membered iodoether **3a**, which is an isomer of **1a**, exhibited no reaction. As a difference producing these contrasting results, the property of proximal C-O bonds can be considered. The C-O bonds of **1a** and **2a** are located at a benzylic position, whereas that of **3a** is located at a homobenzylic position. We also confirmed that the deiodination of **1a** smoothly proceeds in the presence of the radical scavenger galvinoxyl.[6,18] A plausible explanation that accounts for these results is that the deiodination proceeds via the deiodinative ring opening/intramolecular hydroalkoxylation process shown in Scheme 3. That is, the deiodinative ring opening with benzylic C-O bond cleavage of iodoether **A** is caused by the in situ generated $PhSiH_2I$ and produced silyloxy alkene **II**. Then, silyloxy alkene **II** or desilylated hydroxy alkene **C** undergoes recyclization by the intramolecular hydroalkoxylation to provide cyclic ether **B**. It is known from our previous study that the γ- and δ-hydroxy phenyl-substituted alkenes are smoothly cyclized to the corresponding cyclic ethers via the corresponding silyloxy alkenes under silane-iodine conditions.[14] A deuterium labeling study using **2a** and $PhSiD_3$ indicated that the newly introduced hydrogen in **B** originates from $PhSiH_3$.[18] We also examined the deiodination of **4a** and **5a**, which have an electron-donating group (Me) and an electron-withdrawing group (F) on the 4-position of the benzene rings, respectively (Scheme 2). The deiodination reaction of **4a** was faster than that of **2a** and



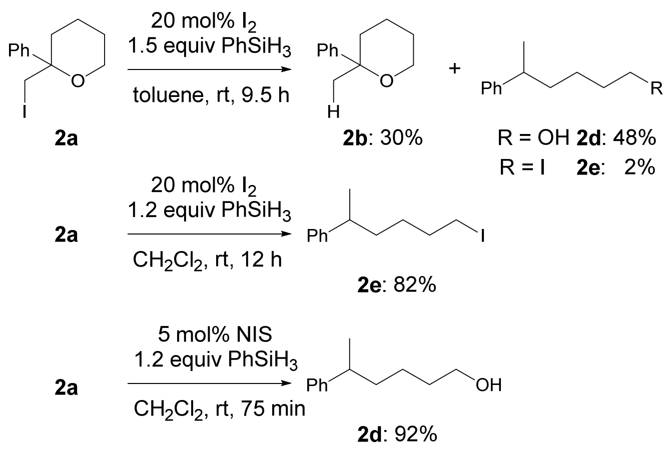
Scheme 3 Plausible mechanism of the deiodination reaction.

completed within 15 min, whereas the reaction of **5a** was slower than that of **2a** and a trace amount of **5b** was observed after 30 min. The reaction rates of the deiodination reactions are correlated with the stability of the benzylic cation. The reaction of **5a** was suddenly accelerated after induction time of 3-6 h. It was difficult to selectively obtain **5b** owing to the concomitant reductive ring opening under the reaction conditions (*vide infra*). A high yield of **5b** was obtained only when the amount of $PhSiH_3$ was reduced to 0.2 equiv, although the proton source is unclear.

During the investigation of the reaction of **2a**, increasing the amount of I_2 to 20 mol% unexpectedly led to a decrease of the yield of cyclic ether **2b** and afforded acyclic saturated alcohol **2d** in moderate yield, together with a small amount of acyclic iodide **2e** (Scheme 4). Furthermore, when the solvent was changed from toluene to CH_2Cl_2, the reaction completed within 12 h to selectively provide acyclic iodide **2e** in high yield. To obtain insight into the solvent effect, the reaction of 1 equiv $PhSiH_3$ and 1 equiv I_2 in toluene-d_8 and that in CD_2Cl_2 were monitored by ^{1}H NMR (Figure 1).[14,16b,19] It was found that while less than 20% of $PhSiH_3$ was converted to $PhSiH_2I$ in toluene-d_8 after 30 min at room temperature, more than 50% of $PhSiH_3$ was converted to $PhSiH_2I$ in CD_2Cl_2 after the same time.[18]



Scheme 2 Deiodination of iodoethers. ^{a} Conditions, 3 mol% I_2, 0.2 equiv $PhSiH_3$, CH_2Cl_2, rt.



