Journal of Organometallic Chemistry, 473 (1994) 335–342

Preparation of vinylgermanes and a germole by the Pd-catalyzed reactions of Me_3GeCn with acetylenes

Naoto Chatani, Tsumoru Morimoto, Toyoshige Muto and Shinji Murai

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565 (Japan)

(Received December 15, 1993; in revised form January 12, 1994)

Abstract

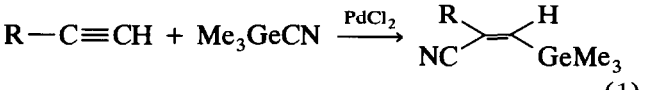
The palladium-catalyzed reaction of trimethylgermyl cyanide (Me_3GeCN, **1**) with terminal acetylenes is studied in detail with particular emphasis focused on functional group compatibility as well as the factor affecting stereoselectivity. The reaction of **1** with terminal aromatic acetylenes in the presence of $PdCl_2$ results in the highly regioselective addition of **1** to the carbon–carbon triple bonds, leading to β-cyano vinylgermanes in high yields. The stereoselectivity depends on the electronic nature of the substituents on the aromatic ring. Whereas the *Z*-stereoselectivity for arylacetylenes having a methoxy group at the *o*- or *p*-position is moderate (60–75%), extremely high *Z*-stereoselectivity (> 96%) is observed for the *m*-methoxyphenylacetylene. For all arylacetylenes with electron-withdrawing groups on the ring quite high selectivities (> 97%) are observed. The reaction of terminal aliphatic acetylenes too affords the adduct with high regio- and stereoselectivity. The reaction of **1** with 1,6-diynes results in unusual cyclization to give a germole as the main product.

Key words: Palladium; Germanium; Acetylene; Catalysis; Cyanide

1. Introduction

In contrast to the well studied vinylsilanes [1] and vinylstannanes [2], the development of vinylgermane chemistry [3] has been slow [4]. New synthetic methods of vinylgermanes are now appearing in recent literature. For example, it was found that hydrogermylation of acetylenes could be catalyzed by a rhodium catalyst [5] or Et_3B [6]. Regioselective germyl-stannylation of acetylenic esters, giving β-stannyl vinylgermanes, provided a new method for the preparation of functionalized vinylgermanes [7]. Double germylation of acetylenes, leading to 1,2-digermylethylenes, could be catalyzed by a palladium complex [8].

We have reported recently a new Pd-catalyzed reaction of trimethylgermyl cyanide (Me_3GeCN, **1**) with acetylenes to give β-cyano vinylgermanes (eqn. (1)) [9]. Both aromatic and aliphatic terminal acetylenes underwent the addition reaction with high regioselectivity. Noteworthy was the simple procedure, *i.e.* bulb-to-bulb distillation, for the isolation of analytically pure samples. The new catalytic reaction (1) has now been studied further with particular emphasis focused on functional group compatibility as well as the factor affecting stereoselectivity, in order to facilitate its use in synthetic organic chemistry. The application of the new catalytic reaction to 1,6-enyne and 1,6-diyne compounds has also been examined.



(1)

2. Results and discussion

2.1. Reaction of terminal acetylenes

The addition of Me_3GeCN (**1**) to terminal acetylenes proceeds in refluxing toluene in the presence of $PdCl_2$ as catalyst. By use of two equivalents of **1** the reactions were complete within 2 h and essentially pure addition products could be isolated in excellent yields by simple distillation. The catalytic reaction of **1** is faster than that of Me_3SiCN [10] which requires 15 h under the same reaction conditions.

Correspondence to: Professor S. Murai or Professor N. Chatani.

0022-328X/94/$7.00
SSDI 0022-328X(94)24459-V

The results of the catalytic addition of **1** to various acetylenes are given in Table 1. We have previously reported [9] that the catalytic reaction tolerates some functional groups including F, Cl, CH_3O, AcO, and CN. We show here that the catalytic reaction exhibits further compatibility with the synthetically more im-

TABLE 1. Palladium-catalyzed addition of Me_3GeCN to acetylenes [a]

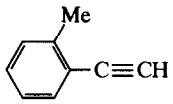
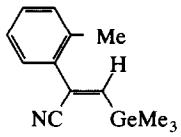
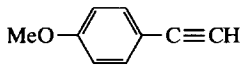
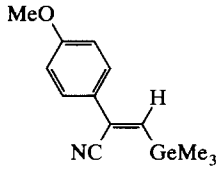
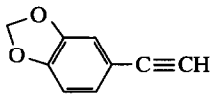
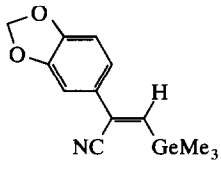
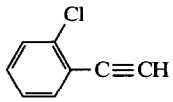
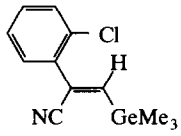
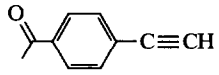
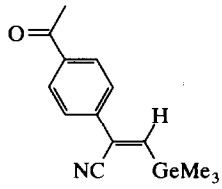
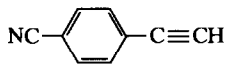
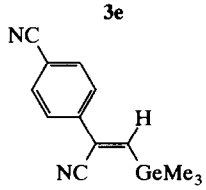
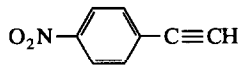
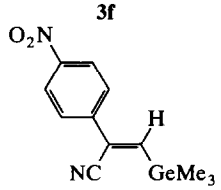
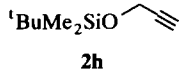
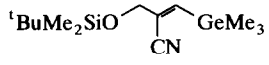
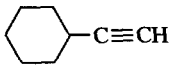
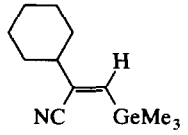
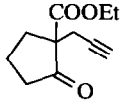
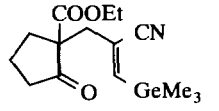
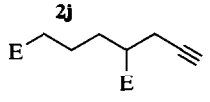
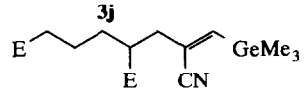
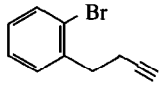
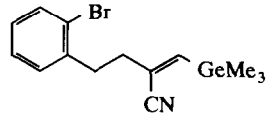
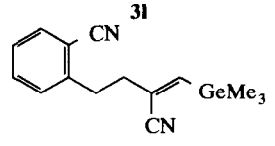
Run	Acetylene	Product	Yield (%) ($Z:E$) [b]
1	 **2a**	 **3a**	88 (93:7)
2	 **2b**	 **3b**	86 (60:40)
3	 **2c**	 **3c**	76 (74:26)
4	 **2d**	 **3d**	97 (98:2)
5	 **2e**	 **3e**	90 (> 99:1)
6	 **2f**	 **3f**	90 (> 99:1)
7	 **2g**	 **3g**	75 (> 99:1)
8	 **2h**	 **3h**	92 (> 99:1)

