JOC Article

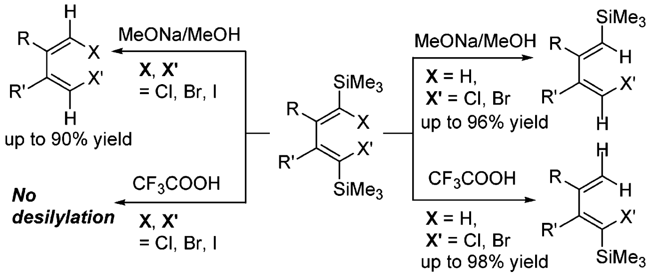
Preparation of Partially Substituted 1-Halo- and 1,4-Dihalo-1,3-dienes via Reagent-Controlled Desilylation of Halogenated 1,3-Dienes

Zhenfeng Xi,*,† Zhiyi Song,† Guangzhen Liu,† Xiaozhong Liu,† and Tamotsu Takahashi*,‡

Bejing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China, and Catalysis Research Center, Graduate School of Pharmaceutical Sciences, Hokkaido University, and SORST, Japan Science and Technology Agency (JST), Kita-Ku, Sapporo 001-0021, Japan

zfxi@pku.edu.cn

Received January 1, 2006



Depending on the desilylation reagents used, 1-halo-1,4-bis(trimethylsilyl)-1,3-butadienes afforded either 1-halo-1-trimethylsilyl-1,3-butadienes or 1-halo-4-trimethylsilyl-1,3-butadienes in excellent yields with excellent selectivity, respectively, when treated with CF_3COOH or with NaOMe. These monosilylated 1,3-butadiene products could be further desilylated to generate their corresponding halobutadienes via the above reagent-controlled desilylation reaction. When 1,4-dihalo-1,4-bis(trimethylsilyl)-1,3-dienes were treated with MeONa/MeOH at room temperature, desilylation of both of the two trimethylsilyl groups took place to afford their corresponding 1,4-dihalo-1,3-dienes in excellent yields. The commonly used desilylation reagent CF_3COOH did not work for these dihalobutadienes.

Introduction

1-Halo-1,3-dienes and 1,4-dihalo-1,3-dienes are a class of useful compounds.[1−4,5f] There are several papers reporting preparative methods for 1-halo-1,3-dienes and 1,4-dihalo-1,3-dienes.[5,6] These methods usually afford all-substituted halo-

---

† Peking University.

‡ Hokkaido University.

(1) (a) Foubelo, F.; Yus, M. *Curr. Org. Chem.* **2005**, *9*, 459−490. (b) Xi, Z. *Eur. J. Org. Chem.* **2004**, 2773−2781. (c) Langer, P.; Freiberg, W. *Chem. Rev.* **2004**, *104*, 4125−4149. (d) Varela, J. A.; Saa, C. *Chem. Rev.* **2003**, *103*, 3787−3801. (e) Hissler, M.; Dyer, P. W.; Reau, R. *Coord. Chem. Rev.* **2003**, *244*, 1−44.

(2) (a) Xi, Z.; Song, Q. *J. Org. Chem.* **2000**, *65*, 9157−9159. (b) Xi, Z.; Song, Q.; Chen, J.; Guan, H.; Li, P. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1913−1916. (c) Song, Q.; Chen, J.; Jin, X.; Xi, Z. *J. Am. Chem. Soc.* **2001**, *123*, 10419−10420. (d) Chen, J.; Song, Q.; Xi, Z. *Tetrahedron Lett.* **2002**, *43*, 3533−3535. (e) Song, Q.; Li, Z.; Chen, J.; Wang, C.; Xi, Z. *Org. Lett.* **2002**, *4*, 4627−4629. (f) Chen, J.; Song, Q.; Li, P.; Guan, H.; Jin, X.; Xi, Z. *Org. Lett.* **2002**, *4*, 2269−2271. (g) Li, G.; Fang, H.; Xi, Z. *Tetrahedron Lett.* **2003**, *44*, 8705−8708. (h) Wang, C.; Song, Q.; Xi, Z. *Tetrahedron* **2004**, *60*, 5207−5214. (i) Mao, G.; Lu, J.; Xi, Z. *Tetrahedron Lett.* **2004**, *45*, 8095−8098. (j) Chen, C.; Xi, C.; Jiang, Y.; Hong, X. *J. Am. Chem. Soc.* **2005**, *127*, 8024−8025. (k) Chen, C.; Xi, C.; Lai, C.; Wang, R.; Hong, X. *Eur. J. Org. Chem.* **2004**, 647−650.

