# Diazidation of Allylsilanes with a Combination of Iodosylbenzene and Trimethylsilyl Azide, and Synthesis of Allyl Azides

Masao ARIMOTO,*[a] Hideo YAMAGUCHI,[a] Eiichi FUJITA,[a] Yoshimitsu NAGAO,[b] and Masahito OCHIAI[b]

*Osaka University of Pharmaceutical Sciences,[a] 10-65 Kawai 2-chome, Matsubara, Osaka 580, Japan and Institute for Chemical Research, Kyoto University,[b] Uji, Kyoto 611, Japan.* *Received May 22, 1989*

**Reaction of allyltrimethylsilanes with iodosylbenzene and trimethylsilyl azide in dichloromethane at −78 °C to room temperature affords vicinal diazides, which undergo fluoride ion-catalyzed β-elimination of azide and trimethylsilyl groups, providing allyl azides in good yields.**

**Keywords** iodosylbenzene; trimethylsilyl azide; allyltrimethylsilane; vicinal diazide; β-elimination; allyl azide

Zbiral and co-workers have reported that the oxidation of simple olefins with (diacetoxyiodo)benzene and trimethylsilyl azide (TMSA) in dichloromethane produces α-azidoketones.[1] For example, cyclohexene gave 2-azidocyclohexanone in 95% yield.[1c] However, such reactions depend on the structure of the olefin. With functionalized olefins such as 1-acetoxy- and 1-chlorocyclohexenes, oxidative ring cleavage occurs to give ω-cyano acid derivatives. With methyl cinnamate, methyl 2,3-diazido-3-phenylpropionate was obtained in low yield (25%).[1a] On the other hand, Moriarty and Khosrowshahi have observed that the treatment of olefins with iodosylbenzene and sodium azide in acetic acid gives 1,2-diazides.[2a]

We recently reported a direct synthesis of allyl azides from allyltrimethylsilanes with a combination of iodosylbenzene, TMSA, and boron trifluoride–diethyl ether in dichloromethane.[3] It was suggested that allyl azide formation probably involves highly reactive allyliodine(III) intermediates **2**,[4] produced by the reactions of allyltrimethylsilanes with initially formed [azido(trimethylsiloxy)iodo]benzene (**1a**), and nucleophilic substitution of **2** with TMSA may give allyl azides (Chart 1).

In this paper, we report that allyltrimethylsilanes react with iodosylbenzene and TMSA in the absence of boron trifluoride–diethyl ether to give good yields of vicinal diazides, useful precursors of allyl azides.

## Results and Discussion

Iodosylbenzene and TMSA by themselves do not react with allyltrimethylsilane **3a** at room temperature. When TMSA was added under nitrogen to a pale yellow suspension of iodosylbenzene in dichloromethane at −78 °C and the mixture was stirred for 3 h at that temperature, a bright orange suspension resulted which was reactive with **3a**. Based on the observation that the treatment of (diacetoxyiodo)benzene with TMSA in dichloromethane produces (acetoxyazidoiodo)benzene,[1b,d] it seems reasonable to consider that iodosylbenzene reacts with TMSA to give either **1a**[3] and/or (diazidoiodo)benzene (**1b**)[2] depending on the relative amounts of TMSA and iodosylbenzene.

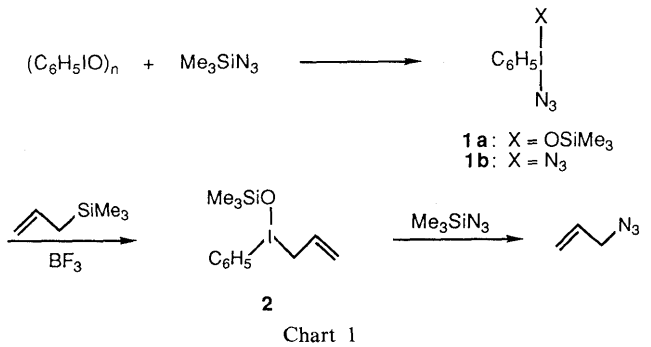
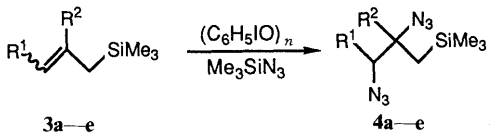



Chart 1

These azidoiodine(III) species were not detected in dichloromethane-$d_2$ at −78 °C by low temperature proton nuclear magnetic resonance ($^1$H-NMR) experiments. They seem to be thermally labile. When the bright orange suspension of iodosylbenzene and TMSA at −78 °C was allowed to warm to −30 °C, the mixture decomposed with evolution of gas, presumably nitrogen, and no longer reacted with allyltrimethylsilanes **3**.

