2 H), 5.01 (s, 2 H); MS *m/z* (relative intensity) 182 ($M^+ + 2$), 180 (M^+), 101 (30), and 45 (100); IR (neat) 2950, 1640, 1430, 1160, 1100, and 1020 cm^{-1}. Anal. Calcd for $C_5H_9BrO_2$: C, 33.17; H, 5.01; Br, 44.14. Found: C, 33.17; H, 5.08; Br, 43.91.

Palladium-Catalyzed Addition of Trimethylgermyl Cyanide to Terminal Acetylenes

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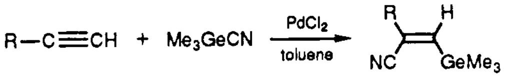
Trimethylsilyl cyanide, Me_3SiCN, has gained considerable recognition as a versatile reagent to introduce cyano groups into organic molecules,[1] and the reaction of Me_3SiCN with a wide variety of substrates such as aldehydes,[2] ketones,[3] acetals,[4] epoxides,[5] and acetylenes[6,7] has been extensively studied. Tributyltin cyanide, Bu_3SnCN, has been found to react with acid halides[8] and aryl halides[9] to give acid cyanides and aryl cyanides, respectively. In contrast, synthetic application of trimethylgermyl cyanide, Me_3GeCN (**1**), has not been developed so far. We now wish to report the Pd-catalyzed addition to **1** to terminal acetylenes with a high regio- and stereoselectivity to give β-cyano alkenylgermanes in high yields (eq 1).



(1)

The results obtained for some terminal acetylenes are shown in Table I. The reaction of phenylacetylene (**2a**) with **1** in the presence of $PdCl_2$ at reflux for 2 h afforded 2-phenyl-3-(trimethylgermyl)-2-propenenitrile (**3a**) in 99% isolated yield with a *Z/E* ratio of 97:3 (entry 1). A decrease in the reaction temperature resulted in a decrease in the yield of **3a** (entries 1–4). When the reaction was carried out at 40 °C, no reaction occurred (entry 4). Palladium complexes such as $Pd(PPh_3)_4$ and $PdCl_2$/DIBAH (*i*-Bu_2AlH) were not effective for the reaction of phenylacetylene with **1**. When Ni(0), generated in situ from the treatment of $NiCl_2$ with DIBAH, was used as a catalyst, the reaction exhibited inverse stereoselectivity (entry 5). The stereochemistry of **3a** was confirmed by the coupling constant between CN and vinyl proton in the ^{13}C NMR spectrum ($^3J_{CN\text{-}H} = 17$ Hz for **3a*Z*** and $^3J_{CN\text{-}H} = 12$ Hz for **3a*E***).[10] The yields were excellent for aromatic acetylenes (entries 1–11). Aliphatic acetylenes also reacted with **1** in the presence of $PdCl_2$ and gave β-cyano alkenylgermanes in high yields (entries 12–15). The reaction was compatible with functional groups such as methoxy, fluoro, chloro, acetoxy, and cyano. The reaction of the internal acetylenes 4-octyne and diphenylacetylene with **1** did not give addition products.

We have previously reported the Pd-catalyzed addition of Me_3SiCN to acetylenes giving β-cyano alkenylsilanes.[6b] The present study reveals that **1** is more reactive than Me_3SiCN. Thus, the present reaction was completed within 2 h, whereas the reaction of Me_3SiCN required at least 15 h to complete under the same reaction conditions as those for the reaction of **2a** with Me_3SiCN. In addition, the reaction of acetylenes with **1** gave a better stereoselectivity than that with Me_3SiCN.

In summary, the present reaction provides a new synthetic method for the preparation of alkenylgermanes[11,12] with a high degree of regio- and stereoselectivity.

Experimental Section

General Method. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker WM 360 spectrometer and are reported in ppm from tetramethylsilane or chloroform as an internal standard on the δ scale. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, quint = quintet, m = multiplet), coupling constant, integration, and interpretation. Infrared spectra were obtained on a Hitachi 260-10 spectrometer. Peaks are reported in units of cm^{-1}. Mass spectra were obtained on a JMS-DX 300 with ionization voltages of 70 eV. Elemental analyses were performed on a Perkin-Elmer 240C by the ISIR Material Analysis Center at Osaka University. Melting points (mp) were determined on a Yanagimoto micro melting point apparatus and uncorrected. Bulb-to-bulb distillations were done on a GTO-250R Sibata glass tube oven; boiling points (bp) refer to air bath temperature and are uncorrected.