(3) (a) Chen, J.; Song, Q.; Wang, C.; Xi, Z. *J. Am. Chem. Soc.* **2002**, *124*, 6238−6239. (b) Fang, H.; Song, Q.; Wang, Z.; Xi, Z. *Tetrahedron Lett.* **2004**, *45*, 5159−5162. (c) Shirley, D. A.; Cameron, M. D. *J. Am. Chem. Soc.* **1952**, *74*, 664−665. (d) Fitt, J. J.; Gschwend, H. W. *J. Org. Chem.* **1979**, *44*, 303−305.

(4) (a) Uemura, M.; Takayama, Y.; Sato, F. *Org. Lett.* **2004**, *6*, 5001−5004. (b) Nakajima, R.; Delas, C.; Takayama, Y.; Sato, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 3023−3025. (c) Yamaguchi, S.; Jin, R.-Z.; Tamao, K.; Sato, F. *J. Org. Chem.* **1998**, *63*, 10060−10062. (d) Fukuhara, K.; Takayama, Y.; Sato, F. *J. Am. Chem. Soc.* **2003**, *125*, 6884−6885. (e) Takayama, Y.; Delas, C.; Muraoka, K.; Sato, F. *Org. Lett.* **2003**, *5*, 365−368. (f) Li, J.-H.; Liang, Y.; Xie, Y.-X. *J. Org. Chem.* **2004**, *69*, 8125−8127. (g) Yamamoto, Y.; Ohno, T.; Itoh, K. *Chem.−Eur. J.* **2002**, *8*, 4734−4741. (h) Trostyanskaya, I. G.; Titskiy, D. Y.; Anufrieva, E. A.; Borisenko, A. A.; Kazankova, M. A.; Beletskaya, I. P. *Russ. Chem. Bull.* **2001**, *50*, 2095−2100. (i) Block, E. *Phosphorus, Sulfur Silicon* **2001**, *171*, 255−277. (j) Block, E.; Birringer, M.; DeOrazio, R.; Fabian, J.; Glass, R. S.; Guo, C.; He, C.; Lorance, E.; Qian, Q.; Schroeder, T. B.; Shan, Z.; Thiruvazhi, M.; Wilson, G. S.; Zhang, X. *J. Am. Chem. Soc.* **2000**, *122*, 5052−5064. (k) Yamaguchi, S.; Jin, R.-Z.; Itami, Y.; Goto, T.; Tamao, K. *J. Am. Chem. Soc.* **1999**, *121*, 10420−10421.

10.1021/jo060003f CCC: $33.50

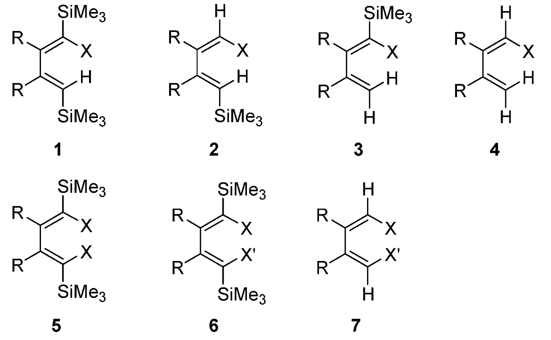
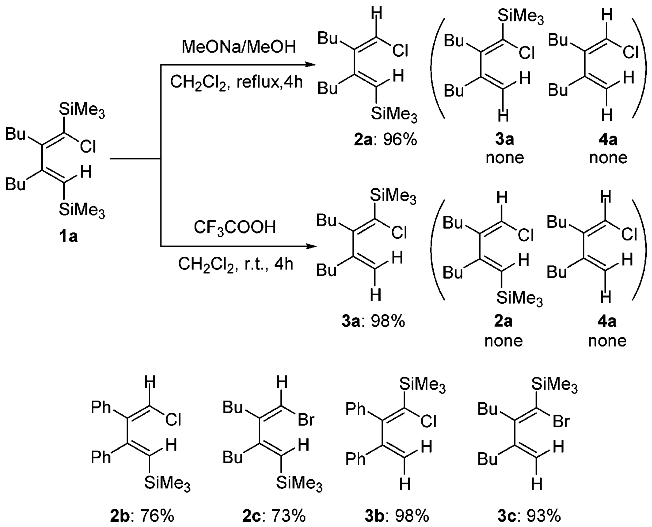


