2220 Bull. Chem. Soc. Jpn. Vol. 80, No. 11, 2220–2225 (2007)

Sequential Addition Reactions of Lithium Acetylides and Grignard Reagents to Selenoiminium Salts Leading to 2-Propynyl Tertiary Amines Bearing a Tetrasubstituted Carbon Center

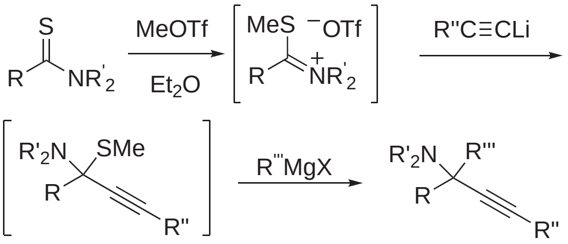
Toshiaki Murai,* Sho Nogawa, and Yuichiro Mutoh

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193

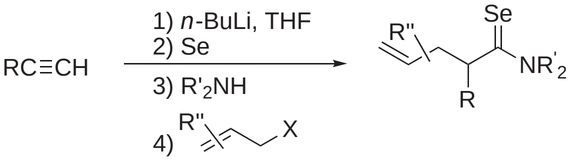
Received June 11, 2007; E-mail: mtoshi@gifu-u.ac.jp

Selenoiminium salts generated in situ from selenoamides and MeOTf were reacted sequentially with lithium acetylides and Grignard reagents to give 2-propynyl tertiary amines bearing a tetrasubstituted carbon center. The lithium acetylides used were generated from (trimethylsilyl)acetylene, phenylacetylene, and 1-hexyne. Among them, that obtained from (trimethylsilyl)acetylene most effectively gave the corresponding products in higher yields. As Grignard reagents, alkyl-, vinyl-, allyl-, and benzylmagnesium halides gave the products with high efficiency, whereas the reaction of arylmagnesium halides did not proceed as well. A variety of 4-penteneselenoamides were synthesized by four-component coupling reactions of terminal acetylenes, elemental selenium, allylic bromides, and secondary amines, and subjected to the sequential addition reactions to give 5-amino-1,6-enynes. The diastereoselectivity of the reaction was found to depend on the substituents at the α-position of selenoamides and Grignard reagents. In the reaction of selenoiminium salts with excess Grignard reagents, amines that incorporated two molecules of Grignard reagents were formed in good yields.

The development of multiple-component coupling reactions leading to valuable compounds is an important issue in modern synthetic chemistry.[1] Recent studies have been focused on new synthetic routes leading to 2-propynylamines. The in situ condensation of aldehydes and amines, followed by the addition reaction of acetylenic nucleophiles gives the corresponding amines.[2] However, these methods are not suitable for the reaction of ketones. Therefore, the resulting 2-propynylamines possess a trisubstituted carbon center adjacent to a nitrogen atom. On the other hand, those with a tetrasubstituted carbon center attached to a nitrogen atom are rarely prepared.[3] Alternatively, we recently developed sequential addition reactions of organolithium and Grignard reagents to thioiminium salts derived from thioamides leading to tertiary 2-propynylamines bearing a tetrasubstituted carbon center (Scheme 1).[4] However, in this reaction, a large excess of Grignard reagents is used, probably because of the low reactivity of in situ-generated *gem*-thioamino compound toward Grignard reagents. Selenium isologues of thioamides, i.e. selenoamides,[5] have been believed to be more reactive than thioamides, but can be handled under air. Therefore, the development of new methods for the synthesis of selenoamides is still an active area.[6] If selenoamides are used instead of thioamides in the reaction in Scheme 1, the reaction is expected to progress to completion under milder reaction conditions. Furthermore, during the course of our studies on thio-,[7] seleno-,[8] and telluroamides,[9] we have devised four-component coupling reactions of terminal acetylenes, elemental selenium, amines, and allylic bromides to give 4-alkenyl selenoamides (Scheme 2).[10] Application of the reactions shown in Scheme 1 to selenoamides in Scheme 2 enables us to provide unprecedented synthetic routes to 5-amino-1,6-enynes. We report here the details of the sequential addition reaction of lithium acetylides and Grignard reagents to selenoiminium salts.



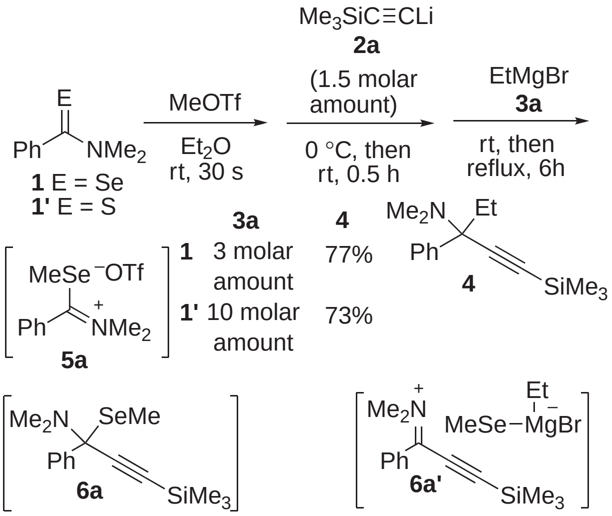
Scheme 1.