Treatment of the β-substituted allylsilane **3a** with the bright orange suspension formed from 1.5 eq of iodosylbenzene and 2 eq of TMSA at −78 °C to room temperature afforded the 1,2-diazide **4a** in 59% yield and a small amount of the ketone **5**. With 3—5 eq of TMSA, the yield of **4a**




**3a—e** **4a—e**

**a**: $R^1$ = H, $R^2$ = *n*-$C_7H_{15}CH(OAc)(CH_2)_2$

**b**: $R^1$ = H, $R^2$ = $C_6H_5(CH_2)_2CH(OAc)CH_2$

**c**: $R^1$ = H, $R^2$ = $CH_2$=$CH(CH_2)_8CH(OAc)CH_2$

**d**: $R^1$ = *n*-$C_{10}H_{21}$, $R^2$ = H

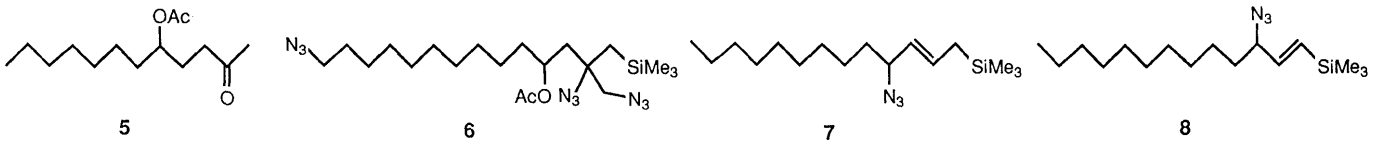
**e**: $R^1$ = $C_6H_5(CH_2)_2$, $R^2$ = H

Chart 2

TABLE I. Synthesis of Vicinal Diazides **4**[a]

| 3 | TMSA (eq) | Reactn. temp.[b] (°C) | 4 | Yield[c] (%) |
|---|---|---|---|---|
| **3a** | 2 | −78 to r.t. | **4a** | 59[d] |
| **3a** | 3 | −78 to −30 | **4a** | 84[d] |
| **3a** | 5 | −78 to r.t. | **4a** | 86 |
| **3b** | 5 | −78 to r.t. | **4b** | 75 |
| **3c** | 5 | −78 to r.t. | **4c** | 48[e] |
| **3d** (81:19)[f] | 5 | −78 to r.t. | **4d** | 46[g] |
| **3e** (83:17)[f] | 5 | −78 to r.t. | **4e** | 52 |

*a*) 1.5 mol eq of iodosylbenzene was used. *b*) r.t. = room temperature. *c*) Isolated yield. *d*) The ketone **5** was isolated as a minor product (5—12% yield). *e*) The triazide **6** was obtained in 8% yield with 19% recovery of **3c**. *f*) (*E*):(*Z*) ratios. *g*) The (*E*)-allyl azides **7** and **8** were isolated in 9% and 5% yields, respectively.



5 6 7 8

Fig. 1

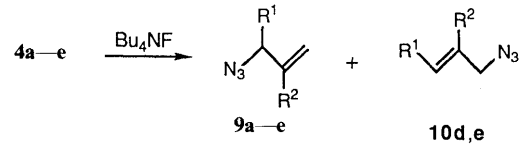
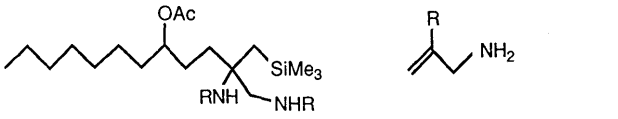


Chart 3



11: R = H 13a: R = $n$-$C_7H_{15}CH(OH)(CH_2)_2$

12: R = $COC_6H_5$ 13b: R = $C_6H_5(CH_2)_2CH(OH)CH_2$

Fig. 2

TABLE II $\beta$-Elimination of Diazides **4**

| Diazide **4** | Allyl azide **9** and **10** | Yield[a] (%) |
|---|---|---|
| **4a** | **9a** | 80 |
| **4b** | **9b** | 73 |
| **4c** | **9c** | 88 |
| **4d** | **9d** + **10d** (36 : 64)[b] | 90 |
| **4e** | **9e** + **10e** (29 : 71)[b] | 84 |

*a*) Isolated yield. *b*) Ratios.

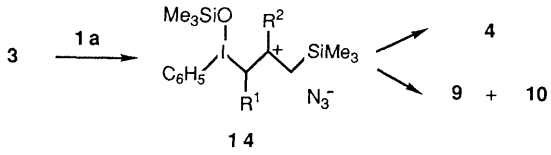


Chart 4

increased to more than 80%. The reaction was monitored by following the disappearance of the orange color, and the products were separated by preparative thin layer chromatography (TLC). The results are summarized in Table I.