Scheme 4 Reductive ring opening of iodoether **2a**.

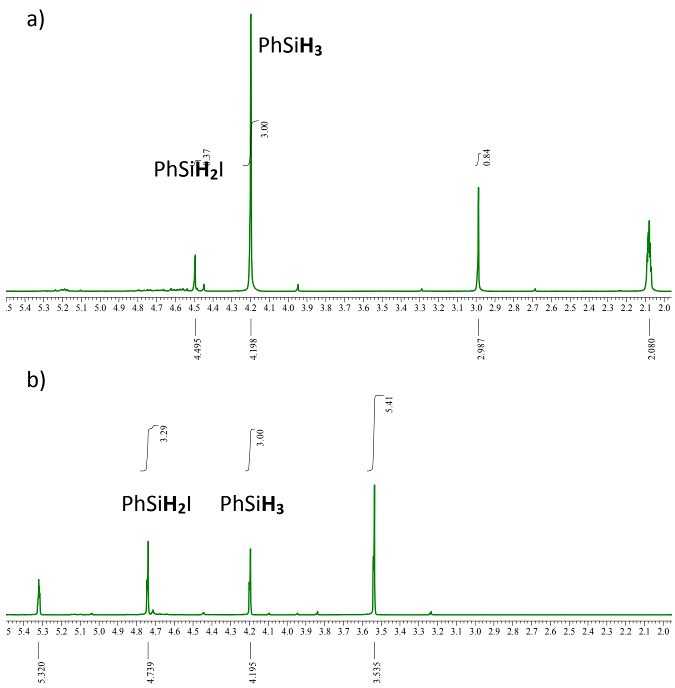
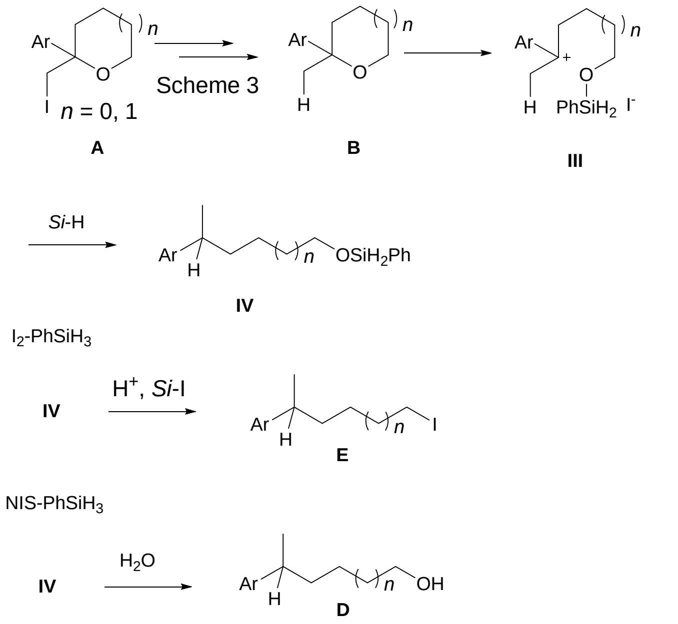