FIGURE 1. Variety of halodienes (X, X′ = Cl, Br, I).

dienes, e.g., 1,2,3,4-tetrasubstituted 1-halo- and 1,4-dihalo-1,3-dienes.[1−6] Synthetic methods for partially substituted halodienes (Figure 1, structures **2**, **3**, **4**, and **7**) are in demand because diversity of halodienes as synthetic intermediates is required for organic synthesis, and the substitution pattern including the number of substituents on the skeleton of 1,3-dienes may have remarkable influence on the reactivity of the 1,3-diene-based reagents, such as lithio-1,3-dienes.[7] Hydrolysis−desilylation of vinylsilanes using CF_3COOH or NaOMe has been well-documented for the preparation of alkenes and vinyl halides.[8] Recently, we have reported an alternative method leading to 1,4-dihalo-2,3-disubstituted-1,3-dienes via desilylation of 1,4-dihalo-1,4-bis(trimethylsilyl)-1,3-dienes using CF_3COOH or NaOMe as desilylation reagents.[9] 1,4-Dihalo-1,4-bis(trimethylsilyl)-1,3-dienes and 1-halo-1,4-bis(trimethylsilyl)-1,3-dienes were readily prepared in good to excellent yields by the zirconocene-mediated coupling of silylated alkynes followed by a halogenation process.[5,6,9,10] In this paper, we would like to report the synthesis of partially substituted halodienes (Figure 1, structures **2**, **3**, **4**, and **7**), including (1) a reagent-controlled regioselective desilylation of 1-halo-1,4-bis(trimethylsilyl)-2,3-disubstituted-1,3-dienes (Figure 1, structure **1**) to prepare 1-halo-4-trimethylsilyl-2,3-disubstituted-1,3-dienes (Figure 1, structure **2**), 1-halo-1-trimethylsilyl-2,3-disubstituted-1,3-dienes (Figure 1, structure **3**), and (*Z*)-1-halo-2,3-disubstituted-1,3-dienes (Figure 1, structure **4**) and (2) the scope of desilylation of 1,4-dihalo-1,4-bis(trimethylsilyl)-2,3-disubstituted-1,3-dienes (Figure 1, structures **5**, **6**) using CF_3COOH or NaOMe as desilylation reagents to afford 1,4-dihalo-2,3-disubstituted-1,3-dienes (Figure 1, structure **7**).

SCHEME 1. Reagent-Controlled Selective Desilylation of 1-Halo-1,4-bis(trimethylsilyl)-1,3-dienes



Results and Discussion

Reagent-Controlled Regioselective Desilylation of 1-Halo-1,4-bis(trimethylsilyl)-2,3-disubstituted-1,3-dienes 1: Preparation of 1-Halo-4-trimethylsilyl-2,3-disubstituted-1,3-dienes 2, 1-Halo-1-trimethylsilyl-2,3-disubstituted-1,3-dienes 3, and (*Z*)-1-Halo-2,3-disubstituted-1,3-dienes 4. As popular protonation−desilylation reagents, CF_3COOH and NaOMe/MeOH have been often used for desilylation of vinylsilanes.[8,9] However, interestingly, we found that, for our 1-halo-1,4-bis(trimethylsilyl)-2,3-disubstituted-1,3-diene systems, these commonly used desilylation reagents, CF_3COOH and NaOMe/MeOH, behaved very differently, resulting in a synthetically useful reagent-controlled desilylation reaction. As demonstrated in Scheme 1, 1-chloro-2,3-dibutyl-1,4-bis(trimethylsilyl)-1,3-diene **1a** afforded 1-chloro-2,3-dibutyl-4-trimethylsilyl-1,3-diene **2a** in 96% isolated yield when treated with NaOMe/MeOH in CH_2Cl_2 at reflux for 4 h. Only the trimethylsilyl group attached to the same carbon as chlorine was desilylated. The other trimethylsilyl group was totally untouched, thus no formation of **3a** and completely desilylated product **4a** were observed. To the contrary, when **1a** was treated with CF_3COOH, the trimethylsilyl group attached to the same carbon as chlorine was totally untouched, resulting in **3a** as the only product in 98% isolated yield via highly selective desilylation of the trimethylsilyl group attached to the =CH moiety. Neither **2a** nor **4a** was formed in this reaction. Products **2b**,**c** and **3b**,**c** could also be prepared in excellent yields.