With 1,13-tetradecadiene **3c**, chemoselective azidation was observed, and the double bond activated with the trimethylsilyl group was preferentially functionalized. Thus, the vicinal diazide **4c** was the major product and was accompanied by an 8% yield of the triazide **6**. The $\gamma$-substituted allylsilane **3d** afforded the 1,2-diazide **4d** in 46% yield and the (*E*)-allyl azides **7** and **8** as minor products. The attempted diazidation of 3-trimethylsilylcyclohex-1-ene led to the formation of a complex mixture of products, and 2,3-diazido-1-trimethylsilylcyclohexane was not isolated.

The $^1$H- and $^{13}$C-NMR spectra support the structures of the 1,2-diazides **4** (see Experimental). All of the diazides **4** were mixtures of two diastereoisomers ($^{13}$C-NMR analysis). The structures were further confirmed by their conversion to the corresponding allyl azides **9** and **10** (Chart 3).

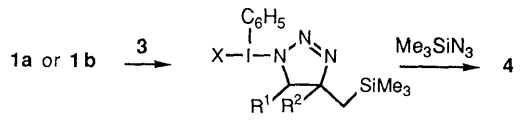
1,2-Elimination of $\beta$-functionalized organosilicon compounds provides a highly efficient and valuable route to olefins of defined stereochemistry.[5] In $\beta$-eliminations mediated by nucleophilic attack at silicon, oxygen (hydroxy, tosyloxy, and acetoxy), sulfur (phenylsulfenyl and phenylsulfonyl), and carbon (cyano) nucleofugal groups have proven to be good leaving groups. We have now found that the azido group of $\beta$-azidosilanes is a good leaving group in fluoride induced eliminations. Exposure of **4a** to tetrabutylammonium fluoride in tetrahydrofuran at room temperature for 10 min caused the $\beta$-elimination of the trimethylsilyl and azido groups to give the allyl azide **9a** in 80% yield. The syntheses of allyl azides from diazides **4** are summarized in Table II.

The diazides **4d** and **4e** yielded mixtures of regioisomers **9** and (*E*)-**10**. The ratio of **9** to **10** is similar to that obtained in reactions of allylsilanes **3d** and **3e** with iodosylbenzene–TMSA–$BF_3$[3] and probably reflects the difference in thermodynamic stability between the regioisomers because of the facile allylic rearrangement of allyl azides at room temperature.[6]

The reduction of azides to amines is documented,[7] and vicinal diazides serve as useful precursors of 1,2-diamines which are otherwise difficult to obtain.[2] For example, hydrogenation of **4a** with Lindlar catalyst in ethanol[8] gave the diamine **11** in 84% yield. The structure of **11** was confirmed by its conversion to the diamide **12**. Furthermore, lithium aluminum hydride reduction of allyl azides **9a** and **9b** gave the corresponding primary allylic amines **13a** and **13b** in good yields. Primary allyl amines are important intermediates in organic synthesis and constitute a partial structure of many biologically active natural products such as gabaculine[9] and cytosinine.[10] The present method provides easy access to primary allyl amines from allylsilanes.

For the oxidation of olefins with iodosylbenzene and sodium azide in acetic acid, yielding vicinal diazides, an ionic reaction pathway involving initial electrophilic attack of hypervalent iodine species analogous to **1** upon the double bond has been proposed.[2] A similar ionic mechanism, shown in Chart 4, involving the formation of allyliodine(III) species can reasonably explain the desilylative azidation of allylsilanes in the presence of $BF_3$ leading to allyl azides directly.[3] The ionic mechanism, however, is not compatible with the formation of vicinal diazides **4** from allylsilanes **3** with iodosylbenzene and TMSA in the absence of $BF_3$. The fact that the allyl azides **9** and **10** expected from the ionic mechanism through facile desilylation of the presumed cationic intermediate **14** were not detected in the reaction provides evidence against the ionic mechanism.

We propose the cycloaddition pathway shown in Chart 5. 1,3-Dipolar cycloadditions of hypervalent azidoiodine(III) species **1a** or **1b** to allylsilanes **3** may produce $\Delta^2$-1,2,3-triazolines **15**. Nucleophilic cleavage of the C5–N bond of **15** with the azido group and concomitant reductive elimina-




**15:** X = $N_3$ or $OSiMe_3$

Chart 5

tion of iodobenzene would give vicinal diazides **4**. Cycloadditions of organic azides to alkenes are well established[11] and are accelerated by electron-withdrawing substituents on the azide.[12] The desilylative Grob fragmentation[13] of **15** may account for the formation of the minor ketone **5**.

## Experimental

Infrared spectra (IR) were recorded with a JASCO IR-A-1 spectrometer. $^1$H- and $^{13}$C-NMR spectra were determined on a Varian XL-300 spectrometer in $CDCl_3$ solution with $(CH_3)_4Si$ as an internal standard. Mass spectra (MS) were taken on a JEOL JMS-DX 300 spectrometer. For column chromatography, Merck Silica gel 60 (70—230 mesh) was used. Preparative TLC was carried out on Merck Silica gel 60 F254. All reactions were performed under nitrogen.