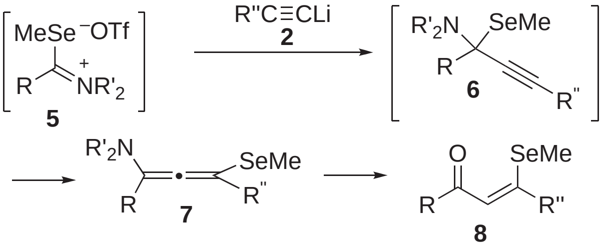
Scheme 2.

Initially, to compare the reactivity of selenoamides with that of thioamides, selenobenzamide **1**[11] was reacted with MeOTf, followed by the addition of lithium (trimethylsilyl)acetylide (1.5 molar amount) (**2a**) and ethylmagnesium bromide (**3a**) (Scheme 3). After aqueous workup, 2-propynylamine **4** was obtained in 77% yield. As expected, the synthesis of **4** was achieved with 3 molar amount. of **3a**, which is in marked contrast to the reaction of the thioiminium salt derived from thiobenzamide **1′**, where 10 molar amount. of **3a** was required. In this reaction, despite the fact that excess organometallic reagents **2a** and **3a** were used, products in which two molecules

Published on the web November 13, 2007; doi:10.1246/bcsj.80.2220



Scheme 3.

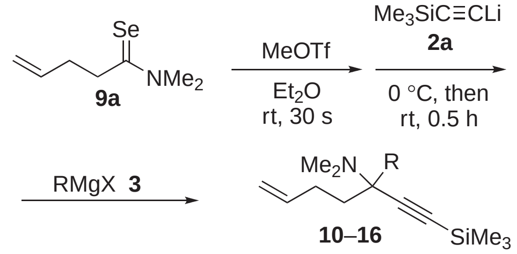


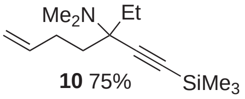
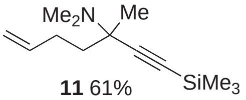
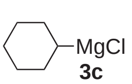
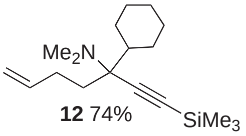
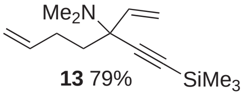
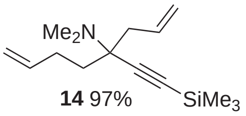
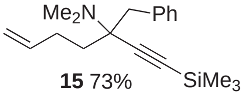
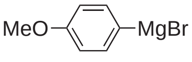
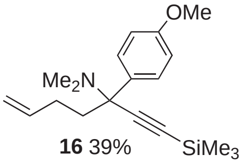
Scheme 4.

of **2a** or **3a** were introduced were not observed. In the initial stage of the reaction, the addition of lithium acetylide **2a** to selenoiminium salt **5a** gives *gem*-selenoamino compound **6a**. The substitution reaction of **6a** with **3a** with the elimination of a MeSe group proceeds smoothly to form **4**. We previously observed that aqueous workup of the reaction mixture of selenoiminium salts **5** and lithium acetylides **2** gave 1-alkenyl ketones **8**,[12] which were probably formed via the 1,3-rearrangement of **6** to **7** followed by the hydrolysis of **7** (Scheme 4), but the corresponding ketones **8** were not detected in the reaction in Scheme 3. This suggested that the substitution reaction of **6a** with **3a** proceeded effectively. In this substitution reaction, it is of interest whether it proceeds by S_N1 or by S_N2 mechanism. No clear results supporting either mechanism are obtained at present. However, on the basis of the Grignard reagents-dependent diastereoselectivity vide infra, iminium salts **6a′** may be formed prior to the addition reaction of Grignard reagents.