Following the above reagent-controlled desilylation procedure, the monosilylated halodienes **2** and **3** could be further desilylated to generate (*Z*)-1-halo-2,3-disubstituted-1,3-dienes

---

(5) Preparative methods for 1,4-dihalo-1,3-diene derivatives: (a) Negishi, E.; Swanson, D. R.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829−2832. (b) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. K.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336−3346. (c) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870−2874. (d) Hill, J. E.; Balaich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911−2924. (e) Yamaguchi, S.; Jin, R.; Tamao, K.; Sato, F. *J. Org. Chem.* **1998**, *63*, 10060−10062. (f) Xi, C.; Huo, S.; Afifi, T. H.; Hara, R.; Takahashi, T. *Tetrahedron Lett.* **1997**, *38*, 4099−4102. (g) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879−933. (h) Snieckus, V. *Bull. Soc. Chim. Fr.* **1988**, 67−78. (i) Beak, P.; Zajdel, W. J.; Reitz, D. B. *Chem. Rev.* **1984**, *84*, 471−523. (j) Narasimhan, N. S.; Mali, R. S. *Synthesis* **1983**, 957−968. (k) Snieckus, V.; Beak, P. *Acc. Chem. Res.* **1982**, *15*, 305−312.

(6) Preparative methods for 1-halo-1,3-diene derivatives: (a) Takahashi, T.; Kondakov, D. Y.; Xi, Z.; Suzuki, N. *J. Am. Chem. Soc.* **1995**, *117*, 5871−5872. (b) Takahashi, T.; Sun, W.; Xi, C.; Ubayama, H.; Xi, Z. *Tetrahedron* **1998**, *54*, 715−726. (c) Ubayama, H.; Sun, W.; Xi, Z.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1998**, 1931−1932.

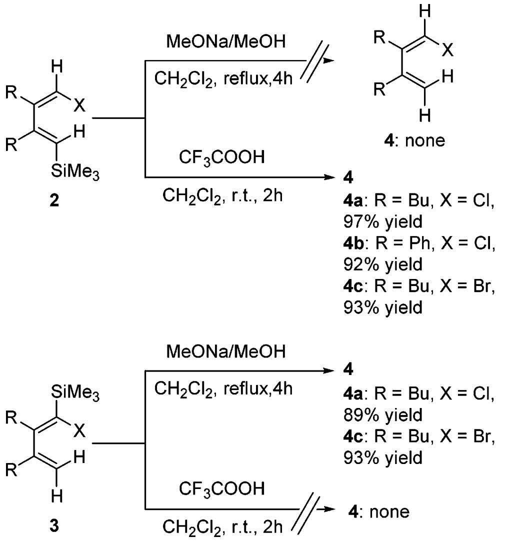
(7) (a) Wang, C.; Lu, J.; Mao, G.; Xi, Z. *J. Org. Chem.* **2005**, *70*, 5150−5156. (b) Dabdoub, M. J.; Dabdoub, V. B.; Guerrero, P. G., Jr.; Silveira, C. C. *Tetrahedron* **1997**, *53*, 4199−4218.