**Materials** 5-Acetoxy-2-(trimethylsilylmethyl)-1-dodecene (**3a**), 4-acetoxy-6-phenyl-2-(trimethylsilylmethyl)-1-hexene (**3b**), and 4-acetoxy-2-(trimethylsilylmethyl)-1,13-tetradecadiene (**3c**) were prepared by the method described previously.[14] 1-Trimethylsilyl-2-tridecene (**3d**) and 5-phenyl-1-trimethylsilyl-2-pentene (**3e**) were prepared by the Wittig reaction developed by Seyferth and his co-workers.[15] (*E*)- and (*Z*)-**3d** (81 : 19): Colorless oil, bp 125—128 °C (4 mmHg). IR ($CHCl_3$): 1645, 1460, 1250, 1150, 850 cm$^{-1}$. $^1$H-NMR $\delta$: 5.44—5.24 (2H, m), 1.99 (2H, q, $J$=6.6 Hz), 1.48 (dd, $J$=8, 1.5 Hz, (*E*)-isomer), 1.41 (dd, $J$=8, 1 Hz, (*Z*)-isomer), 1.38—1.22 (16H), 0.90 (3H, t, $J$=7 Hz), 0.02 (9H, s). MS *m/z* (relative intensity): 254 (85, $M^+$), 239 (41), 127 (21), 99 (44), 85 (24), 73 (100). High-resolution MS: Calcd for $C_{16}H_{34}Si$: 254.2428. Found: *m/z* 254.2428. (*E*)- and (*Z*)-**3e** (83 : 17): Colorless oil, bp 115—117 °C (5 mmHg). IR ($CHCl_3$): 1645, 1605, 1500, 1455, 1250, 1150, 850 cm$^{-1}$. $^1$H-NMR $\delta$: 7.37—7.17 (5H, m), 5.53—5.27 (2H, m), 2.70 (2H, t, $J$=8 Hz), 2.35 (2H, q, $J$=8 Hz), 1.51 (dd, $J$=8, 1.5 Hz, (*E*)-isomer), 1.43 (dd, $J$=8, 1.5 Hz, (*Z*)-isomer), 0.04 (9H, s). MS *m/z* (relative intensity): 218 (32, $M^+$), 203 (25), 127 (47), 91 (33), 73 (100). High-resolution MS: Calcd for $C_{14}H_{22}Si$: 218.1489. Found: *m/z* 218.1498.

**General Procedure for Synthesis of Vicinal Diazides 4** Trimethylsilyl azide (3.0 mmol) was added dropwise to a pale yellow suspension of iodosylbenzene (0.9 mmol) in dichloromethane (5 ml) at −78 °C and the mixture was stirred for 3 h. The mixture turned to a bright orange suspension. Allylsilane **3** (0.6 mmol) was added to the suspension at −78 °C and the reaction temperature was gradually raised to room temperature over 5—6 h. The mixture was poured into cold brine and extracted with dichloromethane. The organic extract was dried ($Na_2SO_4$) and evaporated under reduced pressure. The products were isolated by preparative TLC.

**5-Acetoxy-1,2-diazido-2-(trimethylsilylmethyl)dodecane (4a)** Colorless oil. IR ($CHCl_3$): 2100, 1730, 1250, 845 cm$^{-1}$. $^1$H-NMR $\delta$: 4.86 (1H, m), 3.30 (2H, s), 2.05 (3H, s), 1.70—1.20 (16H), 1.11, 1.00 (2H, AB type, $J$=15 Hz), 0.88 (3H, t, $J$=8 Hz), 0.12 (9H, s). $^{13}$C-NMR $\delta$: 170.7 (s), 73.8 (d), 66.5 (s), 59.2 (t), 59.0 (t), 34.1 (t), 33.9 (t), 33.2 (t), 31.7 (t), 29.4 (t), 29.1 (t), 28.3 (t), 28.2 (t), 25.4 (t), 24.0 (t), 23.8 (t), 22.6 (t), 21.1 (q), 14.0 (q), 0.09 (q). *Anal.* Calcd for $C_{18}H_{36}N_6O_2Si$: C, 54.51; H, 9.15; N, 21.19. Found: C, 54.42; H, 9.26; N, 20.94.