TABLE 1 (continued)

Run	Acetylene	Product	Yield (%) ($Z:E$) [b]
9	 **2i**	 **3i**	87 (> 99:1)
10	 **2j**	 **3j**	96 (> 99:1)
11	 **2k**	 E = COOEt **3k**	94 (> 99:1)
12	 **2l**	 **3l**	49 (98:2)
		 **3m**	35 (98:2)

[a] Reaction conditions: acetylene (1 mmol), Me_3GeCN (1) (2 mmol), $PdCl_2$ (0.1 mmol), toluene (2 ml), reflux, 2 h. [b] Isolated yields.

portant functional groups such as acetal (run 3), aromatic and aliphatic ketones (runs 5 and 10, respectively), aromatic cyano (run 6), aromatic nitro (run 7), propargylic siloxy (run 8), and esters (runs 10 and 11), except for an aromatic bromine bond. Displacement of bromide by cyanide was observed in the case of **2l**, leading to the expected product **3l** in 49% yield along with cyanated **3m** in 35% yield (run 12) [11].

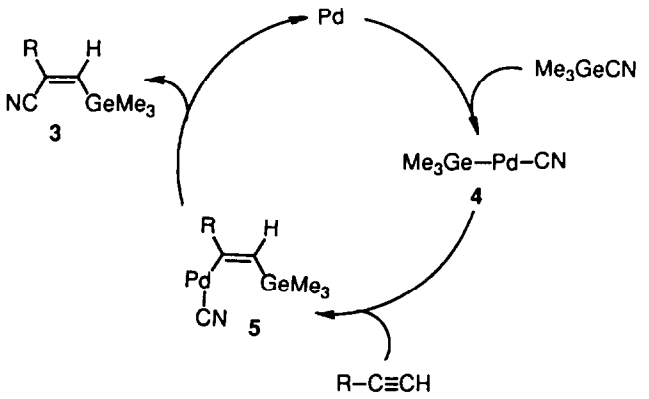
Generally, the catalytic reaction proceeds in the manner of highly-selective *syn* addition to give *Z*-products, *e.g.* $Z/E = 97/3$ for phenylacetylene (R = Ph in eqn. (1)) [9]. As we reported previously, the Z/E ratios for the reaction of *o*- and *m*-methoxyphenylacetylene were 75/25 and 96/4, respectively [9]. The catalytic reactions of *o*-methylphenylacetylene (run 1) and *p*-methoxyphenylacetylene (run 2) were carried out in order find out whether the low Z/E ratio for *o*-methoxyphenylacetylene was due to steric or electronic reasons. The higher Z/E ratio (93/7) of run 1 indicates that there are no steric reasons. Thus, the electronic factor operates for the *p*-methoxy (entry 2) and *o*-methoxy cases (see above and ref. 9), and will be discussed in terms of a description of the mechanism (see below).

For all arylacetylenes with electron withdrawing groups, high stereoselectivity could be observed (runs 5–7). Aliphatic acetylenes also reacted with **1** in the presence of $PdCl_2$ to give the corresponding β-cyano vinylgermanes in high yields with extremely high stereoselectivity (runs 8–12). The reaction of internal acetylenes, *i.e.* 1-phenyl-1-propyne, 4-octyne, and diphenylacetylene, with **1** did not give addition products; the starting materials were recovered. As shown in run 8, a silyl propargyl ether **2h** reacted cleanly. However, a similar reaction of Me_3SiCN with **2h** did not proceed cleanly, but this is not yet fully understood.

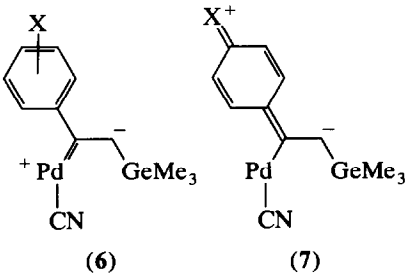
2.2. Reaction mechanism

The proposed reaction mechanism is shown in Scheme 1. The catalytic cycle begins with the oxidative addition of **1** to the Pd catalyst to give a germylpalladium cyanide **4**, although the process is not precedented. The insertion of the coordinated acetylene into the Ge–Pd bond in **4** gives the β-germyl vinylpalladium complex **5** [12], this step being the regio- and stereo-determining step. Complex **5** undergoes reductive elimination to give the final product **3**, regenerating the Pd^0 catalyst. Alternatively, complex **4** can undergo migratory insertion of an acetylene into the Pd–CN bond followed by reductive elimination. This alternative mechanism is less likely because it does not account for