(8) (a) Fleming, I.; Dunogues, J.; Smithers, R. *Org. React.* **1989**, *37*, 57−575. (b) Asaoka, M.; Shima, K.; Takei, H. *J. Chem. Soc., Chem. Commun.* **1988**, 430−431. (c) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371−1448. (d) Hudrlik, P. F.; Kassim, A. M.; Agwaramgbo, E. L. O.; Doonquah, K. A.; Roberts, R. R.; Hudrlik, A. M. *Organometallics* **1993**, *12*, 2367−2369. (e) Ahmar, M.; Duyck, C.; Fleming, I. *Pure Appl. Chem.* **1994**, *66*, 2049−2052.

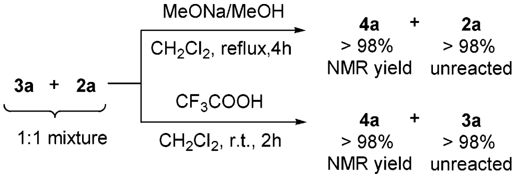
(9) Xi, Z.; Liu, X.; Lu, J.; Bao, F.; Fan, H.; Li, Z.; Takahashi, T. *J. Org. Chem.* **2004**, *69*, 8547−8549.

(10) (a) Ref 5a. (b) Takahashi, T.; Kageyama, M.; Denisov, V.; Hara, R.; Negishi, E. *Tetrahedron Lett.* **1993**, *34*, 687−690. (c) Xi, Z.; Hara, R.; Takahashi, T. *J. Org. Chem.* **1995**, *60*, 4444−4448. (d) Hara, R.; Xi, Z.; Kotora, M.; Xi, C.; Takahashi, T. *Chem. Lett.* **1996**, 1003−1004. (e) Takahashi, T.; Xi, C.; Xi, Z.; Kageyama, M.; Fischer, R.; Nakajima, K.; Negishi, E. *J. Org. Chem.* **1998**, *63*, 6802−6806.

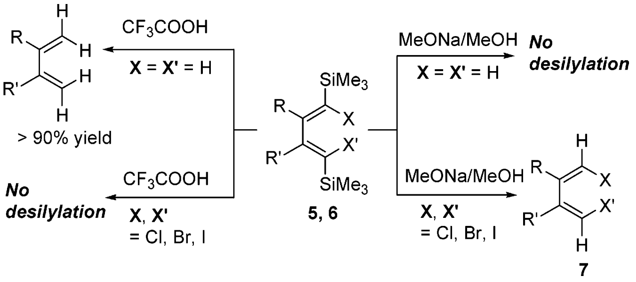
SCHEME 2. Reagent-Controlled Selective Desilylation of 1-Halo-1-(trimethylsilyl)-1,3-dienes and 1-Halo-4-(trimethylsilyl)-1,3-dienes



SCHEME 3. Reagent-Controlled Selective Desilylation of a Mixture of 1-Halo-1-(trimethylsilyl)-1,3-dienes and 1-Halo-4-(trimethylsilyl)-1,3-dienes



SCHEME 4. Desilylation of 1,4-Dihalo-1,4-bis(trimethylsilyl)-1,3-dienes (X, X′ = Cl, Br, I)



4 in high yields with excellent selectivity. As demonstrated in Scheme 2, CF$_3$COOH worked only on **2** whereas NaOMe/MeOH worked only on **3**.

To further demonstrate the usefulness of the above reagent-controlled desilylation reaction, a 1:1 molar ratio mixture of **2a** and **3a** was treated with CF$_3$COOH and NaOMe/MeOH, respectively. As expected, when treated with NaOMe/MeOH, **3a** was completely converted to **4a** leaving **2a** totally untouched (Scheme 3).

The reaction mechanisms of the hydrolysis−desilylation of vinylsilanes have been studied.[11] Retention of configurations has been generally obtained.[11] In the case of CF$_3$COOH-promoted protonation−desilylation, an electrophilic substitution reaction is involved. The presence of the chlorine attached to the same carbon with the trimethylsilyl group depresses the attack of the carbon by an electrophilic group. In the case of NaOMe/MeOH-promoted protonation−desilylation, a nucleophilic substitution reaction is involved, which explains why the trimethylsilyl group attached to the same carbon as chlorine is readily desilylated. Generally, because of the presence of the conjugation system and the electron-withdrawing halogen, desilylation of 1-halo-1,4-bis(trimethylsilyl)-2,3-disubstituted-1,3-dienes becomes more difficult compared with that of vinylsilanes and alkylsilanes.