**4-Acetoxy-1,2-diazido-6-phenyl-2-(trimethylsilylmethyl)hexane (4b)** Colorless oil. IR ($CHCl_3$): 2100, 1740, 1600, 1495, 1250, 835 cm$^{-1}$. $^1$H-NMR $\delta$: 7.34—7.14 (5H, m), 5.16 (1H, m), 3.41—3.27 (2H), 2.64 (2H, t, $J$=8 Hz), 2.07 and 2.05 (total 3H, each s), 2.14—1.74 (4H), 1.20—0.98 (2H), 0.11, 0.10 (total 9H, each s). $^{13}$C-NMR $\delta$: 170.5, 141.1, 141.0, 128.5, 128.3, 126.1, 69.9, 69.8, 65.7, 65.6, 59.2, 58.4, 41.66, 41.3, 37.3, 31.4, 25.1, 24.6, 21.3, 21.2, 0.22. *Anal.* Calcd for $C_{18}H_{28}N_6O_2Si$: C, 55.64; H, 7.26; N, 21.63. Found: C, 55.71; H, 7.54; N, 21.65.

**11-Acetoxy-13,14-diazido-13-(trimethylsilylmethyl)-1-tetradecene (4c)** Colorless oil. IR ($CHCl_3$): 2100, 1730, 1250, 840 cm$^{-1}$. $^1$H-NMR $\delta$: 5.81 (1H, ddt, $J$=17, 10, 7 Hz), 5.08 (1H, m), 5.04—4.90 (2H, m), 3.41—3.26 (2H), 2.06 (3H, s), 2.05—1.90 (3H), 1.80—1.70 (1H, m), 1.55 (2H), 1.46—1.22 (12H), 1.18—0.98 (2H), 0.12, 0.11 (total 9H, each s). $^{13}$C-NMR $\delta$: 170.9, 170.8, 139.4, 114.3, 70.3, 70.1, 65.7, 65.6, 59.2, 58.4, 41.4, 41.0, 35.6, 33.7, 29.3, 29.0, 28.8, 24.9, 24.8, 24.5, 21.3, 21.2, 0.0. *Anal.* Calcd for $C_{20}H_{38}N_6O_2Si$: C, 56.84; H, 9.06; N, 19.88. Found: C, 57.02; H, 9.07; N, 19.71.

**2,3-Diazido-1-trimethylsilyltridecane (4d)** Colorless oil. IR ($CHCl_3$): 2100, 1470, 1250, 860 cm$^{-1}$. $^1$H-NMR $\delta$: 3.42—3.18 (2H, m), 1.70—1.20 (18H, m), 1.06—0.76 (5H, m), 0.09 (9H, s). $^{13}$C-NMR $\delta$: 69.4, 69.1, 64.5, 63.9, 33.2, 32.7, 31.5, 30.9, 30.8, 30.7, 30.6, 27.7, 27.5, 24.0, 20.3, 18.7, 15.4, 0.1. *Anal.* Calcd for $C_{16}H_{34}N_6Si$: C, 56.76; H, 10.12; N, 24.82. Found: C, 56.89; H, 10.20; N, 24.82.

**2,3-Diazido-5-phenyl-1-trimethylsilylpentane (4e)** Colorless oil. IR ($CHCl_3$): 2100, 1250, 860 cm$^{-1}$. $^1$H-NMR $\delta$: 7.36—7.18 (5H, m), 3.46—3.16 (2H, m), 2.94—2.60 (2H, m), 2.08—1.83 (2H, m), 1.04—0.74 (2H), 0.07, 0.04 (total 9H, each s). $^{13}$C-NMR $\delta$: 140.5 (s), 128.7 (d), 128.5 (d), 126.3 (d), 67.0 (d), 66.6 (d), 63.2 (d), 62.9 (d), 33.2 (t), 32.5 (t), 32.3 (t), 31.9 (t), 19.0 (t), 17.7 (t), −1.2 (q), −1.2 (q). *Anal.* Calcd for $C_{14}H_{22}N_6Si$: C, 55.60; H, 7.33; N, 27.79. Found: C, 55.83; H, 7.51; N, 27.94.

**5-Acetoxy-2-dodecanone (5)** Colorless oil. IR ($CHCl_3$): 1730, 1380, 1230, 1020 cm$^{-1}$. $^1$H-NMR $\delta$: 4.86 (1H, m), 2.45 (2H, t, $J$=7.5 Hz), 2.14 (3H, s), 2.04 (3H, s), 2.0—1.45 (4H), 1.40—1.20 (10H), 0.88 (3H, t, $J$=6.7 Hz). MS *m/z* (relative intensity): 242 (2, $M^+$), 199 (92), 182 (40), 143 (100), 83 (40). High-resolution MS: Calcd for $C_{14}H_{26}O_3$: 242.1881. Found: *m/z* 242.1846.