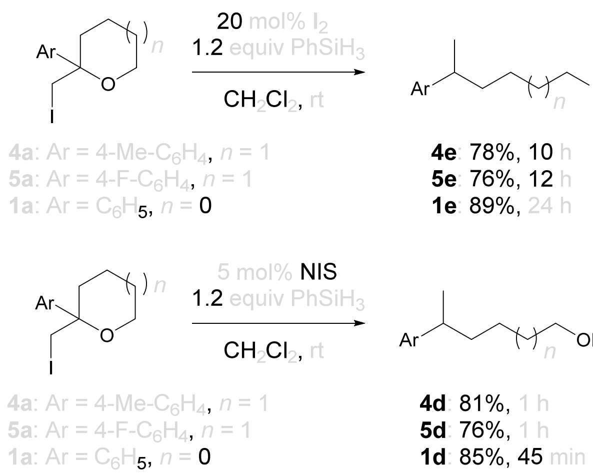
Figure 1 ^{1}H NMR spectra of the reaction mixture of $PhSiH_3$ and I_2 in toluene-d_8 (a) and that in CD_2Cl_2 (b), which were measured 30 min after mixing.

These results indicate that increasing the amount of $PhSiH_2I$ enhanced the reaction and a high yield of acyclic iodide **2e** was consequently provided in CH_2Cl_2. Acyclic iodide **2e** is presumably produced via reductive ring opening (**B** to **IV**) and subsequent iodination reaction (**IV** to **E**) after deiodination (**A** to **B**), as shown in Scheme 5.[12,13d,18] Cyclic ether **2b** and acyclic alcohol **2d** as intermediates are detectable by TLC analysis. Although Panek *et al.* reported the reductive ring opening of aryl pyranosides using $Sc(OTf)_3$ and Et_3SiH,[20] it is interesting that similar reductive ring opening of the cyclic ethers efficiently occurs under $PhSiH_2I$-mediated conditions. Also note that it is not a stoichiometric amount but only a catalytic amount of I_2 that is required for the transformation from iodoether **2a** to acyclic iodide **2e**, which means that the iodide atom of **2e** originates from not only I_2 but also iodoether **2a**. 1 equiv of I_2 is released on the process of deiodinative ring opening of iodoether **2a** and $PhSiH_2I$ is generated from the I_2 and $PhSiH_3$ (Scheme 3). As the results, the iodine atom of **2a** is reintroduced into acyclic iodide **2e**. Next, we treated iodoether **2a** with $PhSiH_3$ and NIS in CH_2Cl_2 (Scheme 4). Our previous study suggested that the reaction of $PhSiH_3$ and NIS also produces $PhSiH_2I$ together with succinimide.[14]

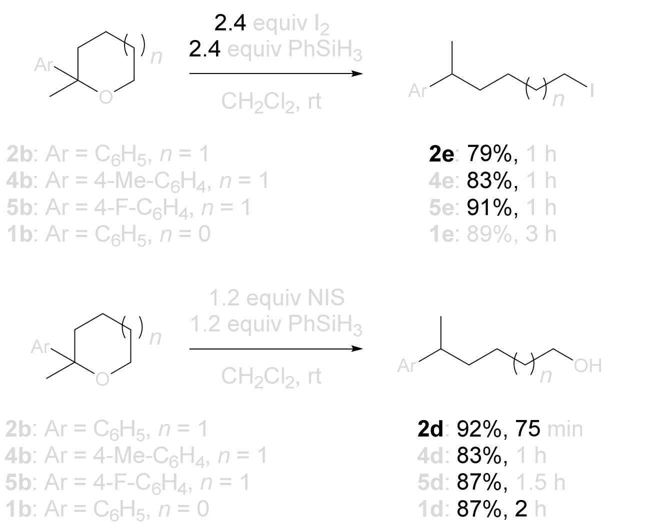


Scheme 5 Plausible reaction mechanism of the transformation from iodoether **A**.