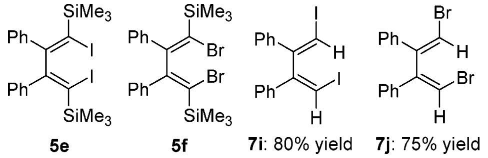


FIGURE 2. Formation of dihalodienes with (*Z,E*) stereochemistry.

Desilylation of 1,4-Dihalo-1,4-bis(trimethylsilyl)-2,3-disubstituted-1,3-dienes 5 and 1,4-Mixed Dihalo-1,4-bis(trimethylsilyl)-2,3-disubstituted-1,3-dienes 6: Preparation of 2,3-Disubstituted 1,4-Dihalo-1,3-dienes 7. The above reagent-controlled desilylation reaction could also be applied to 1,4-dihalo-1,4-bis(trimethylsilyl)-2,3-disubstituted-1,3-dienes **5** (Scheme 4, X = X′) and 1,4-mixed dihalo-1,4-bis(trimethylsilyl)-2,3-disubstituted-1,3-dienes **6** (Scheme 4, X ≠ X′). When X = X′ = H, desilylation of the two trimethylsilyl groups using CF$_3$COOH proceeded smoothly to afford their corresponding 2,3-disubstituted 1,3-butadienes in excellent yields, but NaOMe/MeOH did not work at all for these compounds without halide substituents. On the contrary, when both X and X′ are halides, either identical (structure **5**) or different (structure **6**), NaOMe/MeOH could work as the desilylation reagent to generate (*Z,Z*)-1,4-dihalo-1,3-dienes or (*Z,Z*)-1,4-mixed dihalo-1,3-dienes in high yields. However, CF$_3$COOH did not work at all for these compounds with halide substituents. This reagent-controlled desilylation can also be explained by the presence of the conjugation system and the electron-withdrawing halides, as mentioned above. Results are given in Table 1. The stereochemistry of **7a**,**b** and **7e**,**f** was determined by nuclear Overhauser effects (NOEs).[12] The structure of **7d** has been determined by single-crystal X-ray structural analysis (see Supporting Information).

Interestingly, when 2,3-diphenyl-1,3-dienes **5e** and **5f** (Figure 2) were treated with NaOMe/MeOH, desilylation took place to afford (*Z,E*)-1,4-diiodo-2,3-diphenyl-1,3-diene **7i** and (*Z,E*)-1,4-dibromo-2,3-diphenyl-1,3-diene **7j** as the sole products in 80% and 75% isolated yields, respectively. The structure of **7i** has been determined by single-crystal X-ray structural analysis (see Supporting Information).

Conclusion

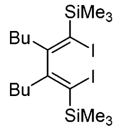
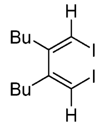
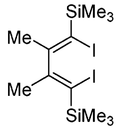
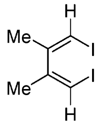
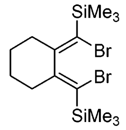
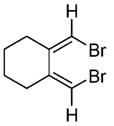
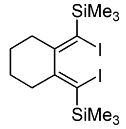
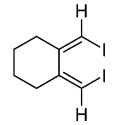
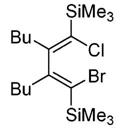
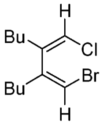
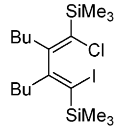
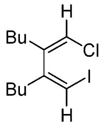
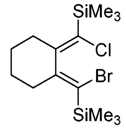
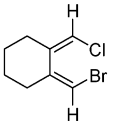
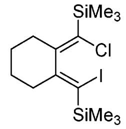
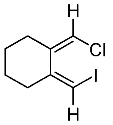
We have developed a reagent-controlled desilylation of 2,3-disubstituted 1-halo-1,4-bis(trimethylsilyl)- and 1,4-dihalo-1,4-bis(trimethylsilyl)-1,3-dienes using either CF$_3$COOH or NaOMe as the desilylation reagent. These starting halo 1,3-dienes could be readily prepared in good to excellent yields by the zir-

---

[11] Reaction mechanisms of the hydrolysis−desilylation of vinylsilanes have been studied. Retention of configurations has been generally obtained. See: (a) Hudrlik, P. F.; Schwartz, R. H.; Hogan, J. C. *J. Org. Chem.* **1979**, *44*, 155−157. (b) Utimoto, K.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* **1975**, *33*, 2825−2828. (c) Koenig, K. E.; Weber, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 3416−3418.