**4-Acetoxy-1,2,14-triazido-2-(trimethylsilylmethyl)tetradecane (6)** Colorless oil. IR ($CHCl_3$): 2100, 1730, 1250, 845 cm$^{-1}$. $^1$H-NMR $\delta$: 5.08 (1H, m), 3.37, 3.34 (2H, AB type, $J$=14 Hz), 3.25 (2H, t, $J$=6.9 Hz), 2.07, 2.06 (total 3H, each s), 2.06—1.90 (1H, m), 1.80—1.72 (1H, m), 1.68—1.22 (18H), 1.18—0.98 (2H), 0.12, 0.12 (total 9H, each s). $^{13}$C-NMR $\delta$: 170.8, 70.3, 70.2, 65.7, 65.6, 59.2, 58.4, 51.4, 41.4, 41.0, 35.6, 29.3, 29.0, 28.7, 26.6, 24.9, 24.9, 24.5, 21.3, 21.2, 0.0. *Anal.* Calcd for $C_{20}H_{39}N_9O_2Si$: C, 51.58; H, 8.44; N, 27.07. Found: C, 51.91; H, 8.44; N, 26.69.

**(*E*)-4-Azido-1-trimethylsilyl-2-tridecene (7)** Colorless oil. IR ($CHCl_3$): 2100, 1660, 1470, 1250, 860 cm$^{-1}$. $^1$H-NMR $\delta$: 5.69 (1H, ddt, $J$=15, 1.5, 8 Hz), 5.21 (1H, ddt, $J$=15, 8, 1.5 Hz), 3.75 (1H, q, $J$=8 Hz), 1.53 (2H, dd, $J$=8, 1.5 Hz), 1.60—1.20 (16H), 0.88 (3H, t, $J$=6.8 Hz), 0.03 (s, 9H). *Anal.* Calcd for $C_{16}H_{33}N_3Si$: C, 65.03; H, 11.26; N, 14.22. Found: C, 64.96; H, 11.28; N, 14.34.

**(*E*)-3-Azido-1-trimethylsilyl-1-tridecene (8)** Colorless oil. IR ($CHCl_3$): 2100, 1620, 1470, 1250, 995, 870, 845 cm$^{-1}$. $^1$H-NMR $\delta$: 5.90, 5.85 (2H, AB type, $J$=18 Hz, Higher-field signals appear as d. $J$=6 Hz), 1.60—1.20 (18H), 0.88 (3H, t, $J$=7 Hz), 0.09 (9H, s). MS *m/z*: 252, 126, 73. High-resolution MS: Calcd for $C_{15}H_{30}NSi$: 252.2148 ($M^+ - Me - N_2$). Found: *m/z* 252.2150.

**General Procedure for Fluoride Ion-Induced β-Elimination of Vicinal Diazides 4** A solution of tetrabutylammonium fluoride (0.46 mmol) in tetrahydrofuran (0.5 ml) was added to a solution of **4** (0.38 mmol) in tetrahydrofuran (5 ml) in the presence of 4 Å molecular sieves. The mixture was stirred at room temperature for 10—15 min. The reaction was monitored by TLC ($CHCl_3$). The mixture was poured into cold water and extracted with diethyl ether. The organic extract was dried ($Na_2SO_4$) and evaporated under reduced pressure. The products were isolated by preparative TLC.

**5-Acetoxy-2-azidomethyl-1-dodecene (9a)**[3] Colorless oil. IR ($CHCl_3$): 2110, 1740, 1655, 1380, 1250, 915 cm$^{-1}$. $^1$H-NMR $\delta$: 5.05 (1H, s), 4.99 (1H, s), 4.88 (1H, quintet, $J$=6 Hz), 3.74 (2H, s), 2.10 (2H, m), 2.05 (3H, s), 1.71 (2H, dt, $J$=8.5, 6.5 Hz), 1.64—1.20 (12H), 0.88 (3H, t, $J$=7 Hz). MS *m/z* (relative intensity): 281 (2, $M^+$), 239 (10), 210 (20), 192 (20), 122 (38), 108 (100), 94 (86). *Anal.* Calcd for $C_{15}H_{27}N_3O_2$: C, 64.02; H, 9.67; N, 14.93. Found: C, 64.31; H, 9.42; N, 14.99.

**4-Acetoxy-2-azidomethyl-6-phenyl-1-hexene (9b)**[3] Colorless oil. IR ($CHCl_3$): 2120, 1740, 1655, 1605, 1380, 1250, 1035, 920 cm$^{-1}$. $^1$H-NMR $\delta$: 7.36—7.15 (5H, m), 5.10 (1H, s), 5.07 (1H, m), 5.03 (1H, s), 3.80, 3.73 (2H, AB type, $J$=14 Hz), 2.65 (2H, m), 2.36 (2H, d, $J$=7 Hz), 2.02 (3H, s), 1.90 (2H, m). *Anal.* Calcd for $C_{15}H_{19}N_3O_2$: C, 65.91; H, 7.01; N, 15.37. Found: C, 66.04; H, 6.87; N, 15.50.