Next, selenoamides **9** derived from the four-component coupling reaction in Scheme 2 were subjected to the sequential reactions. The results of the reaction of 4-penteneselenoamide **9a**, lithium (trimethylsilyl)acetylide **2a**, and Grignard reagents **3** are shown in Table 1. The reaction of the selenoiminium salt derived from **9a** and MeOTf with **2a** went to completion within 0.5 h below room temperature. On the other hand, the reaction conditions leading to the desired amines depended on the substituents on the Grignard reagents. The addition of aliphatic Grignard reagents, such as methyl, ethyl, and cyclohexylmagnesium halides **3a**–**3c**, proceeded at room temperature to give the corresponding amines **10**–**12** in good yields (Entries 1–3). The use of vinyl-, allyl-, and benzylmagnesium halides **3d**–**3f** also took place in a similar fashion under the same reaction conditions to lead to **13**–**15** (Entries 4–6). In particular, crude product **14** prepared from **3e** was highly pure and further purification was not necessary (Entry 5). On the other hand, the reaction of aromatic magnesium halides required higher reaction temperatures and longer reaction times. For example, to the reaction mixture of **9a**, MeOTf, and **2a** was added 4-methoxyphenylmagnesium bromide (**3g**), and the mixture was stirred at reflux for 6 h (Entry 7). Nevertheless, the corresponding amine **16** was formed in only 39% yield.

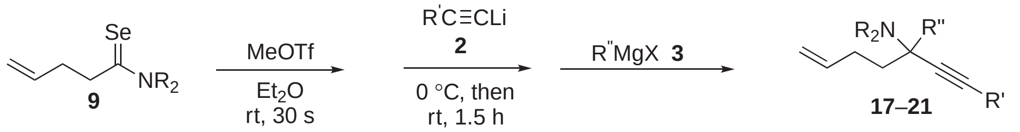
Table 1. Reaction of Selenoamide **9a** with MeOTf, Lithium Acetylide **2a**, and Grignard Reagents **3**[a)]

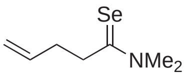
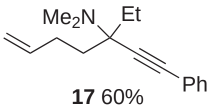
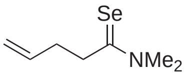
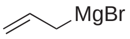
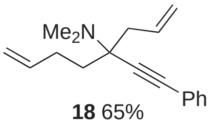
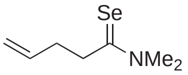
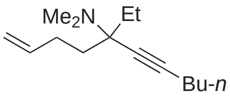
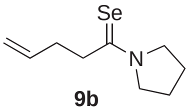
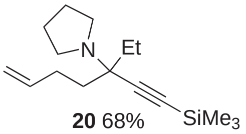
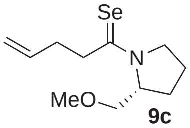
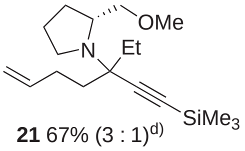


Entry	3 conditions	Product Yield/%[b)]
1[c)]	EtMgBr **3a** rt, 2 h	 **10** 75%
2[c)]	MeMgBr **3b** rt, 2 h	 **11** 61%
3[c)]	 **3c** rt, 2 h	 **12** 74%
4[c)]	$CH_2=CHMgCl$ **3d** rt, 2 h	 **13** 79%
5[c)]	$CH_2=CHCH_2MgBr$ **3e** rt, 2 h	 **14** 97%
6	$PhCH_2MgCl$ **3f** rt, 2 h	 **15** 73%
7	 **3g** reflux, 6 h	 **16** 39%

a) All reactions were carried out with selenoamide **9a** (0.50 mmol), MeOTf (1 molar amount), lithium acetylide **2a** (1.5 molar amount), and Grignard reagents **3** (3 molar amount) in Et_2O (5 mL) unless otherwise noted. b) Isolated yield. c) The reaction was carried out with **9a** (1.0 mmol).

Table 2. Reaction of Selenoamides **9** with MeOTf, Lithium Acetylides **2**, and Grignard Reagents **3**[a)]



Entry	Selenoamide **9**	**2**	**3** Conditions	Product Yield/%[b)]
1[c)]	 **9a**	PhC≡CLi **2b**	EtMgBr **3a** rt, then reflux, 22 h	 **17** 60%
2	 **9a**	PhC≡CLi **2b**	 **3e** rt, then reflux, 2 h	 **18** 65%
3	 **9a**	*n*-BuC≡CLi **2c**	EtMgBr **3a** rt, 17 h	 **19** 47%
4	 **9b**	Me$_3$SiC≡CLi **2a**	EtMgBr **3a** rt, then reflux, 2 h	 **20** 68%
5	 **9c**	Me$_3$SiC≡CLi **2a**	EtMgBr **3a** rt, then reflux, 6 h	 **21** 67% (3 : 1)[d)]

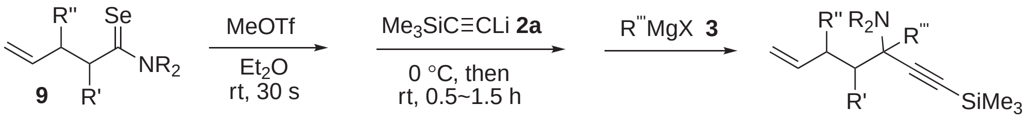
a) All reactions were carried out with selenoamides **9** (0.50 mmol), MeOTf (1 molar amount), lithium acetylides **2** (1.5 molar amount), and Grignard reagents **3** (3 molar amount) in Et$_2$O (5 mL) unless otherwise noted. b) Isolated yield. c) Selenoamide **9a** (0.75 mmol) was used. d) The yield was determined by NMR spectra. The product was given as a mixture of two stereoisomers after column chromatography. A diastereomeric ratio is shown in parenthesis.