the lower selectivities for aromatic acetylenes having electron-donating groups and it also does not account for the formation of cyclized products starting from 1,6-enynes. The lower stereoselectivity observed for *o*- and *p*-methoxyphenylacetylenes can be rationalized by isomerization of the vinylpalladium intermediate **5**. Complex **5** suffers from steric congestion between the trimethylgermyl group and the palladium moiety. Thus, **5***Z* undergoes partial isomerization to **5***E* via a twitterionic carbene complex **6**. Electron-donating methoxy group stabilizes the twitterion **6** by the contribution of the structure **7** [13] and therefore accelerates the rate of isomerization leading to low *Z*/*E* ratio of the products. Alternatively, another molecule of acetylene having an electron-withdrawing group may act as the π-acid ligand that facilitates reductive elimination [14] in **5** to produce a *Z*-isomer. However, as high *Z*/*E* ratios are observed not only for electron-decicient aromatic acetylenes but also for aliphatic acetylenes (runs 9–12), which are relatively weak π-acids, the latter explanation might not be appropriate.



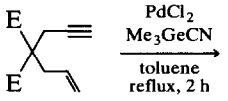
Scheme 1.



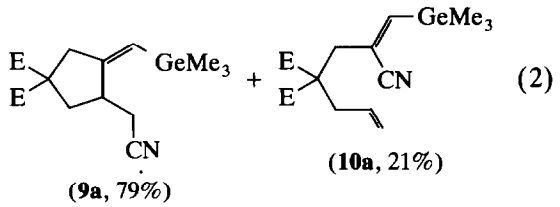
(6) (7)

2.3. Reaction of 1,6-enynes

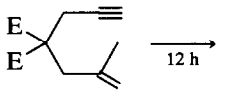
The applicability of the current reaction towards enynes has been examined. With acetylenes having an olefin function in a suitable position, formation of a carbocyclic framework containing useful functional groups could be anticipated. Furthermore, the structure of the cyclized products, if obtained, could give useful information on the reaction mechanism involved. The reaction of 1,6-enyne **8a** with **1** in the presence of a catalytic amount of $PdCl_2$ gave the cyclization product **9a** in 79% yield, along with the uncyclized adduct **10a** in 21% yield (eqn. (2)). Although various palladium complexes were used as catalyst to improve the selectivity of **9a**, satisfactory results have so far not been obtained. Introduction of a methyl group into the olefin moiety did not lead to selective cyclization (eqn. (3)). The structure of the products support the proposed mechanism involving the insertion of acetylene into the Ge–Pd bond in **4**, leading to vinylpalladium species such as **5** and **11**. The intermediate **11** undergoes intramolecular carbometallation to give **12** and further reductive elimination yields the cyclized product **9a**.



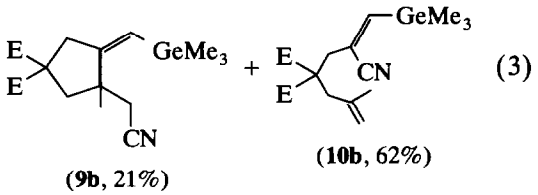
(8a)



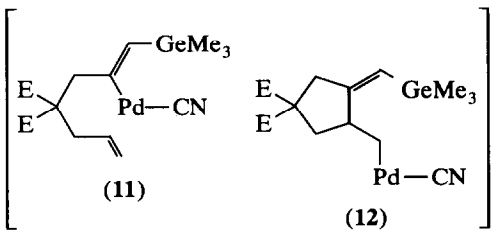
(9a, 79%) (10a, 21%) (2)



(8b)



(9b, 21%) (10b, 62%) (3)

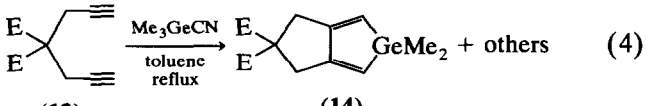


(11) (12)

2.4. Reaction of 1,6-diynes

We examined also the Pd-catalyzed cyclization reaction of 1,6-diynes with **1**. The reaction of diethyl dipropargylmalonate (**13**) with **1**, using $PdCl_2$ as the catalyst, gave the germole **14** as an unexpected product

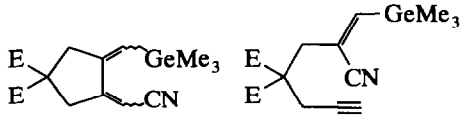
along with usual addition products such as **15** and **16** (eqn. (4)). Although modifications in the catalytic system only marginally affect the product distribution, as shown in eqn. (4), $Pd(CN)_2$ was primarily effective for the predominant formation of the germole **14**. Geminal substitution has a marked effect on selectivity of formation of germole derivatives. The substrates possessing the simple tether, *e.g.* 1,6-heptadiyne or dipropargyl ether, did not give any corresponding germole, but simple addition products (not shown; similar to **15** and **16**) instead. The mechanism of the formation of **14** is not clear at the present time. Although the reaction suffers from substrate limitations and low selectivity, it provides a new entry to a germole [15].



(4)

(13) (14)

Catalyst	Time	14	Others
$PdCl_2$	2 h	51%	35%
$PdBr_2$	1 h	41%	68%
$Pd(OAc)_2$	2 h	28%	63%
$Pd(CN)_2$	20 h	77%	16%



(15) (16)

2.5. Conclusion

It has been shown that a variety of vinylgermanes can be synthesized by the $PdCl_2$-catalyzed reaction of terminal acetylenes with **1** with a high degree of regio- and stereoselectivity. Various functional groups such as methoxy, methylenedioxy, fluoro, chloro, acetoxy, cyano, ethoxycarbonyl, and even acetyl and nitro groups were compatible with this reaction, which is notably efficient. The reaction of 1,6-enynes with **1** resulted in intramolecular cyclization. However, the reaction of 1,6-diynes give a germole derivative.