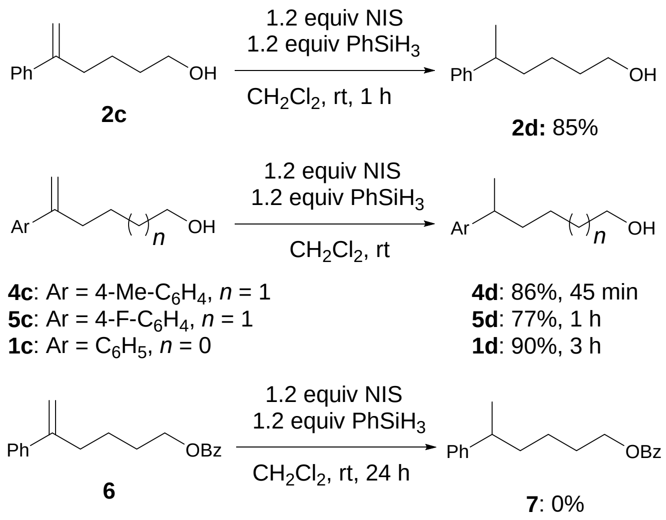
A prolonged reaction time only resulted in the production of a small amount of acyclic iodide **2e**. While the $PhSiH_3$–I_2 protocol provides acyclic iodide **2e**, the $PhSiH_3$–NIS protocol gives acyclic alcohol **2d** from iodoether **2a**. The difference may originate from the existence of HI generated from the reaction of $PhSiH_3$ with I_2, which could promote the iodination of acyclic alcohol **2d**. 4-Me- and 4-F-phenyl-substituted iodoethers **4a** and **5a** and 5-membered iodoether **1a** were treated with 20 mol% I_2 and 1.2 equiv $PhSiH_3$ and with 5 mol% NIS and 1.2 equiv $PhSiH_3$ (Scheme 6). All of the iodoethers afforded the corresponding acyclic iodides in high yields by the $PhSiH_3$–I_2 protocol and afforded the corresponding acyclic alcohols by the $PhSiH_3$–NIS protocol. The



Scheme 6 Reductive ring opening of iodoethers **4a**, **5a**, and **1a**.



Scheme 7 Reductive ring opening of cyclic ethers.



Scheme 8 Formal hydrogenation of phenyl-substituted olefins.

substituents on the benzene ring and the ring size of the cyclic ethers did not have a significant effect on the reaction times and yields.

Because cyclic ether **B** is considered as an intermediate in the above cascade reactions, the reductive ring opening from cyclic ether **B** to acyclic alcohol **D** and acyclic iodide **E** is assumed to proceed according to the reaction pathway in Scheme 5. Although the combination of a catalytic amount of I_2 and a stoichiometric amount of $PhSiH_3$ resulted in no reaction, 2.4 equiv of I_2 and 2.4 equiv $PhSiH_3$ effectively caused the cascade reductive ring opening/iodination reaction of **2b** to provide the corresponding acyclic iodide **2e** in high yield (Scheme 7). Similarly, 1.2 equiv of NIS and 1.2 equiv of $PhSiH_3$ caused the reductive ring opening to selectively yield the corresponding acyclic alcohol **2d**. Cyclic ethers **4b**, **5b**, and **1b** also afforded the corresponding acyclic iodides by the treatment of I_2 and $PhSiH_3$ in high yields as well as the corresponding alcohols by the treatment of NIS and $PhSiH_3$.

Hydroxy alkene **C** is also a putative intermediate of the cascade reaction from iodoether **A** to acyclic alcohol **D** (see Scheme 3 and 5). It is assumed that the cascade intramolecular hydroalkoxylation/reductive ring opening reaction of γ-hydroxy alkene **2c** occurred to provide saturated alcohol **2d**, which is a formal hydrogenation without hydrogen gas. On the basis of this assumption, γ-hydroxy alkene **2c** was treated with 1.2 equiv of NIS and 1.2 equiv of $PhSiH_3$ (Scheme 8). Thus, the saturated alcohol **2d** was obtained in high yield. 4-Me- and 4-F-phenyl-substituted alkenes **4c** and **5c** and alkene shorter by one carbon **1c** were smoothly reduced to the corresponding saturated alcohols, whereas benzoyl ester **6** did not afford the saturated alcohol **7** under the same conditions within 24 h.