Various types of selenoamides **9** and lithium acetylides **2** were also used, and the results are shown in Table 2. The addition reaction of lithium acetylides **2b** and **2c** derived from phenylacetylene and 1-hexyne to the selenoiminium salt derived from **9a** was complete within 1.5 h, but longer reaction times and higher temperatures were necessary for the addition reaction of Grignard reagents **3a** and **3e** (Entries 1–3), unlike the case of **2a** shown in Table 1. Generally, lithium acetylide **2a** derived from (trimethylsilyl)acetylene showed higher efficiency in the reaction. The substituents on the nitrogen atom of starting selenoamides **9** also affected the reaction conditions. For the reaction of **9b** and **9c**, the addition of Grignard reagent **3a** was achieved at reflux (Entries 4 and 5). In the latter case, two diastereomers were obtained in a ratio of 3 to 1.

The stereochemical aspects of the present reaction were elucidated with 2- or 3-substituted 4-penteneselenoamides **9d**–**9h**. The results are shown in Table 3. Due to the high efficiency of the reaction of lithium acetylide **2a** as noted above, **2a** was added to the selenoiminium salts derived from **9d**–**9h**. For 2-phenyl selenoamide **9d**, one of two diastereomers was predominantly formed, and the ratio depended on the Grignard reagents used (Entries 1–3). The replacement of a *N*,*N*-dimethyl group with a pyrrolidinyl group did not improve the stereoselectivity (Entry 4). The 2-methyl selenoamide **9f** showed relatively lower selectivity (Entry 5), whereas in the reaction of 2-cyclohexenyl selenoamide **9g**, the formation of only a single stereoisomer was observed in ^{1}H and ^{13}C NMR spectra (Entry 6). In contrast to these successful results, 2-*t*-butyl selenoamide **9i** did not undergo sequential addition reactions to give the desired amine **29** (Scheme 5). In place of the Grignard reagent **3a**, a hydrogen atom was introduced to the carbon atom attached to the nitrogen atom to give **30** in 29% yield. To determine the origin of the hydrogen atom, a reaction mixture consisting of **9i**, MeOTf, and **2a** was trapped with D$_2$O, but the incorporation of deuterium atom was not observed, and the amine **30** was formed again in 29% yield. This shows that the formation of **30** was independent of the presence of **3a**. Additionally, the deposition of red selenium was not observed, which implied that the MeSe group in in situ-formed *gem*-selenoamino compound **31** was eliminated as a divalent selenium species. Therefore, **31** may undergo 1,3-shift of the hydrogen atom on the methyl group to the carbon atom adjacent to the nitrogen atom to lead to the formation of **30** and decomposed products of selenoformaldehyde,[13] although further studies are necessary to clarify this possibility (Scheme 6).

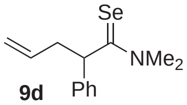
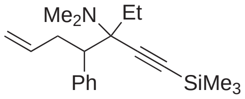
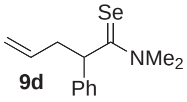
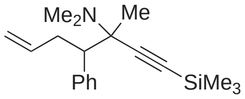
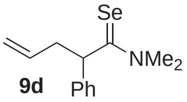
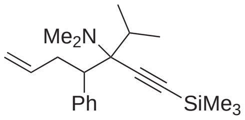
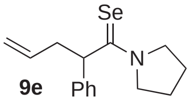
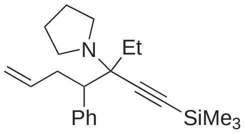
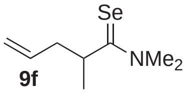
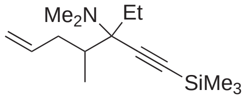
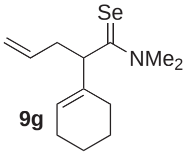
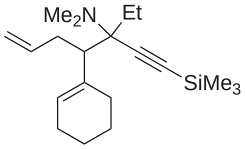
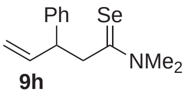
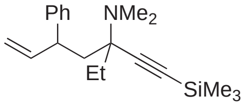
Finally, the reverse sequential addition reaction, i.e. the

Table 3. Reaction of 2- or 3-Substituted 4-Penteneselenamides **9** with MeOTf, Lithium Acetylide **2a**, and Grignard Reagents **3**[a)]