3. Experimental details

3.1. General methods

^1H NMR and ^{13}C NMR spectra were recorded on a JEOL 270 spectrometer and are reported in ppm relative to 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, q = quartet, 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 or Shimadzu GCMS-QP 1000 with ionization voltages of 70 eV. Elemental analyses were performed by the Instrumental Analysis Center, Faculty of Engineering, Osaka University. Melting points (mp) were determined on a Yanagimoto micro melting point apparatus and have not been corrected. Bulb-to-bulb distillations were done on a Sibata glass tube oven GTO-250R; boiling points (bp) refer to air bath temperature and have not been corrected.

3.2. Material

Cyclohexylacetylene (**2i**), 4-octyne, 1-phenyl-1-propyne, and diphenylacetylene are commercially available. Preparation of (2-methyl)- (**2a**), (4-methoxy)- (**2b**), (3,4-methylenedioxy)- (**2c**), and ((2-chloro)phenyl)acetylene (**2d**) was by Corey's method [16]. (4-Acetyl)- (**2e**), (4-cyano)- (**2f**), and ((4-nitro)phenyl)acetylene (**2g**) were prepared from the Pd-catalyzed coupling reaction of haloarenes with trimethylsilylacetylene, followed by hydrolysis [17]. Acetylene **2j** was prepared by treatment of 2-(carboethoxy)cyclopentanone with NaH, followed by addition of propargyl bromide. Acetylene **2k** was prepared by treatment of 2-(carboethoxy)cyclopentanone with NaOEt in EtOH followed by addition of propargyl bromide. Acetylene **2l** was prepared from treatment of 2-bromobenzyl iodide with allenyl Grignard [18]. Trimethylgermyl cyanide (**1**) was prepared according to the literature [19].

3.3. General procedure

In a 10-ml round-bottomed flask were placed acetylene (1 mmol) Me_3GeCN (2 mmol, 288 mg), and toluene (2 ml). To the mixture was then 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*. Distillation of the residue by Kugelrohr distillation gave essentially pure β-cyano vinylgermanes **3**. The physical properties of new compounds are given below.

3.4. 2-(2-Methylphenyl)-3-trimethylgermyl-(Z)-prop-2-enenitrile (3a)

Bp 80–90°C (2 Torr); ^1H NMR ($CDCl_3$) δ 0.49 (s, 9H, $GeCH_3$), 2.42 (s, 3H, CH_3), 6.89 (s, 1H, CH=), 7.19–7.26 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ −1.60 ($GeCH_3$), 19.99 (CH_3), 118.07 (CN), 126.32, 127.87, 128.74, 128.94, 130.65, 135.11, 137.10 (Ar, C=), 157.14 (CH=); IR (neat) 3068, 3024, 2984, 2916, 2812, 2212, 1604, 1568, 1486, 1462, 1416, 1386, 1298, 1240, 1214, 1192, 1160, 1114, 1034, 998, 972, 946, 860, 834, 768, 730; MS, *m/z* 261 (M^+ for ^{74}Ge, 0), 246 ($M^+ - Me$, 75), 130 (100); Anal. Calcd for $C_{13}H_{17}NGe$: C, 60.08; H, 6.59; N, 5.39. Found: C, 60.16; H, 6.74; N, 5.64.

3.5. 2-(4-Methoxyphenyl)-3-trimethylgermyl-prop-2-enenitrile (3b)

Bp 70–80°C (3 Torr); ^{1}H NMR ($CDCl_3$)δ [0.19 (s, *E*), 0.47 (s, *Z*), 9H, $GeCH_3$], 3.83 (s, 3H, CH_3O), [6.99 (s, *E*), 7.15 (s, *Z*), 1H, CH=], [6.88–6.92, 7.29–7.32, 7.51–7.55 (m, 4H, Ar)]; ^{13}C NMR ($CDCl_3$)δ [−1.57, −0.44, ($GeCH_3$)], [55.33, 55.38, (CH_3O)], [118.04, 119.16 (CN)], 113.89, 114.15, 126.84, 127.55, 127.87, 129.43, 147.75, 153.38 (Ar, C=), [160.43, 160.52 (CH=)]; IR (neat) 2976, 2916, 2844, 2216, 1610, 1582, 1558, 1514, 1468, 1446, 1420, 1308, 1256, 1180, 1116, 1034, 998, 974, 832, 770, 728; MS, *m/z* 277 (M^+ for ^{74}Ge, 20), 262 (M^+ − Me, 100); Anal. Calcd for $C_{13}H_{17}NOGe$: C, 56.60; H, 6.21; N, 5.08. Found: C, 56.46; H, 6.48; N, 5.19.

3.6. 2-(3,4-Methylenedioxyphenyl)-3-trimethylgermyl-prop-2-enenitrile (3c)

Bp 105–110°C (3 Torr), Mp 62–66°C; ^{1}H NMR ($CDCl_3$) δ [0.21 (s, *E*), 0.47 (s, *Z*), 9H, $GeCH_3$], [6.00 (s, *Z*), 6.02 (s, *E*), 2H, OCH_2O], 6.80–6.95 (m, 3H, Ar); ^{13}C NMR ($CDCl_3$)δ [−1.60 (*Z*), −0.44 (*E*), ($GeCH_3$)], 101.57, 105.33, 108.23, 108.31, 117.90, 120.29, 122.24, 126.75, 129.30, 148.34, 148.45, 148.68, 154.10 (Ar, CN, CH=, C=); IR (KBr) 2980, 2912, 2220, 1560, 1508, 1494, 1450, 1354, 1286, 1240, 1104, 1046, 986, 946, 884, 854, 836, 816, 798, 772, 742; MS, *m/z* 291 (M^+ for ^{74}Ge, 39), 276 (M^+ − Me, 100); Anal. Calcd for $C_{13}H_{15}NO_2Ge$: C, 53.87; H, 5.22; N, 4.83. Found: C, 53.68; H, 5.22; N, 4.92.