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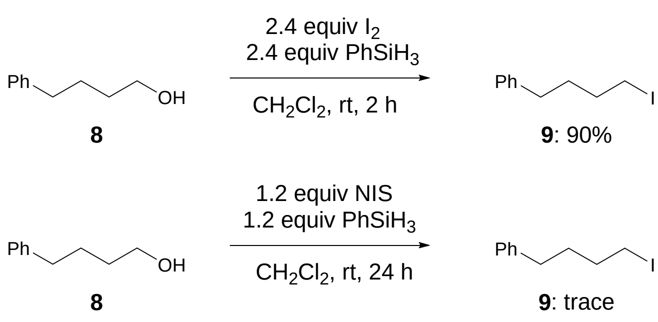
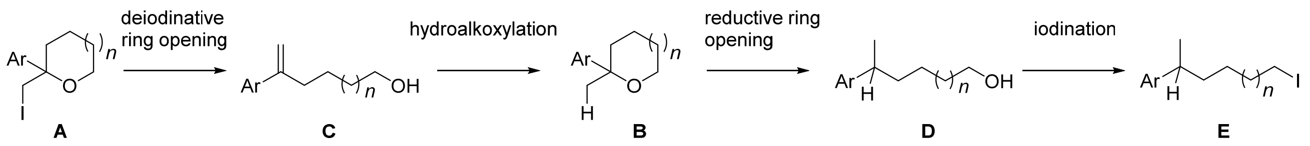
Finally, we examined the iodination of alcohol **8** employing the $PhSiH_3$–I_2 and $PhSiH_3$–NIS protocols (Scheme 9).[13e,21] As expected from the results so far obtained, the iodination of **8** was efficiently caused by $PhSiH_3$ and I_2 to provide iodide **9** in high yield, while $PhSiH_3$ and NIS afforded a trace amount of iodide **9** even after 24 h.

As summarized in Scheme 10, $PhSiH_3$–I_2 and $PhSiH_3$–NIS generate highly reactive $PhSiH_2I$, which is able to mediate our previously reported intramolecular hydroalkoxylation as well as diverse transformations such as the deiodination of iodoethers, the reductive ring opening of iodoethers and cyclic ethers, and the formal hydrogenation of a γ-hydroxy phenyl-substituted alkene. The $PhSiH_3$–I_2 protocol causes the iodination of alcohols.



Scheme 9 Reaction of alcohol 8 with $PhSiH_3$-I_2 and $PhSiH_3$-NIS.



A ⟶ **B** deiodination (deiodinative ring opening/hydroalkoxylation): $PhSiH_3$, cat I_2
C ⟶ **B** hydroalkoxylation [ref 14]: cat $PhSiH_3$, cat I_2
A ⟶ **D** deiodination/reductive ring opening: $PhSiH_3$, cat NIS
A ⟶ **E** deiodination/reductive ring opening/iodination: $PhSiH_3$, cat I_2
B ⟶ **D** reductive ring opening: $PhSiH_3$, NIS
B ⟶ **E** reductive ring opening/iodination: $PhSiH_3$, I_2
C ⟶ **D** formal hydrogenation (hydroalkoxylation/reductive ring opening): $PhSiH_3$, NIS
D ⟶ **E** iodination: $PhSiH_3$, I_2

Scheme 10. Summary of $PhSiH_2I$–mediated transformation.