R' = aryl, alkyl; R'' = Hor
R' = H, R'' = aryl

22–28

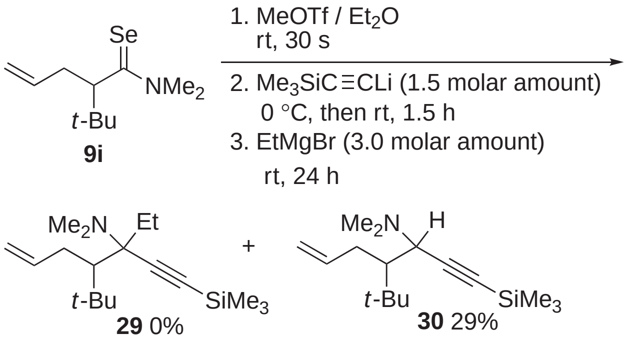
Entry	Selenoamide	Grignard reagent conditions		Products / Yield[b)]
1	 **9d**	EtMgBr **3a** rt, 21 h		**22** 68% (9:1)
2	 **9d**	MeMgBr **3b** reflux, 3 h		**23** 47% (5:1)
3	 **9d**	*i*-PrMgCl **3h** rt, 15 h		**24** 76% (6:1)
4	 **9e**	EtMgBr **3a** rt, 22 h		**25** 71% (7:1)
5	 **9f**	EtMgBr **3a** rt, 21 h		**26** 51% (2:1)
6	 **9g**	EtMgBr **3a** rt, 21 h		**27** 51% (single isomer)
7	 **9h**	EtMgBr **3a** rt, 2 h		**28** 87% (1:1)

a) All reactions were carried out with selenoamides **9** (0.50 mmol), MeOTf (0.50 mmol), lithium acetylides **2** (0.75 mmol), and Grignard reagents **3** (1.5 mmol) in $\mathrm{Et_2O}$ (5 mL) unless otherwise noted. b) The products were obtained as mixture of diastereomers. Although the relative stereochemistry of the products was not determined, their ratio was determined by ^{1}H NMR spectra of crude products, and is shown in parentheses.

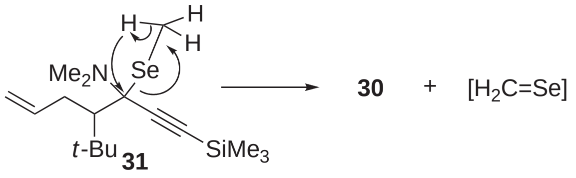
addition of Grignard reagents prior to the addition of lithium acetylides, was carried out. Grignard reagent **3a** (1.5 molar amount) was added to selenoiminium salt **32** generated from **9a** and MeOTf, and the mixture was stirred for 0.5 h. Lithium acetylide **2a** (3 molar amount) was then added to give amine **34** in 58% yield along with amine **10**, where both **3a** and **2a** were incorporated (Scheme 7). In this reaction, two molecules of **3a** were introduced into the product **34** with high efficiency, whereas the introduction of **2a** proceeded with low efficiency. This indicated that *gem*-selenoamino compound **33**, which was formed by the addition of **3a** to **32**, was highly reactive toward Grignard reagents. In fact, the reaction of **32** with 3 molar amount of Grignard reagents effectively gave the products **34**–**36** which incorporated two molecules of Grignard reagents, in good to high yields (Scheme 8).

Conclusion

In summary, we have demonstrated the sequential addition reaction of lithium acetylides and Grignard reagents to selenoiminium salts derived from selenoamides and MeOTf. The reaction proceeded under milder reaction conditions compared to a similar reaction using thioiminium salts to give tertiary



Scheme 5.

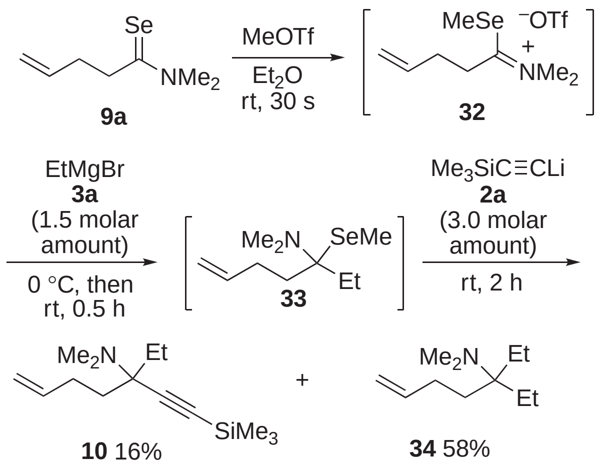


Scheme 6.