3.7. 2-(2-Chlorophenyl)-3-trimethylgermyl-(Z)-prop-2-enenitrile (3d)

Bp 60–70°C (3 Torr); ^{1}H NMR ($CDCl_3$) δ 0.50 (s, 9H, $GeCH_3$), 7.08 (s, 1H, CH=), 7.27–7.39 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ −1.66 ($GeCH_3$), 117.40 (CN), 125.39, 127.18, 130.13, 130.19, 131.99, 135.81 (Ar, C=), 159.24 (CH=); IR (neat) 3072, 2984, 2916, 2812, 2220, 1596, 1576, 1474, 1442, 1298, 1240, 1210, 1162, 1128, 1062, 1034, 974, 950, 858, 834, 780, 754, 726; MS, *m/z* 281 (M^+ for ^{74}Ge, 1), 266 (M^+ − Me, 100); Anal. Calcd for $C_{12}H_{14}NClGe$: C, 51.42; H, 5.03; N, 5.00; Cl, 12.65. Found: C, 51.23; H, 5.14; N, 5.22; Cl, 12.61.

3.8. 2-(4-Acetylphenyl)-3-trimethylgermyl-(Z)-prop-2-enenitrile (3e)

Bp 100–110°C (3 Torr), Mp 70–72°C; ^{1}H NMR ($CDCl_3$)δ 0.51 (s, 9H, $GeCH_3$), 2.62 (s, 3H, CH_3), 7.48 (s, 1H, CH=), 7.68 (d, J = 8.6 Hz, 2H, Ar), 7.98 (d, J = 8.6 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$)δ −1.63 ($GeCH_3$), 26.65 (CH_3), 117.40 (CN), 125.70, 126.55, 128.88, 137.40, 138.73 (Ar, C=), 154.30 (CH=), 197.19 (C=O); IR (KBr) 2988, 2916, 2224, 1682, 1604, 1578, 1514, 1464, 1406, 1356, 1310, 1270, 1242, 1210, 1184, 1118, 1076, 1014, 978, 962, 882, 832, 774; MS, *m/z* 289 (M^+ for ^{74}Ge, 9), 274 (M^+ − Me, 100); Anal. Calcd for $C_{14}H_{17}NOGe$: C, 58.41; H, 5.95; N, 4.87. Found: C, 58.45; H, 5.96; N, 5.01.

3.9. 2-(4-Cyanophenyl)-3-trimethylgermyl-(Z)-prop-2-enenitrile (3f)

Bp 80–90°C (3 Torr), Mp 98–100°C; ^{1}H NMR ($CDCl_3$)δ 0.51 (s, 9H, $GeCH_3$), 7.50 (s, 1H, CH=), 7.70 (s, 4H, Ar); ^{13}C NMR ($CDCl_3$)δ −1.66 ($GeCH_3$), 112.94 (CN), 117.00 (CN), 118.15, 125.91, 126.14, 132.68, 138.69 (Ar, C=), 155.80 (CH=); IR (KBr) 2988, 2920, 2228, 1608, 1576, 1552, 1462, 1410, 1314, 1302, 1238, 1212, 1178, 1126, 1014, 976, 832, 772, 706; MS, *m/z* 272 (M^+ for ^{74}Ge, 7), 257 (M^+ − Me, 100); Anal. Calcd for $C_{13}H_{14}N_2Ge$: C, 57.65; H, 5.21; N, 10.34. Found: C, 57.73; H, 5.18; N, 10.34.

3.10. 2-(4-Nitrophenyl)-3-trimethylgermyl-(Z)-prop-2-enenitrile (3g)

Bp 110–120°C (3 Torr); ^{1}H NMR ($CDCl_3$)δ 0.53 (s, 9H, $GeCH_3$), 7.57 (s, 1H, CH=), 7.76 (d, J = 9.0 Hz, 2H, Ar), 8.27 (d, J = 9.0 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$)δ −1.66 ($GeCH_3$), 116.99 (CN), 124.17, 125.61, 126.42, 140.40, 148.10 (Ar, C=), 156.85 (CH=); IR (neat) 2988, 2924, 2324, 1600, 1562, 1524, 1462, 1410, 1342, 1304, 1234, 1188, 1108, 1008, 978, 848, 750; MS, *m/z* 292 (M^+ for ^{74}Ge, 0), 279 (M^+ − Me, 13), 130 (100); Anal. Calcd for $C_{12}H_{14}N_2O_2Ge$: C, 49.56; H, 4.85; N, 9.63. Found: C, 49.71; H, 4.85; N, 9.92.

3.11. 2-(t-Butyldimethylsilyloxy)methyl-3-trimethylgermyl-(Z)-prop-2-enenitrile (3h)

Bp 40–50°C (3 Torr); ^{1}H NMR ($CDCl_3$)δ 0.10 (s, 6H, $SiCH_3$), 0.40 (s, 9H, $GeCH_3$), 0.91 (s, 9H, CH_3), 4.22 (d, J = 1.7 Hz, 2H, CH_2O), 6.88 (t, J = 1.7 Hz, 1H, CH=); ^{13}C NMR ($CDCl_3$)δ −5.37 ($SiCH_3$), −1.71 ($GeCH_3$), 18.34 (CH_3), 25.78 (C), 65.37 (CH_2O), 117.60 (CN), 127.26 (C=), 149.53 (CH=); IR (neat) 2964, 2940, 2864, 2220, 1602, 1476, 1412, 1394, 1364, 1258, 1134, 1090, 1008, 940, 838, 780; MS, *m/z* 315 (M^+ for ^{74}Ge, 0), 300 (M^+ − Me, 1), 119 (100); Anal. Calcd for $C_{13}H_{27}NOSiGe$: C, 49.72; H, 8.67; N, 4.46. Found: C, 49.44; H, 8.81; N, 4.76.