Conclusions

The deiodination of iodoether **A** was rationalized by the deiodinative ring opening/intramolecular hydroalkoxylation mechanism mediated by $PhSiH_2I$. Stemming from the mechanistic study, we also found a series of $PhSiH_2I$-mediated reactions under $PhSiH_3$–I_2 and $PhSiH_3$–NIS protocols. Iodoether **A** and cyclic ether **B** as well as alcohol **D** are converted to acyclic iodide **E** under $PhSiH_3$–I_2 protocols, whereas iodoether **A,** cyclic ether **B**, hydroxy alkene **C** are converted to acyclic alcohol **D** under $PhSiH_3$–NIS protocols. These results indicate that $PhSiH_2I$ acts as silyl iodide species having the properties of a Lewis acid and an iodide donor and as a hydrosilane species having the property of a hydride donor in these reactions. Further studies on the silane-iodine system are ongoing in our laboratory.

Experimental

General considerations

All reagents were obtained from commercial source and used without further purification. Reactions were carried out in a glass flask with a plastic cap. Column chromatography was performed on silica gel (Cica silica gel 60N). ^1H and ^{13}C NMR were obtained for samples in $CDCl_3$ on a JEOL 400 MHz spectrometer at room temperature. ^1H NMR chemical shifts are reported in terms of chemical shift (δ, ppm) relative to the singlet at 7.26 ppm for chloroform. ^{13}C NMR chemical shifts were fully decoupled and are reported in terms of chemical shift (δ, ppm) relative to the triplet at 77.0 ppm for $CDCl_3$.

Representative procedure

Deiodination of iodoether A. I_2 (1.4 mg, 5.6 μmol) and $PhSiH_3$ (34 μl, 0.28 mmol) were added to a solution of **2a** (56 mg, 0.19 mmol) in toluene (2 ml) at room temperature. After stirring for 30 min, the reaction mixture was quenched with sat. $Na_2S_2O_3$ and extracted with Et_2O (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/Et_2O = 100:1) to afford **2b** (27 mg, 82%) as colorless oil. Analytical data of **1b** and **2b** were consistent with reported data.[12]

2-Methyl-2-(4-methylphenyl)tetrahydrofuran (4b). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, 2H, J = 8.0 Hz), 7.17 (d, 2H, J = 8.0 Hz), 3.74-3.67 (m, 1H), 3.47 (td, 1H, J = 11.6, 4.8 Hz), 2.35 (s, 3H), 2.28 (dt, 1H, J = 13.6, 3.2 Hz), 1.76-1.36 (m, 5H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 136.0, 129.1, 126.0, 75.9, 62.7, 34.6, 32.9, 26.0, 21.0, 20.1; IR (neat, cm^{-1}): 2937; HRMS (ESI, m/z) Calcd. for $C_{13}H_{18}NaO$ $[M+Na]^+$: 213.1255, found 213.1259.

2-Methyl-2-(4-fluorophenyl)tetrahydrofuran (5b). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40-7.34 (m, 2H), 7.06-7.01 (m, 2H), 3.75-3.69 (m, 1H), 3.45 (ddd, 1H, J = 11.6, 10.6, 3.2 Hz), 2.28-2.21 (m, 1H), 1.78-1.41 (m, 5H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6 (d, J = 244.4 Hz), 141.1 (d, J = 2.8 Hz), 127.5 (d, J = 7.6 Hz), 115.0 (d, J = 21.0 Hz), 75.5, 62.6, 34.6, 32.5, 25.9, 20.0; IR (neat, cm^{-1}): 2939; HRMS (DART, m/z) Calcd. for $C_{12}H_{19}FNO$ $[M+NH_4]^+$: 212.1451, found 212.1476.

Tandem deiodination/reductive ring opening/iodination reaction from iodoether A to acyclic iodide E. I_2 (8.4 mg, 0.033 mmol) and $PhSiH_3$ (24 μl, 0.19 mmol) were added to a solution of **2a** (50 mg, 0.17 mmol) in CH_2Cl_2 (0.5 ml) at room temperature. After stirring 12 h, the reaction mixture was quenched with H_2O and extracted with Et_2O (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/Et_2O = 100:1) to afford **2e** (39 mg, 82%) as colorless oil.