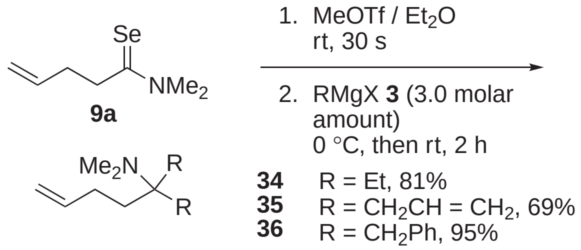
amines bearing a tetrasubstituted carbon center adjacent to a nitrogen atom. Application of the present reaction to 4-penteneselenoamides led to 5-amino-1,6-enynes, which are not readily accessible by other known methods. Substrate-dependent diastereoselectivity was observed, and a bulky substituent, such as a *t*-butyl group, disturbed the desired reaction. The order of the addition of two organometallic reagents is important. When Grignard reagents were added prior to the addition of lithium acetylides, products that incorporated two molecules of Grignard reagents, were predominantly formed.

Experimental

Typical Procedure for Sequential Addition Reactions of Lithium Acetylides and Grignard Reagents to Selenoiminium Salts. To an Et_2O (5.0 mL) solution of selenoamide **9a** (0.19 g, 1.0 mmol) was added MeOTf (0.11 mL, 1.0 mmol) at room temperature, and the mixture was stirred for 30 s. To this was added lithium acetylide **2a**, prepared from (trimethylsilyl)acetylene (0.21 mL, 1.5 mmol) and *n*-butyllithium (1.6 M hexane solution, 0.94 mL, 1.5 mmol) in Et_2O (5.0 mL) at 0 °C, and the resulting mixture was stirred for 0.5 h at room temperature. Ethylmagnesium bromide (**3a**) (1.0 M THF solution, 3.0 mL, 3.0 mmol) was then added, and the mixture was further stirred for 2 h at this temperature. The resulting mixture was poured into a saturated aqueous solution of NH_4Cl, washed with brine, and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:ethyl acetate = 100:1–10:1) to give **10** (0.175 g, 75%) as a brown oil; IR (neat) 3078, 2959, 2865, 2823, 2783, 2156, 1823, 1641, 1456, 1415, 1378, 1333, 1283, 1249, 1163, 1118, 1094, 1040, 1019, 993, 964, 910, 843, 760, 698, 661, 628, 572, 545, 475, 424, 405 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 9H, $SiCH_3$), 0.93 (t, $J = 7.3$ Hz, 3H, CH_3), 1.54–1.64 (m, 2H, CH_2C), 1.64–1.74 (m, 2H, CH_2CH_3), 2.04–2.12 (m, 2H, $CH_2{=}CHCH_2$), 2.25 (s, 6H, NCH_3), 4.95 (dd, $J = 9.5$, 1.5 Hz, 1H, $CH_2{=}CH$), 5.04 (dd, $J = 17.1$, 1.5 Hz, 1H, $CH_2{=}CH$), 5.84 (ddt, $J = 17.1$, 10.3, 6.3 Hz, 1H, $CH_2{=}CH$); ^{13}C NMR ($CDCl_3$) δ 0.3 ($SiCH_3$), 8.4 (CH_3), 27.6, 28.2, 33.6 (CH_2), 39.4 (NCH_3), 65.8 (C), 88.6, 106.7 (C≡C), 114.2 ($CH_2{=}CH$), 138.7 ($CH_2{=}CH$); MS (EI) *m/z* 208 ($M^+ - CH_2CH_3$); HRMS calcd for $C_{13}H_{24}NSi$ ($M^+ - CH_3$) 222.1678, found: 222.1709.



Scheme 7.



Scheme 8.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area (No. 19020020, "Advanced Molecular Transformations of Carbon Resources") from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information

Detailed experimental procedures and spectroscopic data for new compounds; this material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

References

1 For recent reviews of multiple-component coupling reactions: a) H. Nemoto, *J. Synth. Org. Chem. Jpn.* **2004**, *62*, 347. b) Y. Ishii, S. Sakaguchi, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 909. c) S. Kamijo, Y. Yamamoto, *J. Synth. Org. Chem. Jpn.* **2004**, *62*, 682. d) C. Wei, Z. Li, C.-J. Li, *Synlett* **2004**, 1472. e) K. Yamada, Y. Yamamoto, K. Tomioka, *J. Synth. Org. Chem. Jpn.* **2004**, *62*, 1158. f) G. Balme, *Angew. Chem., Int. Ed.* **2004**, *43*, 6238. g) M. Kimura, *J. Synth. Org. Chem. Jpn.* **2006**, *64*, 130. h) G. Guillena, D. J. Ramón, M. Yus, *Tetrahedron: Asymmetry* **2007**, *18*, 693. i) M. Vrettou, A. A. Gray, A. R. E. Brewer, A. G. M. Barrett, *Tetrahedron* **2007**, *63*, 1487.