3.12. 2-Cyclohexyl-3-trimethylgermyl-(Z)-prop-2-enenitrile (3i)

Bp 70–80°C (3 Torr); ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 9H, $GeCH_3$), 1.12–1.36 (m, 5H, CH_2), 1.66–1.83 (m, 5H, CH_2), 2.09–2.13 (m, 1H, CH), 6.53 (d, J = 1.2 Hz, 1H, CH=); ^{13}C NMR ($CDCl_3$) δ −1.66 ($GeCH_3$), 25.57, 25.84, 31.47 (CH_2), 46.10 (CH), 118.50 (CN), 134.06 (C=), 148.51 (CH=); IR (neat) 2975, 2934, 2858, 2214, 1585, 1453, 1415, 1238, 990, 895, 833; MS, *m/z*

253 (M^+ for ^{74}Ge, 0), 238 ($M^+ - Me$, 100); Anal. Calcd for $C_{12}H_{21}NGe$: C, 57.22; H, 8.40; N, 5.56. Found: C, 57.63; H, 8.65; N, 5.83.

*3.13. 2-(1-Ethoxycarbonyl-2-oxocyclopentyl)methyl-3-trimethylgermyl-(Z)-prop-2-enenitrile (**3j**)*

Bp 70–80°C (3 Torr); ^1H NMR ($CDCl_3$)δ 0.38 (s, 9H, $GeCH_3$), 1.26 (t, $J = 7.0$ Hz, 3H, CH_3), 1.92–2.13 (m, 3H, CH_2), 2.18–2.33 (m, 1H, CH_2), 2.39–2.52 (m, 1H, CH_2), 2.55 (dd, $J = 14.3$, 1.1 Hz, 1H, CH_2C=), 2.58–2.70 (m, 1H, CH_2), 3.02 (dd, $J = 14.3$, 1.1 Hz, 1H, CH_2C=), 4.16 (q, $J = 7.0$ Hz, 4H, CH_2O), 6.71 (t, $J = 1.1$ Hz, 1H, CH=); ^{13}C NMR ($CDCl_3$)δ −1.88 ($GeCH_3$), 13.96 (CH_3), 19.52, 31.99, 37.55, 41.46 (CH_2), 60.16, 61.84 (CH_2O, C), 118.68 (CN), 122.78 (C=), 158.00 (CH=), 169.37, 212.94 (C=O); IR (neat) 2984, 2916, 2220, 1758, 1728, 1634, 1584, 1470, 1452, 1410, 1368, 1322, 1298, 1268, 1238, 1200, 1162, 1118, 1023, 962, 924, 834, 772; MS, m/z 339 (M^+ for ^{74}Ge, 0), 324 ($M^+ - Me$, 12), 119 (100); Anal. Calcd for $C_{15}H_{23}NO_3Ge$: C, 53.31; H, 6.86; N, 4.15. Found: C, 53.41; H, 6.76; N, 4.37.

*3.14. 2-[2-Cyano-3-(trimethylgermyl)-2-propenyl]hexanoic acid diethyl ester (**3k**)*

Bp 130–140°C (3 Torr); ^1H NMR ($CDCl_3$)δ 0.36 (s, 9H, $GeCH_3$), 1.24 (t, $J = 7.1$ Hz, 6H, CH_3), 1.45–1.70 (m, 4H, CH_2), 2.25–2.77 (m, 5H, CH_2, CH), 4.10 (q, $J = 7.1$ Hz, 4H, CH_2O), 4.14 (q, $J = 7.1$ Hz, 4H, CH_2O), 6.62 (t, $J = 1.7$ Hz, 1H, CH=); ^{13}C NMR ($CDCl_3$)δ −1.88 ($GeCH_3$), 14.12, 14.17 (CH_3), 22.30, 31.04, 33.79, 40.79, 43.81, (CH_2, CH), 60.24, 60.54 (CH_2O), 118.23 (CN), 124.98 (C=), 154.36 (CH=), 172.94, 174.06 (C=O); IR (neat) 2980, 2920, 2220, 1736, 1628, 1590, 1450, 1422, 1378, 1352, 1298, 1240, 1180, 1096, 1028, 940, 834, 772; MS, m/z 385 (M^+ for ^{74}Ge, 0), 370 ($M^+ - Me$, 92), 119 (100); Anal. Calcd for $C_{17}H_{29}NO_4Ge$: C, 53.17; H, 7.61; N, 3.65. Found: C, 52.68; H, 7.63; N, 3.89.

*3.15. 2-[(2-Bromophenyl)ethyl]-3-trimethylgermyl-(Z)-prop-2-enenitrile (**3l**)*

Bp 80–90°C (3 Torr); ^1H NMR ($CDCl_3$)δ 0.35 (s, 9H, $GeCH_3$), 2.60 (t, $J = 7.3$ Hz, 2H, CH_2), 2.99 (t, $J = 7.3$ Hz, 2H, CH_2), 6.47 (s, 1H, CH=), 7.05–7.11 (m, 1H, Ar), 7.19–7.25 (m, 2H, Ar), 7.53 (d, $J = 7.8$ Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$)δ −1.78 ($GeCH_3$), 34.64 (CH_2), 38.51 (CH_2), 118.70 (CN), 124.26, 126.58, 127.44, 128.13, 130.83, 132.89, 139.16 (Ar, C=), 152.96 (CH=); IR (neat) 3068, 2980, 2920, 2220, 1590, 1572, 1476, 1444, 1418, 1344, 1298, 1240, 1208, 1160, 1120, 1090, 1026, 948, 914, 834, 748, 720; MS, m/z 354 (M^+ for ^{74}Ge, 0.3), 338 (100); Anal. Calcd for $C_{14}H_{18}NBrGe$: C, 47.66; H, 5.14; N, 3.97. Found: C, 47.75; H, 5.18; N, 4.01.