(6-Iodohexan-2-yl)benzene(2e). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.27 (m, 2H), 7.20-7.16 (m, 3H), 3.13 (td, 2H, J = 6.8, 2.0 Hz), 2.67 (sext, 1H, J = 6.8 Hz), 1.84-1.76 (m, 2H), 1.61-1.53 (m, 2H), 1.43-1.24 (m, 2H), 1.24 (d, 2H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 128.3, 127.0, 126.0, 39.8, 37.2, 33.6, 28.6, 22.3, 6.9; IR (neat, cm^{-1}): 2957, 2929; HRMS (DART, m/z) Calcd. for $C_{12}H_{21}IN$ [M+NH$_4$]$^+$: 306.0719, found 306.0716 .

1-(6-Iodohexan-2-yl)-4-methylbenzene(4e). yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11-7.05 (m, 4H), 3.12 (td, 2H, J = 7.2, 2.0 Hz), 2.64 (sext, 1H, J = 6.8 Hz), 2.32 (s, 3H), 1.83-1.80 (m, 2H), 1.60-1.51 (m, 2H), 1.40-1.25 (m, 2H), 1.21 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 135.3, 129.0, 126.8, 39.3, 37.2, 33.7, 28.7, 22.4, 21.0, 6.9; IR (neat, cm^{-1}): 2927; HRMS (DART, m/z) Calcd. for $C_{13}H_{23}IN$ [M+NH$_4$]$^+$: 320.0875, found 320.0873.

1-Fluoro-4-(6-iodohexane-2-yl)benzene (5e). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.10 (m, 2H), 6.99-6.95 (m, 2H), 3.13 (t, 2H, J = 7.4 Hz), 2.66 (sext, 1H, J = 6.8 Hz), 1.83-1.75 (m, 2H), 1.58-1.53 (m, 2H), 1.38-1.25 (m, 2H), 1.22 (d, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2 (d, J = 243.4 Hz), 142.8 (d, J = 2.8 Hz), 128.1 (d, J = 7.6 Hz), 115.2 (d, J = 21.0), 39.1, 37.3, 33.5, 28.5, 22.4, 6.8; IR (neat, cm^{-1}): 2958; HRMS (DART, m/z) Calcd. for $C_{12}H_{20}FIN$ [M+NH$_4$]$^+$: 324.0624, found 324.0612.

(5-Iodopentan-2-yl)benzene (2e). Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (m, 2H), 7.21-7.17 (m, 3H), 3.13 (t, 2H, J = 6.8 Hz), 2.71 (sext, 1H, J = 6.8 Hz), 1.76-1.68 (m, 4H), 1.26 (d, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.8, 128.4, 126.9, 126.1, 39.2, 39.0, 31.6, 22.4, 7.1; IR (neat, cm^{-1}): 2958; HRMS (DART, m/z) Calcd. for $C_{11}H_{19}IN$ [M+NH$_4$]$^+$: 292.0562, found 292.0554.

Tandem deiodination/reductive ring opening reaction from iodoether A to acyclic alcohol D. After a solution of NIS (1.5 mg, 8.4 μmol) and $PhSiH_3$ (32 μl, 0.26 mmol) in CH_2Cl_2 (1.0 ml) was stirred for 30 min, a solution of **2a** (51 mg, 0.17 mmol) in CH_2Cl_2 (0.68 ml) was added at room temperature. The reaction mixture was stirred for 75 min, and then was quenched with H_2O and extracted with Et_2O (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/Et_2O = 5:1) to afford **2d** (27 mg, 92%) as colorless oil.

5-Phenylhexane-1-ol (2d). colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (m, 2H), 7.19-7.16 (m, 3H), 3.59 (t, 2H, J = 6.4 Hz), 2.68 (sext, 1H, J = 7.2 Hz), 1.64-1.50 (m, 4H), 1.24 (s, 3H), 1.37-1.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 128.3, 126.9, 125.8, 62.8, 39.9, 38.1, 32.8, 23.8, 22.3; IR (neat, cm^{-1}): 3333; HRMS (ESI, m/z) Calcd. for $C_{12}H_{18}NaO$: 201.1255 ([M+Na]$^+$), found 201.1263 ([M+Na]$^+$).