Materials. Phenylacetylene (**2a**), 1-octyne (**2h**), 5-hexynenitrile (**2j**), 4-octyne and diphenylacetylene are commercially available. Preparation of (4-fluorophenyl)- (**2b**), (4-chlorophenyl)- (**2c**), (3-methoxyphenyl)- (**2d**), (2-methoxyphenyl)- (**2e**), (2-naphthyl)- (**2f**), and (1-naphthyl)acetylene (**2g**) has already been reported in a previous paper.[6b] Trimethylgermyl cyanide (**1**) was prepared by the literature procedure.[13]

2-Phenyl-3-(trimethylgermyl)-(*Z*)-prop-2-enenitrile (3a*Z*). In a 20-mL round-bottomed flask were placed phenylacetylene (1 mmol, 0.11 mL), Me_3GeCN (2 mmol, 0.27 mL), and toluene (2 mL). To the solution was added $PdCl_2$ (0.1 mmol, 18 mg), and the mixture was heated at reflux under nitrogen. After 2 h, the solvent was removed in vacuo, and distillation of the residue by Kugelrohr distillation gave pure 2-phenyl-3-(trimethylgermyl)-2-propenenitrile (**3a**) (245 mg, 99%): bp 95–100 °C (0.35 Torr); ^1H NMR ($CDCl_3$) δ 0.49 (s, 9 H, $GeCH_3$), 7.31 (s, 1 H, CH=), 7.59

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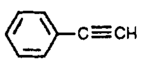
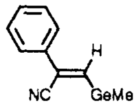
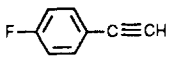
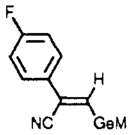
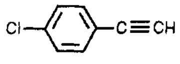
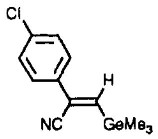
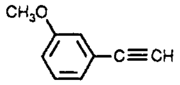
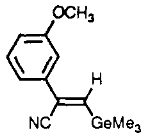
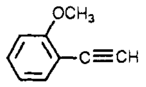
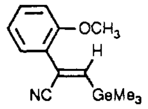
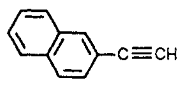
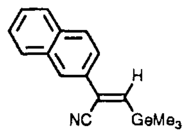
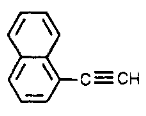
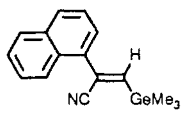
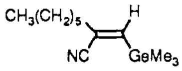
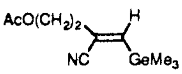
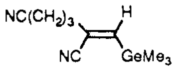
Table I. Addition of Trimethylgermyl Cyanide (1) to Terminal Acetylenes[a]

entry	acetylene	cat.	temp, time	product	yield[b], %	*Z*:*E*[c]
1	 **2a**	$PdCl_2$	reflux, 2 h	 **3a**	99	97:3
2	**2a**	$PdCl_2$	80 °C, 20 h	**3a**	90	98:2
3	**2a**	$PdCl_2$	60 °C, 20 h	**3a**	76	99:1
4	**2a**	$PdCl_2$	40 °C, 20 h	**3a**		
5	**2a**	$NiCl_2$/DIBAH	reflux, 2 h	**3a**	98	25:75
6	 **2b**	$PdCl_2$	reflux, 2 h	 **3b**	65	95:5
7	 **2c**	$PdCl_2$	reflux, 2 h	 **3c**	97	98:2
8	 **2d**	$PdCl_2$	reflux, 2 h	 **3d**	96	96:4
9	 **2e**	$PdCl_2$	reflux, 2 h	 **3e**	88	75:25
10	 **2f**	$PdCl_2$	reflux, 2 h	 **3f**	91	94:6
11	 **2g**	$PdCl_2$	reflux, 2 h	 **3g**	96	92:8
12	$CH_3(CH_2)_5{-}C{\equiv}CH$ **2h**	$PdCl_2$	reflux, 2 h	 **3h**	89	98:2
13	**2h**	$NiCl_2$/DIBAH	reflux, 20 h	**3h**	49	84:16
14	$AcO(CH_2)_2{-}C{\equiv}CH$ **2i**	$PdCl_2$	reflux, 2 h	 **3i**	88	75:25
15	$NC(CH_2)_3{-}C{\equiv}CH$ **2j**	$PdCl_2$	reflux, 2 h	 **3j**	91	94:6