*3.16. 2-[(2-Cyanophenyl)ethyl]-3-trimethylgermyl-(Z)-prop-2-enenitrile (**3m**)*

Bp 80–90°C (3 Torr); ^1H NMR ($CDCl_3$)δ 0.35 (s, 9H, $GeCH_3$), 2.66 (dt, $J = 7.8$, 1.5 Hz, 2H, CH_2), 3.10 (t, $J = 7.8$ Hz, 2H, CH_2), 6.53 (t, $J = 1.5$ Hz, 1H, CH=), 7.30–7.36 (m, 2H, Ar), 7.53 (t, $J = 7.6$ Hz, 1H, Ar), 7.65 (t, $J = 6.8$ Hz, 1H, Ar); ^{13}C NMR ($CDCl_3$)δ −1.81 ($GeCH_3$), 32.96, 39.20 (CH_2), 112.33 (CN), 117.74, 118.45, 125.87, 127.12, 130.07, 132.85, 133.00, 143.68 (Ar, CN, C=), 153.87 (CH=); IR (neat) 3072, 2980, 2920, 2876, 2228, 1602, 1590, 1490, 1454, 1418, 1342, 1304, 1288, 1240, 1214, 1164, 1110, 1090, 1042, 1010, 958, 836, 762, 710; MS, m/z 300 (M^+ for ^{74}Ge, 0), 285 ($M^+ - Me$, 100); Anal. Calcd for $C_{15}H_{18}N_2Ge$: C, 60.27; H, 6.07; N, 9.37. Found: C, 59.88; H, 6.10; N, 9.17.

*3.17. (3-Cyanomethyl)-4-[(trimethylgermyl)methylene]-1,1-cyclopentanedicarboxylic acid diethyl ester (**9a**)*

^1H NMR ($CDCl_3$)δ 0.28 (s, 9H, $GeCH_3$), 1.24 (t, $J = 7.0$ Hz, 3H, CH_3), 1.27 (t, $J = 7.0$ Hz, 3H, CH_3), 4.20 (q, $J = 7.0$ Hz, 4H, CH_2O), 5.69 (m, 1H, CH=); ^{13}C NMR ($CDCl_3$)δ −0.44 ($GeCH_3$), 13.99 (CH_3), 23.73, 38.77, 38.86, 43.78, 58.30 (CH_2, CH), 61.69, 61.87 (CH_2O), 77.18 (C), 118.20 (CN), 126.11 (CH=), 154.99 (C=), 171.06 (C=O), 171.58 (CO); IR (neat) 2982, 2942, 2912, 2250, 2218, 1734, 1634, 1469, 1450, 1429, 1391, 1368, 1283, 1245, 1188, 1161, 1097, 1074, 1019, 900, 862, 831, 766, 721; MS, m/z 383 (M^+ for ^{74}Ge, 0), 368 ($M^+ - Me$, 100); Anal. Calcd for $C_{17}H_{27}NO_4Ge$: C, 53.45; H, 7.12; N, 3.67. Found: C, 53.15; H, 7.20; N, 3.82.

*3.18. [2-Cyano-3-(trimethylgermyl)-2-propenyl]-2-propenylpropanedioic acid diethyl ester (**10a**)*

^1H NMR ($CDCl_3$)δ 0.38 (s, 9H, $GeCH_3$), 1.27 (t, $J = 7.1$ Hz, 6H, CH_3), 2.72 (dt, $J = 7.3$, 1.0 Hz, 2H, CH_2), 2.89 (d, $J = 1.0$ Hz, 2H, CH_2), 4.20 (t, $J = 7.1$ Hz, 4H, CH_2O), 5.11–5.14 (m, 1H, CH=), 5.16–5.20 (m, 1H, CH=), 5.57–5.73 (m, 1H, CH=), 6.70 (t, $J = 1.0$ Hz, 1H, CH=); IR (neat) 2982, 2912, 2218, 1737, 1645, 1582, 1468, 1447, 1391, 1368, 1281, 1242, 1208, 1185, 1095, 1067, 926, 863, 833, 773.

*3.19. (3-Cyanomethyl)-3-methyl-4-[(trimethylgermyl)methylene]-1,1-cyclopentanedicarboxylic acid diethyl ester (**9b**)*

^1H NMR ($CDCl_3$)δ 0.29 (s, 9H, $GeCH_3$), 1.25 (t, $J = 7.1$ Hz, 3H, CH_3), 1.26 (t, $J = 7.1$ Hz, 3H, CH_3), 1.32 (s, 3H, CH_3), 2.21 (d, $J = 14.1$ Hz, 1H, CH_2), 2.47 (d, $J = 6.8$ Hz, 2H, CH_2), 2.67 (d, $J = 14.1$ Hz, 1H,

CH_2), 3.15 (d, $J = 2.0$ Hz, 2H, CH_2), 4.20 (q, $J = 7.1$ Hz, 4H, CH_2O), 5.62 (t, $J = 2.0$ Hz, 1H, CH=).

*3.20. [2-Cyano-3-(trimethylgermyl)-2-propenyl]-(2-methyl-2-propenyl)propanedioic acid diethyl ester (**10b**)*

^{1}H NMR ($CDCl_3$)δ 0.37 (s, 9H, $GeCH_3$), 1.26 (t, $J = 7.1$ Hz, 6H, CH_3), 1.68 (m, 3H, CH_3), 2.77 (s, 2H, CH_2), 2.94 (d, $J = 1.0$ Hz, 2H, CH_2), 4.20 (q, $J = 7.1$ Hz, 4H, CH_2O), 4.78 (m, 1H, CH_2=). 4.90 (t, $J = 1.6$ Hz, 1H, CH_2=), 6.72 (t, $J = 1.1$ Hz, 1H, CH=); IR (neat) 3084, 2984, 2940, 2916, 2916, 2216, 1738, 1648, 1582, 1450, 1392, 1370, 1332, 1296, 1270, 1240, 1204, 1184, 1106, 1096, 1076, 1020, 900, 864, 834, 774; Anal. Calcd for $C_{18}H_{29}NO_4Ge$: C, 54.59; H, 7.38; N, 3.54. Found: C, 54.46; H, 7.64; N, 3.89.