[12] Ashe, A. J., III; Al-Ahmad, S.; Piloted, S.; Puranik, D. B. *Organometallics* **1995**, *14*, 2689−2698.

TABLE 1. Formation of Dihalodienes from MeONa/MeOH-Mediated Desilylation of 1,4-Dihalo-1,4-bis(trimethylsilyl)-1,3-dienes

entry	1,4-dihalo-1,4-bis(trimethylsilyl)-1,3-diene **5**, **6**		Product **7**		Yield (%)[a]
1		**5a**		**7a**	81
2		**5b**		**7b**	84
3		**5c**		**7c**	86
4		**5d**		**7d**	85
5		**6a**		**7e**	75
6		**6b**		**7f**	90
7		**6c**		**7g**	86
8		**6d**		**7h**	79

[a] Isolated yields.

conocene-mediated coupling of silylated alkynes followed by the halogenation process. Partially substituted halo 1,3-dienes such as products **2**, **3**, **4**, and **7**, which are useful but otherwise difficult to obtain, were prepared in excellent yields with excellent selectivity.

Experimental Section

Typical Procedure for Selective Desilylation of 1,4-Disilylated 1-Monohalo-2,3-disubstituted-1,3-butadienes to Prepare (*Z*,*E*)-1-Monohalo-4-trimethylsilyl-2,3-disubstituted-1,3-butadienes 2. A solution of 1,4-disilylated 1-monohalo-2,3-disubstituted-1,3-butadienes (1.0 mmol in 4.0 mL of CH_2Cl_2) and freshly prepared CH_3ONa in CH_3OH (7.5 mL, 2.0 M) was refluxed for 4 h. After being cooled to room temperature, the reaction mixture was added to 10.0 mL of saturated $NaHCO_3$ and was extracted with ether (3 × 10.0 mL). The combined organic layer was washed with water, NH_4Cl, and saturated NaCl and dried over $MgSO_4$. The solvent was evaporated in vacuo to give crude products. Chromatography using petroleum ether or a mixture of petroleum and methylene chloride as the eluent provided the corresponding pure product **2**.

((1*E*,3*Z*)-2-Butyl-3-(chloromethylene)hept-1-enyl)trimethylsilane 2a: colorless liquid, isolated yield 96% (261 mg); ^{1}H NMR ($CDCl_3$) δ 0.72−0.77 (m, 6H), 1.14−1.95 (m, 8H), 1.93−1.21 (m, 4H), 5.19 (s, 1H), 5.65 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.6, 13.8, 21.8, 22.7, 29.5, 30.5, 34.0, 34.5, 110.6, 129.6, 146.8, 153.8; IR (film) ν_{max}/cm^{-1} 2955, 2923, 2852, 1463, 1248, 859, 837; UV/vis λ_{max}/nm 243.6; HRMS calcd for $C_{15}H_{29}ClSi$ 272.1727, found 272.1720.

Typical Procedure for Selective Desilylation of 1,4-Disilylated 1-Monohalo-2,3-disubstituted-1,3-butadienes to Prepare (*Z*,*E*)-1-Monohalo-1-trimethylsilyl-2,3-disubstituted-1,3-butadienes 3. To a solution of 1,4-disilylated 1-monohalo-2,3-disubstituted-1,3-butadienes (1.0 mmol in 4.0 mL of CH_2Cl_2) was added dropwise 1.0 mmol TFA at room temperature, and the mixture was stirred for 1 h at the same temperature. The resulting mixture was neutralized with 10.0 mL of saturated $NaHCO_3$ and was extracted with ether (3 × 10.0 mL). The combined organic layer was washed with water and brine. After drying over $MgSO_4$ and evaporation of the solvent, column chromatography on silica gel with petroleum afforded the desired product **3**.