[a] Reaction conditions: acetylene (1 mmol), Me_3GeCN (2 mmol), catalyst (0.1 mmol), and toluene (2 mL) under nitrogen. [b] Isolated yields based on acetylene. [c] Determined by GC analysis.

(dd, J = 1.7, 0.6 Hz, 2 H, Ph), 7.37 (m, 3 H, Ph); ^{13}C NMR ($CDCl_3$) δ -1.59 ($GeCH_3$), 117.91 (CN), 125.54, 127.56, 128.87, 129.36, 134.88, 150.09 (CH=); IR (neat) 3060, 2990, 2910, 2800, 2210, 1585, 1560, 1500, 1450, 1420, 1240, 975, 830, 760, 690; MS, m/z 247 (M^+ for ^{74}Ge). Anal. Calcd for $C_{12}H_{15}NGe$: C, 58.63; H, 6.15; N, 5.70. Found: C, 58.41; H, 6.15; N, 5.77.

2-Phenyl-3-(trimethylgermyl)-(*E*)-prop-2-enenitrile (3a*E*). In a 20-mL reaction flask was placed $NiCl_2$ (0.1 mmol, 13 mg), and then 1 N DIBAH (i-Bu_2AlH) in hexane (0.1 mmol, 0.1 mL) was added. Toluene (2 mL), phenylacetylene (1 mmol, 0.11 mL), and Me_3GeCN (2 mmol, 0.27 mL) were added to the flask, and the mixture was stirred at reflux for 2 h. The solvent was removed in vacuo, and the residue was distilled by Kugelrohr distillation to give a mixture of **3a*Z*** and **3a*E***, the ratio of which was 25:75. Unfortunately, **3a*E*** could not be obtained in pure form. The ^1H NMR spectra and ^{13}C NMR spectrum were obtained from the mixture and the most of peaks are obscured by minor isomer **3a*Z***. ^1H NMR ($CDCl_3$) δ 0.16 (s, 9 H, $GeCH_3$), 7.10 (s, 1 H, CH=); ^{13}C NMR ($CDCl_3$) δ -1.41 ($GeCH_3$), 118.70 (CN).

2-(4-Fluorophenyl)-3-(trimethylgermyl)-(*Z*)-prop-2-ene-

nitrile (3b): bp 110 °C (0.5 Torr); ^{1}H NMR ($CDCl_3$) δ 0.49 (s, 9 H, $GeCH_3$), 7.09 (dd, J = 9.1, 8.3 Hz, 2 H, Ar), 7.25 (s, 1 H, CH=), 7.58 (dd, J = 9.1, 5.2 Hz, 2 H, Ar); IR (neat) 2975, 2920, 2210, 1600, 1550, 1510, 1410, 1300, 1240, 1165, 1105, 1015, 975, 830, 770, 725; MS, m/z 265 (M^+ for ^{74}Ge). Anal. Calcd for $C_{12}H_{14}NFGe$: C, 54.63; H, 5.35; N, 5.31. Found: C, 54.75; H, 5.07; N, 5.57.

2-(4-Chlorophenyl)-3-(trimethylgermyl)-(*Z*)-prop-2-enenitrile (3c): mp 49–50 °C; ^{1}H NMR ($CDCl_3$) δ 0.49 (s, 9 H, $GeCH_3$), 7.30 (s, 1 H, CH=), 7.36 (dd, J = 6.7, 2.0 Hz, 2 H, Ar), 7.52 (dd, J 6.7, 2.0 Hz, 2 H, Ar); IR (Nujol) 2220, 1590, 1570, 1555, 1495, 1470, 1405, 1380, 1240, 1100, 1015, 980, 875, 820, 775; MS, m/z 281 (M^+ for ^{74}Ge). Anal. Calcd for $C_{12}H_{14}NClGe$: C, 51.41; H, 5.03; N, 5.00; Cl, 12.65. Found: C, 51.61; H, 5.01; N, 5.11; Cl, 12.39.