2 For recent examples: a) C. Wei, C.-J. Li, *J. Am. Chem. Soc.* **2003**, *125*, 9584. b) N. E. Leadbeater, H. M. Torenius, H. Tye, *Mol. Diversity* **2003**, *7*, 135. c) N. Gommermann, C. Koradin, K. Polborn, P. Knochel, *Angew. Chem., Int. Ed.* **2003**, *42*, 5763. d) L. Shi, Y.-Q. Tu, M. Wang, F.-M. Zhang, C.-A. Fan, *Org. Lett.*

2004, *6*, 1001. e) Z. Li, C. Wei, L. Chen, R. S. Varma, C.-J. Li, *Tetrahedron Lett.* **2004**, *45*, 2443. f) J. S. Yadav, B. V. S. Reddy, V. Naveenkumar, R. S. Rao, K. Nagaiah, *New J. Chem.* **2004**, *28*, 335. g) B. M. Choudary, C. Sridhar, M. L. Kantam, B. Sreedhar, *Tetrahedron Lett.* **2004**, *45*, 7319. h) T. F. Knopfel, P. Aschwanden, T. Ichikawa, T. Watanabe, E. M. Carreira, *Angew. Chem., Int. Ed.* **2004**, *43*, 5971. i) S. B. Park, H. Alper, *Chem. Commun.* **2005**, 1315. j) B. M. Trost, M. T. Rudd, *J. Am. Chem. Soc.* **2005**, *127*, 4763. k) Q. Xu, E. Rozners, *Org. Lett.* **2005**, *7*, 2821. l) Y. Yamamoto, H. Hayashi, T. Saigoku, H. Nishiyama, *J. Am. Chem. Soc.* **2005**, *127*, 10804. m) N. Gommermann, P. Knochel, *Chem. Commun.* **2005**, 4175. n) B. Sreedhar, P. S. Reddy, B. V. Prakash, A. Ravindra, *Tetrahedron Lett.* **2005**, *46*, 7019. o) M. L. Kantam, B. V. Prakash, C. R. V. Reddy, B. Sreedhar, *Synlett* **2005**, 2329. p) X. Guinchard, Y. Vallee, J.-N. Denis, *Org. Lett.* **2005**, *7*, 5147. q) N. Gommermann, P. Knochel, *Synlett* **2005**, 2799. r) L. Zani, S. Alesi, P. G. Gozzi, C. Bolm, *J. Org. Chem.* **2006**, *71*, 1558. s) A. Bisai, V. K. Singh, *Org. Lett.* **2006**, *8*, 2405. t) N. Gommermann, P. Knochel, *Chem. Eur. J.* **2006**, *12*, 4380. u) K. Mohan Reddy, N. Seshu Babu, I. Suryanarayana, P. S. Sai Prasad, N. Lingaiah, *Tetrahedron Lett.* **2006**, *47*, 7563. v) N. Gommermann, P. Knochel, *Org. Synth.* **2007**, *84*, 1. w) P. Li, L. Wang, *Tetrahedron* **2007**, *63*, 5455.

3 a) C. W. Kruse, R. F. Kleinschmidt, *J. Am. Chem. Soc.* **1961**, *83*, 216. b) G. F. Hennion, A. C. Perrino, *J. Org. Chem.* **1961**, *26*, 1073. c) N. R. Easton, D. R. Cassidy, R. D. Dillard, *J. Org. Chem.* **1963**, *28*, 448. d) G. F. Hennion, C. V. DiGiovanna, *J. Org. Chem.* **1965**, *30*, 3696. e) H. Frey, G. Kaupp, *Synthesis* **1990**, 931. f) R. Geri, C. Polizzi, L. Lardicci, A. M. Caporusso, *Gazz. Chim. Ital.* **1994**, *124*, 241. g) R. Nussbaumer, I. Leitner, K. Mraz, A. Stuetz, *J. Med. Chem.* **1995**, *38*, 1831. h) I. A. Poplavskaya, T. B. Dembitskaya, *Zh. Org. Khim.* **1995**, *31*, 665. i) D. Semeril, J. Le Norte, C. Bruneau, P. H. Dixneuf, A. F. Kolomiets, S. N. Osipov, *New J. Chem.* **2001**, *25*, 16. j) M. Z. Ovakimyan, S. K. Barsegyan, M. G. Indzhikyan, *Russ. J. Chem.* **2002**, *72*, 1938. k) J. W. Lane, R. L. Halcomb, *Org. Lett.* **2003**, *5*, 4017. l) H. Fukumoto, K. Takahashi, J. Ishihara, S. Hatakeyama, *Angew. Chem., Int. Ed.* **2006**, *45*, 2731. m) A. Arcadi, F. Marinelli, L. Rossi, M. Verdecchia, *Synthesis* **2006**, 2019.