(*Z*)-(2-Butyl-1-chloro-3-methylenehept-1-enyl)trimethylsilane 3a: colorless liquid, isolated yield 98% (267 mg); ^{1}H NMR ($CDCl_3$) δ 0.60−0.67 (m, 6H), 1.02−1.17 (m, 8H), 1.83−1.96 (m, 4H), 4.45 (d, J = 1.2 Hz, 1H), 4.75 (d, J = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.5, 13.58, 13.60, 22.2, 29.0, 30.5, 33.9, 34.2, 111.5, 128.6, 148.5, 154.4; IR (film) ν_{max}/cm^{-1} 2957, 2928, 2872, 1466, 1250, 889, 840; UV/vis λ_{max}/nm 244.0; HRMS calcd for $C_{15}H_{29}ClSi$ 272.1727, found 272.1720. Anal. Calcd for $C_{15}H_{29}ClSi$: C, 72.93%; H, 6.76%. Found: C, 72.90%; H, 6.78%.

Typical Procedure for Preparation of 4 by Further Desilylation of 2. Further desilylation of **2** to **4** by TFA was carried out under conditions similar to those described for **3**.

Typical Procedure for Preparation of 4 by Further Desilylation of 3. Further desilylation of **3** to **4** by TFA was carried out under conditions similar to those described for **2**.

(*Z*)-5-(Chloromethylene)-6-methylenedecane 4a: colorless liquid, isolated yield 97% (195 mg); ^{1}H NMR ($CDCl_3$) δ 0.87−0.93 (m, 6H), 1.26−1.42 (m, 8H), 2.10−2.17 (m, 4H), 4.61 (d, J = 1.2 Hz, 1H), 4.83 (d, J = 1.2 Hz, 1H), 5.85 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.6, 13.6, 22.2, 29.0, 30.5, 33.9, 34.2, 111.4, 128.6, 148.6, 154.4; IR (film) ν_{max}/cm^{-1} 2958, 2931, 2872, 1466, 1250, 902, 843; UV/vis λ_{max}/nm 2442.2; HRMS calcd for $C_{12}H_{21}Cl$ 200.1332, found 200.1330.

Typical Procedure for Preparation of (*Z*,*Z*)-1,4-Dihalo-2,3-disubstituted-1,3-butene Derivatives 7. A solution of silylated 1,4-dihalo-2,3-disubstituted-1,3-butadienes (1.0 mmol in 4.0 mL of CH_2Cl_2) and freshly prepared CH_3ONa in CH_3OH (15.0 mL, 2.0 M) was stirred overnight at room temperature. The reaction mixture was added to 10.0 mL of saturated $NaHCO_3$ and extracted with ether (3 × 10.0 mL). The combined organic layer was washed with water, NH_4Cl, and saturated NaCl and dried over $MgSO_4$. The solvent was evaporated in vacuo to give crude products. Chromatography using petroleum ether or a mixture of petroleum and methylene chloride as the eluent provided the corresponding pure product **7**.

(5*Z*,6*Z*)-5,6-Bis(iodomethylene)decane 7a: colorless liquid, isolated yield 81% (339 mg); ^{1}H NMR ($CDCl_3$) δ 0.92 (t, J = 7.2 Hz, 6H), 1.32−1.53 (m, 8H), 2.23 (t, J = 7.6 Hz, 4H), 6.13 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.8, 22.4, 29.2, 35.3, 102.8, 144.6; IR (film) ν_{max}/cm^{-1} 2952, 2927, 2865, 1455, 1297, 1210, 775, 694; UV/vis λ_{max}/nm 242.0; HRMS calcd for $C_{12}H_{20}I_2$ 417.9654, found 417.9650.

Acknowledgment. This work was supported by the National Natural Science Foundation of China, the Major State Basic Research Development Program (G2000077502-D), and Dow Corning Corporation. Cheung Kong Scholars Program, Qiu Shi

Science and Technologies Foundation, and BASF are gratefully acknowledged.

Supporting Information Available: Characterization data for all products except an illustrative example, copies of ^{1}H and ^{13}C NMR spectra for all isolated compounds and crystallographic data, positional and thermal parameters, and lists of bond lengths and angles for **7d** and **7i**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO060003F