2-(3-Methoxyphenyl)-3-(trimethylgermyl)-(*Z*)-prop-2-enenitrile (3d): bp 115 °C (0.2 Torr); ^{1}H NMR ($CDCl_3$) δ 0.48 (s, 9 H, $GeCH_3$), 3.84 (s, 3 H, CH_3O), 6.91 (ddd, J = 7.5, 2.0, 0.8 Hz, 1 H, Ar), 7.11 (t, J = 2.0 Hz, 1 H, Ar), 7.19 (ddd, J = 7.5, 2.0, 0.8 Hz, 1 H, Ar), 7.30 (s, 1 H, CH=), 7.30 (t, J = 7.5 Hz, 1 H, Ar); IR (neat) 2975, 2910, 2830, 2210, 1600, 1580, 1560, 1490, 1465, 1455, 1430, 1290, 1285, 1255, 1240, 1190, 1180, 1165, 1050, 990, 830, 775, 685; MS, m/z 277 (M^+ for ^{74}Ge). Anal. Calcd for $C_{13}H_{17}NGeO$: C, 56.60; H, 6.21; N, 5.08. Found: C, 56.62; H, 6.09; N, 5.29.

2-(2-Methoxyphenyl)-3-(trimethylgermyl)-(*Z*)-prop-2-enenitrile (3e): bp 120 °C (0.4 Torr); ^{1}H NMR ($CDCl_3$) δ 0.45 (s, 9 H, $GeCH_3$), 3.89 (s, 3 H, CH_3O), 7.15 (s, 1 H, CH=), 6.90–7.34 (m, 4 H, Ar); IR (neat) 3070, 2975, 2910, 2830, 2800, 2220, 1600, 1580, 1490, 1465, 1455, 1295, 1250, 1200, 1180, 1165, 1120, 1050, 1030, 1000, 970, 935, 860, 830, 750, 720; MS, m/z 277 (M^+ for ^{74}Ge). Anal. Calcd for $C_{13}H_{17}NOGe$: C, 56.60; H, 6.21; N, 5.08. Found: C, 56.56; H, 5.94; N, 5.22.

2-(2-Naphthyl)-3-(trimethylgermyl)-(*Z*)-prop-2-enenitrile (3f): bp 140 °C (0.08 Torr); mp 72–73 °C; ^{1}H NMR ($CDCl_3$) δ 0.52 (s, 9 H, $GeCH_3$), 7.45 (s, 1 H, CH=), 7.50–8.90 (m, 7 H, Ar); IR (Nujol) 2980, 2970, 2850, 2220, 1595, 1555, 1460, 1380, 1275, 1240, 1130, 890, 855, 840, 820, 810, 770, 740; MS, m/z 297 (M^+ for ^{74}Ge). Anal. Calcd for $C_{16}H_{17}NGe$: C, 64.94; H, 5.79; N, 4.73. Found: C, 64.74; H, 5.66; N, 4.80.

2-(1-Naphthyl)-3-(trimethylgermyl)-(*Z*)-prop-2-enenitrile (3g): bp 140 °C (0.25 Torr); ^{1}H NMR ($CDCl_3$) δ 0.55 (s, 9 H, $GeCH_3$), 7.11 (s, 1 H, CH=), 7.43–8.03 (m, 7 H, Ar); IR (neat) 3060, 2970, 2910, 2790, 2220, 1590, 1565, 1510, 1415, 1395, 1360, 1260, 1240, 1170, 1090, 1050, 1025, 945, 860, 830, 800, 775; MS, m/z 297 (M^+ for ^{74}Ge). Anal. Calcd for $C_{16}H_{17}NGe$: C, 64.94; H, 5.79; N, 4.73. Found: C, 65.04; H, 5.61; N, 4.80.