**4-Acetoxy-2-azidomethyl-1,13-tetradecadiene (9c)** Colorless oil. IR ($CHCl_3$): 2100, 1730, 1640, 1250, 1020, 915 cm$^{-1}$. $^1$H-NMR $\delta$: 5.81 (1H, ddt, $J$=17, 10, 7 Hz), 5.10 (1H, s), 5.08—4.90 (4H), 3.81, 3.76 (2H, AB type, $J$=12 Hz), 2.33 (2H, m), 2.10—1.98 (2H), 2.02 (3H, s), 1.62—1.22 (14H). *Anal.* Calcd for $C_{17}H_{29}N_3O_2$: C, 66.42; H, 9.51; N, 13.67. Found: C, 66.64; H, 9.70; N, 13.66.

**3-Azido-1-tridecene (9d) and (*E*)-1-Azido-2-tridecene (10d)**[3] 36 : 64. Colorless oil. IR ($CHCl_3$): 2120, 1680, 1470, 1380, 1090, 970 cm$^{-1}$. $^1$H-NMR $\delta$: 5.75 (1H, C2-H of **9d** and C3-H of **10d**), 5.51 (dtt, $J$=16, 6, 1.5 Hz, C2-H of **10d**), 5.29—5.23 (m, Cl-$H_2$ of **9d**), 3.80 (q, $J$=7 Hz, C3-H of **9d**), 3.69 (d, $J$=6 Hz, Cl-$H_2$ of **10d**), 2.08 (2H, q, $J$=7 Hz, C4-$H_2$ of **9d**

and **10d**), 1.60—1.20 (16H), 0.88 (3H, t, $J=7$ Hz, C13-$H_3$ of **9d** and **10d**). *Anal.* Calcd for $C_{13}H_{25}N_3$: C, 69.90; H, 11.28; N, 18.81. Found: C, 69.93; H, 11.43; N, 18.93.

**3-Azido-5-phenyl-1-pentene (9e) and (*E*)-1-Azido-5-phenyl-2-pentene (10e)**[3] 29:71. Colorless oil. IR ($CHCl_3$): 2100, 1680, 1610, 1460, 1250, 975 $cm^{-1}$. $^1$H-NMR $\delta$: 7.32—7.16 (5H, m, aromatic-$H_5$ of **9e** and **10e**), 5.78 (1H, C2-H of **9e** and C3-H of **10e**), 5.55 (dtt, $J=15$, 7, 1.5 Hz, C2-H of **10e**), 5.32—5.25 (m, C1-$H_2$ of **9e**), 3.82 (q, $J=7$ Hz, C3-H of **9e**), 3.69 (d, $J=6$ Hz, C1-$H_2$ of **10e**), 2.76—2.62 (2H, C5-$H_2$ of **9e** and **10e**), 2.41 (q, $J=7$ Hz, C4-$H_2$ of **10e**), 1.85 (m, C4-$H_2$ of **9e**). *Anal.* Calcd for $C_{11}H_{13}N_3$: C, 70.56; H, 7.00; N, 22.44. Found: C, 70.38; H, 7.02; N, 22.55.

**Reduction of 4a with Lindlar Catalyst** Hydrogenation[8] of **4a** (59 mg, 0.15 mmol) with Lindlar catalyst (5% Pd/$CaCO_3$, 24 mg) in ethanol (5 ml) gave 5-acetoxy-1,2-diamino-2-(trimethylsilylmethyl)dodecane (**11**) (43 mg, 84% yield). Its structure was confirmed by the conversion to the diamide **12**: IR ($CHCl_3$): 3440, 3320, 1720, 1650, 1530, 1490, 1250, 840, 700 $cm^{-1}$. $^1$H-NMR $\delta$: 8.07 (1H), 7.98—7.76 (4H, m), 7.56—7.20 (6H, m), 7.28, 6.95 (total 1H, each s), 4.82, 4.50 (total 1H, m), 3.92—3.50 (2H), 2.0, 1.98 (total 3H, each s), 0.87 (3H, t, $J=6.8$ Hz), 0.13, 0.11 (total 9H, each s).

**Lithium Aluminum Hydride Reduction of 9a** Reduction of **9a** (20 mg, 0.07 mmol) with lithium aluminum hydride (14 mg, 0.35 mmol) in diethyl ether (2 ml) at room temperature for 1 h afforded 2-aminomethyl-5-hydroxy-1-dodecene (**13a**) (9.3 mg, 62% yield), colorless oil. IR ($CHCl_3$): 3670, 3600, 3380, 1650, 1460, 900 $cm^{-1}$. $^1$H-NMR $\delta$: 4.95, 4.86 (each 1H), 3.61 (1H, m), 3.27 (2H), 2.21 (2H, m), 1.72—1.18 (15H), 0.89 (3H, t, $J=7.2$ Hz).