4 a) T. Murai, Y. Mutoh, Y. Ohta, M. Murakami, *J. Am. Chem. Soc.* **2004**, *126*, 5968. b) T. Murai, R. Toshio, Y. Mutoh, *Tetrahedron* **2006**, *62*, 6312.

5 For recent reviews: a) A. J. Moore, in *Comprehensive Organic Functional Group Transformations II*, ed. by A. R. Katritzky, R. J. K. Taylor, Elsevier Ltd., Oxford, **2005**, Vol. 5, p. 519. b) C. Flynn, L. Haughton, in *Comprehensive Organic Functional Group Transformations II*, ed. by A. R. Katritzky, R. J. K. Taylor, Elsevier Ltd., Oxford, **2005**, Vol. 5, p. 571. c) T. Murai, in *Topics in Current Chemistry*, ed. by S. Kato, Springer GmbH, Heidelberg, **2005**, p. 247. d) M. Koketsu, H. Ishihara, *Curr. Org. Synth.* **2007**, *4*, 15. e) M. Koketsu, H. Ishihara, in *Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium, Tellurium*, ed. by F. A. Devillanova, Royal Society of Chemistry, Cambridge, **2007**, pp. 145–194.

6 a) J. Bethke, K. Karaghiosoff, L. A. Wessjohan, *Tetrahedron Lett.* **2003**, *44*, 6911. b) V. Saravanan, C. Mukherjee, S. Das, S. Chandrasekaran, *Tetrahedron Lett.* **2004**, *45*, 681. c) G. Hua, Y. Li, A. M. Z. Alexandra, J. D. Woollins, *Org. Lett.* **2006**, *8*, 5251.

7 a) T. Murai, H. Aso, Y. Tatematsu, Y. Itoh, H. Niwa, S. Kato, *J. Org. Chem.* **2003**, *68*, 8514. b) T. Murai, H. Niwa, T. Kimura, F. Shibahara, *Chem. Lett.* **2004**, *33*, 508. c) T. Murai, Y. Ohta, Y. Mutoh, *Tetrahedron Lett.* **2005**, *46*, 3637. d) T. Murai, H. Sano, H. Kawai, H. Aso, F. Shibahara, *J. Org. Chem.* **2005**, *70*, 8148. e) T. Murai, Y. Mutoh, K. Fukushima, *Lett. Org. Chem.* **2006**, *3*, 409. f) F. Shibahara, A. Kitagawa, E. Yamaguchi, T. Murai, *Org. Lett.* **2006**, *8*, 5621. g) T. Murai, F. Asai, *J. Am. Chem. Soc.* **2007**, *129*, 780. h) F. Shibahara, A. Suenami, A. Yoshida, T. Murai, *Chem. Commun.* **2007**, 2354.

8 a) T. Murai, H. Aso, S. Kato, *Org. Lett.* **2002**, *4*, 1407. b) T. Murai, M. Ishizuka, A. Suzuki, S. Kato, *Tetrahedron Lett.* **2003**, *44*, 1343. c) Y. Mutoh, T. Murai, *Org. Lett.* **2003**, *5*, 1361. d) T. Murai, A. Fujishima, C. Iwamoto, S. Kato, *J. Org. Chem.* **2003**, *68*, 8514. e) Y. Mutoh, T. Murai, *Organometallics* **2004**, *23*, 3907.

9 a) Y. Mutoh, T. Murai, S. Yamago, *J. Am. Chem. Soc.* **2004**, *126*, 16696. b) Y. Mutoh, T. Murai, S. Yamago, *J. Organomet. Chem.* **2007**, *692*, 129.

10 T. Murai, T. Ezaka, S. Kato, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1193.

11 M. Koketsu, Y. Okayama, H. Aoki, H. Ishihara, *Heteroat. Chem.* **2002**, *13*, 195.

12 T. Murai, Y. Mutoh, S. Kato, *Org. Lett.* **2001**, *3*, 1993.

13 Selenoformaldehyde has been reported to be an unstable species, but can be trapped with dienes: a) H. Bock, S. Aygen, P. Rosmus, B. Solouki, E. Weissflog, *Chem. Ber.* **1984**, *117*, 187. b) R. H. Judge, D. C. Moule, *J. Am. Chem. Soc.* **1984**, *106*, 5406. c) R. D. Brown, P. D. Godfrey, D. McNaughton, *Chem. Phys. Lett.* **1985**, *118*, 29. d) G. A. Krafft, P. T. Meinke, *J. Am. Chem. Soc.* **1986**, *108*, 1314. e) F. S. Guziec, Jr., L. J. Guziec, in *Comprehensive Organic Functional Group Transformation*, ed. by A. R. Katritzky, O. Meth-Cohn, C. W. Rees, Pergamon, Oxford, **1995**, Vol. 3, pp. 381–401.