2-Hexyl-3-(trimethylgermyl)-(*Z*)-prop-2-enenitrile (3h): bp 105 °C (0.25 Torr); ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 9 H, $GeCH_3$), 0.82 (t, J = 6.7 Hz, 3 H, CH_3), 1.23 (m, 6 H, CH_2), 1.48 (quint, J = 7.5 Hz, 2 H, CH_2), 2.21 (td, J = 7.5, 1.2 Hz, 2 H, CH_2C=), 6.47 (t, J = 1.2 Hz, 1 H, CH=); IR (neat) 2960, 2930, 2850, 2210, 1585, 1465, 1455, 1410, 1380, 1260, 1240, 1090, 1015, 830, 765; MS, m/z 255 (M^+ for ^{74}Ge). Anal. Calcd for $C_{12}H_{23}NGe$: C, 56.76; H, 9.13; N, 5.52. Found: C, 56.91; H, 8.93; N, 5.80.

2-(2-(Acetyloxy)ethyl)-3-(trimethylgermyl)-(*Z*)-prop-2-enenitrile (3i): bp 90–95 °C (0.3 Torr); ^{1}H NMR ($CDCl_3$) δ 0.40 (s, 9 H, $GeCH_3$), 2.06 (s, 3 H, CH_3CO), 2.60 (td, J = 6.3, 1.2 Hz, 2 H, CH_2C=), 4.25 (t, J = 6.3 Hz, 2 H, CH_2O), 6.68 (t, J = 1.2 Hz, 1 H, CH=); IR (neat) 2980, 2910, 2220, 1740, 1590, 1455, 1435, 1385, 1365, 1235, 1120, 1040, 835, 770; MS, m/z 242 ($M^+ - 15$ for ^{74}Ge). Anal. Calcd for $C_{10}H_{17}NO_2Ge$: C, 46.95; H, 6.70; N, 5.47. Found: C, 47.03; H, 6.59; N, 5.46.

2-(3-Cyanopropyl)-3-(trimethylgermyl)-(*Z*)-prop-2-enenitrile (3j): bp 100 °C (0.25 Torr); ^{1}H NMR ($CDCl_3$) δ 0.40 (s, 9 H, $GeCH_3$), 1.94 (quint, J = 7.1 Hz, 2 H, CH_2), 2.39 (t, J = 7.1 Hz, 2 H, CH_2C=), 2.48 (t, J = 7.1 Hz, 2 H, CH_2CN), 6.71 (s, 1 H, CH=); IR (neat) 2975, 2920, 2800, 2245, 2220, 1590, 1260, 1425, 1240, 1165, 1110, 980, 840, 770; MS, m/z 223 ($M^+ - 15$ for ^{74}Ge). Anal. Calcd for $C_{10}H_{16}N_2Ge$: C, 50.71; H, 6.81; N, 11.83. Found: C, 50.62; H, 6.51; N, 12.02.

Acknowledgment. We acknowledge the ISIR Material Analysis Center at Osaka University for measurement of the ^{1}H NMR, ^{13}C NMR, and mass spectra and for elemental analyses.

A Convenient Preparation of 3-Alkylcyclopentenones from Alkylcyclopentadienes

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Improved syntheses of cyclopentenones are being continually developed, in part, because alkylated cyclopentenones have figured prominently in synthetic approaches to, for example, triquinane and prostaglandin natural products.[2] Existing approaches to 3-alkylcyclopentenones **5**, one of the more important types of these compounds, are numerous and include, inter alia, Pauson–Khand and Nazarov type cyclizations and intramolecular aldol condensations.[3-5] In connection with other ongoing projects we needed to prepare a variety of these compounds on a large scale in an efficient manner. Most existing methods for the synthesis of these compounds require expensive starting materials, are inefficient, or involve conditions not compatible with certain functional groups. We report here a three-step sequence to compounds **5** from alkylcyclopentadienes **1**, which seems broadly applicable to the synthesis of these compounds.

Results

The alkylcyclopentadienes (**1a–f**) used in this work were prepared from cyclopentadiene using one of two methods. Simple alkylation of an appropriate cyclopentadienide salt was suitable for the efficient (80–90%) preparation of compounds **1a–c** bearing a primary alkyl group (Scheme I).[6] Those substrates containing a secondary or a tertiary alkyl group were more effectively produced via a two-step sequence (eq 1). Condensation of cyclopentadiene with 3-pentanone or cyclohexanone according to the method of Little et al. provided, in high yield, intermediate fulvenes **2a** or **2b**.[7a,b] Reduction of the derived fulvenes, with $LiAlH_4$, provided compounds **1d** and **1e** whereas addition of methyllithium to compound **2a** gave cyclopentadiene

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