5-(4-Fluorophenyl)hexane-1-ol (5 d). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14-7.09 (m, 2H), 6.99-6.93 (m, 2H), 3.57 (t, 2H, J = 6.4 Hz), 2.67 (sext, 1H, J = 6.8 Hz), 1.59-1.46 (m, 4H), 1.34-1.16 (m, 2H), 1.21 (d, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1 (d, J = 243.4 Hz), 143.0 (d, J = 2.8 Hz), 128.1 (d, J = 7.6 Hz), 114.9 (d, J = 21.0), 62.8, 39.2, 38.2, 32.7, 23.7, 22.4; IR (neat, cm^{-1}): 3335; HRMS (DART, m/z) Calcd. for $C_{12}H_{21}FNO$ [M+NH$_4$]$^+$: 214.1608, found 214.1631.

4-Phenylpentan-1-ol (1d). colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (m, 2H), 7.20-7.16 (m, 3H), 3.58 (t, 2H, J = 6.4 Hz), 2.70 (sext, 1H, J = 7.2 Hz), 1.68-1.62 (m, 2H), 1.58-1.37 (m, 2H), 1.26 (d, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 128.3, 127.0, 126.0, 63.0, 39.8, 34.4, 31.0, 22.4; IR (neat, cm^{-1}): 3348; HRMS (ESI, m/z) Calcd. for $C_{11}H_{16}NaO$ [M+Na]$^+$: 187.1099, found 187.1111.

Reductive ring opening/iodination reaction from cyclic ether B to acyclic iodide E. I_2 (136 mg, 0.54 mmol) and $PhSiH_3$ (66 μl, 0.54 mmol) were added to a solution of **2b** (39 mg, 0.22 mmol) in CH_2Cl_2 (0.75 ml) at room temperature. After stirring for 1 h, the reaction mixture was quenched with H_2O and extracted with Et_2O (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/Et_2O = 100:1) to afford **2e** (51 mg, 78%) as colorless oil.

Tandem deiodination/reductive ring opening reaction from cyclic ether B to acyclic alcohol D. After a solution of NIS (46 mg, 0.26 mmol) and $PhSiH_3$ (32 μl, 0.26 mmol) in CH_2Cl_2 (0.5 ml) was stirred for 30 min, a solution of **2b** (38 mg, 0.22 mmol) in CH_2Cl_2 (0.22 ml) was added at room temperature. The reaction mixture was stirred for 75 min, and then was quenched with H_2O and extracted with Et_2O (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/Et_2O = 5:1) to afford **2d** (31 mg, 80%) as colorless oil

Formal hydrogenation from hydroxy alkene C to acyclic alcohols D. After a solution of NIS (51 mg, 0.30 mmol) and $PhSiH_3$ (37 μl, 0.30 mmol) in CH_2Cl_2 (0.5 ml) was stirred for 30 min, a solution of **2c** (44 mg, 0.25 mmol) in CH_2Cl_2 (0.22 ml) was added at room temperature. The reaction mixture was stirred for 1 h, and then was quenched with H_2O and extracted with Et_2O (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/Et_2O = 5:1) to afford **2d** (38 mg, 85%) as colorless oil.

Iodination of 4-phenyl-1-butanol. A solution of I_2 (238 mg, 0.94 mmol) and $PhSiH_3$ (115 μl, 0.94 mmol) was stirred for 1.5 h, and **8** (59 mg, 0.39 mmol) was added to the mixture at room temperature. After stirring for 2 h, the reaction mixture was quenched with sat. $NaHCO_3$ and extracted with Et_2O (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane/Et_2O = 100:1) to afford **9** (92 mg, 90%) as colorless oil.

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