*3.21. Germole **14***

^{1}H NMR ($CDCl_3$)δ 0.38 (s, 6H, $GeCH_3$), 1.24 (t, $J = 7.0$ Hz, 6H, CH_3), 3.03 (d, $J = 1.6$ Hz, 4H, CH_2), 4.19 (q, $J = 7.0$ Hz, 4H, CH_2O), 5.82 (t, $J = 1.6$ Hz, 2H, CH=); ^{13}C NMR ($CDCl_3$)δ -3.31 ($GeCH_3$), 13.99 (CH_3), 38.16 (CH_2), 60.53 (C), 61.48 (CH_2O), 121.13 (CH=), 156.79 (C=), 171.48 (C=O); IR (neat) 2988, 2916, 1738, 1675, 1560, 1465, 1455, 1420, 1395, 1370, 1278, 1240, 1186, 1155, 1095, 1064, 864, 836, 804, 705; Anal Calcd for $C_{15}H_{22}O_4Ge$: C, 53.16; H, 6.54. Found: C, 52.88; H, 6.70.

Acknowledgements

This work is supported in part by grants from the Ministry of Education, Science, and Culture, Japan. N.C. is grateful to Watanabe Foundation for genius financial support.

References and notes

1 E. Colvin, *Silicon in Organic Synthesis*, Butterworths, London, 1981; P. Magnus and T.S. Sarkar, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 7, Pergamon, Oxford, 1982; W.P. Weber, *Silicon Reagents for Organic Synthesis*, Spring-Verlag, Berlin, 1983.

2 M. Pereyre, J.-P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, 1989; J.L. Wardell, in P.G. Harrison (ed.), *Chemistry of Tin*, Blackie & Son, London, 1989, Chap. 10.

3 For a paper on the transformation of alkenylgermanes to alkenyl halides, see: H. Oda, Y. Morizawa, K. Oshima and H. Nozaki, *Tetrahedron Lett.*, *25* (1984) 3221; E. Piers and P.C. Marais, *J. Org. Chem.*, *55* (1990) 3454.

4 D. Barton and W.D. Ollis, in G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Vol. 3, Pergamon, Oxford, 1979.

5 F. Wada, S. Abe, N. Yonemaru, K. Kikukawa and T. Matsuda, *Bull. Chem. Soc. Jpn.*, *64* (1991) 1701.

6 Y. Ichinose, K. Nozaki, K. Wakamatsu, K. Oshima and K. Utimoto, *Tetrahedron Lett.*, *28* (1987) 3709; K. Nozaki, Y. Ichinose, K. Wakamatsu, K. Oshima and K. Utimoto, *Bull. Chem. Soc. Jpn.*, *63* (1990) 2268.

7 E. Piers and R.T. Skerlj, *J. Chem. Soc., Chem. Commun.*, (1987) 1025.

8 T. Tsumuraya and W. Ando, *Organometallics*, *8* (1989) 2286; T. Hayashi, H. Yamashita, T. Sakakura, Y. Uchimaru and M. Tanaka, *Chem. Lett.*, (1991) 245.

9 N. Chatani, N. Horiuchi and T. Hanafusa, *J. Org. Chem.*, *55* (1990) 3393.

10 N. Chatani and T. Hanafusa, *J. Chem. Soc., Chem. Commun.*, (1985) 838; N. Chatani, T. Takeyasu, N. Horiuchi and T. Hanafusa, *J. Org. Chem.*, *55* (1988) 3539.

11 The Pd-catalyzed reaction of aryl iodides with Me_3SiCN leading to aryl cyanides has been reported previously: N. Chatani and T. Hanafusa, *J. Org. Chem.*, *51* (1986) 4714.

12 Insertion of C=C and C ≡ C bonds to a Ge–Pd bond is postulated in the Pd-catalyzed reactions of olefins and acetylenes with digermanes. See ref 8. Recently, silylpalladation of an acetylene with a Si–Pd–I species was reported. H. Yamashita, M. Tanaka and M. Goto, *Organometallics*, *12* (1993) 988. See also a recent review on silylmetalation. S. Murai and N. Chatani, *J. Synth. Org. Chem. Jpn.*, *51* (1993) 421.

13 Recently, isomerization via a similar twitterion carbene type complex was proposed by Ojima and Alper. I. Ojima, N. Clos, R.J. Donovan and P. Ingallina, *Organometallics*, *9* (1990) 3127; D. Zargarian and H. Alper, *Organometallics*, *10* (1991) 2914.

14 H. Kurosawa, M. Emoto, H. Ohnishi, K. Miki, N. Kasai, K. Tatsumi and A. Nakamura, *J. Am. Chem. Soc.*, *109* (1987) 6333.

15 For recent papers on the preparation of germoles, see: P.J. Fagan and W.A. Nugent, *J. Am. Chem. Soc.*, *110* (1988) 2310; T. Tsumuraya and W. Ando, *Organometallics*, *9* (1990) 869. H. Brauer and W.P. Neumann, *Synlett.*, (1991) 431. J.-D. Andriamizaka, C. Couret and J. Escudié, *J. Organomet. Chem.*, 419 (1991) 57.

16 E.J. Corey and P.L. Fuchs, *Tetrahedron Lett.*, (1972) 3769.

17 S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, (1980) 627.

18 R.-T. Wang, F.-L. Chou and F.-T. Lou, *J. Org. Chem.*, *55* (1990) 4846.

19 E.W. Abel, D.A. Armitoge and D.B. Brady, *J. Organomet. Chem.*, *5* (1966) 130.