**Lithium Aluminum Hydride Reduction of 9b** Reduction of **9b** (19 mg, 0.07 mmol) with lithium aluminum hydride (14 mg, 0.35 mmol) in diethyl ether (3 ml) at room temperature for 1 h afforded 2-aminomethyl-4-hydroxy-6-phenyl-1-hexene (**13b**) (10.3 mg, 72% yield), colorless oil. IR ($CHCl_3$): 3380, 1645, 1495, 1455, 910 $cm^{-1}$. $^1$H-NMR $\delta$: 7.34—7.14 (5H, m), 4.97, 4.90 (each 1H), 3.65 (1H, m), 3.37, 3.23 (2H, AB type, $J=13.2$ Hz), 2.92—2.62 (2H, m), 2.44 (1H, dd, $J=13.5$, 2.6 Hz), 2.20 (1H, dd, $J=13.5$, 8.6 Hz), 1.90—1.70 (2H).

## References


1) *a*) J. Ehrenfreund and E. Zbiral, *Tetrahedron*, **28**, 1697 (1972); *b*) E. Zbiral, *Synthesis*, **1972**, 285; *c*) J. Ehrenfreund and E. Zbiral, *Justus Liebigs Ann. Chem.*, **1973**, 290; *d*) E. Zbiral and G. Nestler, *Tetrahedron*, **26**, 2945 (1970); *e*) E. Zbiral, G. Nestler, and K. Kischa, *ibid.*, **26**, 1427 (1970).
2) *a*) R. M. Moriarty and J. S. Khosrowshahi, *Tetrahedron Lett.*, **27**, 2809 (1986); *b*) *Idem*, *Synth. Commun.*, **17**, 89 (1987); *c*) R. M. Moriarty, R. K. Vaid, V. T. Ravikumar, B. K. Vaid, and T. E. Hopkins, *Tetrahedron*, **44**, 1603 (1988).
3) M. Arimoto, H. Yamaguchi, E. Fujita, M. Ochiai, and Y. Nagao, *Tetrahedron Lett.*, **28**, 6289 (1987).
4) M. Ochiai and Y. Nagao, *Yuki Gosei Kagaku Kyokai Shi*, **44**, 660 (1986).
5) *a*) E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London, 1981, p. 141; *b*) A. W. P. Jarvie, *Organometal. Chem. Rev., Sect. A*, **6**, 153 (1970); *c*) T.-H. Chan, *Acc. Chem. Res.*, **10**, 442 (1977); *d*) S. L. Jones and C. J. M. Stirling, *J. Chem. Soc., Chem. Commun.*, **1988**, 1153; *e*) I. Fleming, J. Goldhill, and D. A. Perry, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 1563; *f*) T. Shono, H. Ohmizu, and N. Kise, *Chem. Lett.*, **1980**, 1517; *g*) H. Nishiyama, M. Matsumoto, H. Sakaguchi, and K. Itoh, *Tetrahedron Lett.*, **27**, 1599 (1988).
6) *a*) A. Gagneux, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **82**, 5956 (1960); *b*) C. A. Werf and V. L. Heasley, *J. Org. Chem.*, **31**, 3534 (1966).
7) T. Sheradsky, "The Chemistry of the Azido Group," ed. by S. Patai, John Wiley and Sons, Inc., New York, 1971, Chapter 6.
8) E. J. Corey, K. C. Nicolaou, D. Balanson, and Y. Machida, *Synthesis*, **1975**, 590.
9) K. Kobayashi, S. Miyazawa, A. Terahara, H. Mishima, and H. Kurihara, *Tetrahedron Lett.*, **1976**, 537.
10) T. Kondo, H. Nakai, and T. Goto, *Tetrahedron*, **29**, 1801 (1973).
11) R. A. Abramovitch and E. P. Kyba, "The Chemistry of the Azido Group," ed. by S. Patai, John Wiley and Sons, Inc., New York, 1971, Chapter 5.
12) W. Lwowski, "1,3-Dipolar Cycloaddition Chemistry," Vol. 1, ed. by A. Padwa, John Wiley and Sons, Inc., New York, 1984, Chapter 5.
13) *a*) C. A. Grob and P. W. Schiess, *Angew. Chem. Internat. Edit.*, **6**, 1 (1967); *b*) C. A. Grob, *ibid.*, **8**, 535 (1969).
14) *a*) M. Ochiai, E. Fujita, M. Arimoto, and H. Yamaguchi, *Tetrahedron Lett.*, **24**, 777 (1983); *b*) *Idem, Chem. Pharm. Bull.*, **33**, 989 (1985).
15) D. Seyferth, K. R. Wursthorn, and R. E. Mammarella, *J. Org. Chem.*, **42**, 3104 (1977).