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Synthesis of stanna- and germa-cycloheptatrienes

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Abstract

The first preparations of C-unsubstituted stannacycloheptatriene and germacycloheptatriene, analogues of cycloheptatriene, are described with their spectroscopic properties. A stannacyclohexadienyl anion derived from stannacyclohexadiene by treatment with lithium di-isopropylamide was allowed to react with chlorocarbene generated from dichloromethane and n-butyllithium, and this led to the formation of the corresponding stannacycloheptatriene. The disproportionation reaction between the stannacyclohexadiene and dichlorodimethylgermane gave the corresponding germacyclohexadiene in reasonable yield. In a similar manner, the reaction of the germacyclohexadienyl anion with chlorocarbene yielded C-unsubstituted germacycloheptatriene.

Introduction

Recently, we reported the first synthesis of C-unsubstituted silacycloheptatrienes (silepin) such as **1a**, together with their spectroscopic and chemical properties [1–3]. The silepin can be routinely prepared by ring enlargement of 1-sila-2,4-cyclohexadiene (**2a**) with concomitant introduction of one more double bond into the ring. This has been accomplished by the reaction of the silacyclohexadienyl anion **3a** with dichloromethane in the presence of BuLi (Scheme 1). Since our knowledge of stannacycloheptatriene (stannepin) [4–5] and germacycloheptatriene (germepin) [6] has been limited to benzo-fused and dibenzo-fused systems, respectively, we have extended successfully our studies of silepin **1a** to include other Group 14 element heteropins, such as stannepin **1b** and germepin **1c** [3,7*]. Further, by means of ligand exchange, **1b** has been found to be transformed bora-cycloheptatriene (borepin), the neutral analogue of tropylium ion [7*–9].

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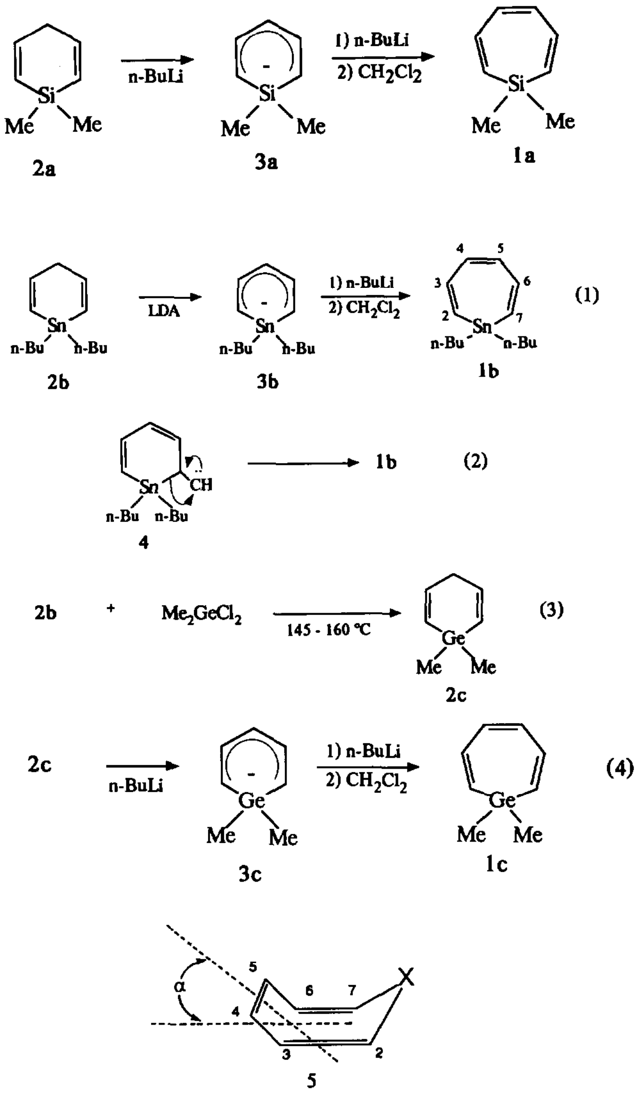
* Reference number with an asterisk indicates a note in the list of references.



Scheme 1.

Results and discussion

*Preparation of 1,1-di-n-butyl-1-stannacyclohepta-2,4,6-triene (1,1-di-n-butylstannepin) (**1b**)*

By analogy with the synthesis of silepin, stannacyclohexadiene **2b** is expected to act as a precursor of stannepin **1b**. The starting material, 1,1-di-n-butyl-1-stannacyclohexa-2,5-diene (**2b**) was prepared by hydrostannation of 1,4-pentadiyne with dibutylstannane [10,11]. Although silacyclohexadienyl anion **3a** is prepared by abstraction of a proton from silacyclohexadiene **2a** with BuLi, the same method may not be applicable to **2b**, since the vinyl–tin bond is reported to be cleaved readily by alkyllithium [11]. This difficulty can be overcome by employing a base with low nucleophilicity such as lithium di-isopropyl amide (LDA). To a solution of 1.4 equiv. of LDA in ether was added **2b** at 0°C. The solution changed colour gradually from yellow to green. After 1 h the solution was cooled to −78°C and 4.0 equiv. of BuLi followed by 3.0 equiv. of CH_2Cl_2 were added. The resulting mixture was allowed to warm to room temperature and turned brown with precipitation of salt. After hydrolysis and the usual workup, the reaction mixture was submitted to TLC on silica gel to give stannepin **1b** as a colourless oil in 33% yield.

The structure of **1b** is deduced from spectroscopic data. The ^1H NMR spectrum of **1b** shows an [AA'BB'CC'] pattern due to the six ring protons centred at δ 6.08, 6.21 and 7.07 ppm. These signals have been analyzed by means of spectral simulation (Fig. 1 and Table 1). The ^{13}C NMR spectrum of **1b** shows three doublets at δ 132.5, 133.4 and 142.0 ppm due to the secondary olefinic carbons together with signals ascribable to those of butyl groups. No molecular ion peak was obtained in the mass spectrum of **1b** but the peak at m/z 255 (46%) corresponding to loss of a butyl group from $C_{14}H_{24}{}^{120}Sn$ was observed instead.

From the close similarity between the Si–C and the Sn–C bonds in electronic properties, the key step of the formation of **1b** is considered to be 1,2-migration of the stannyl group to the carbene centre as shown in **4** derived from the reaction of **3b** and chlorocarbene [1–3].

Preparation of 1,1-dimethyl-1-germacyclohepta-2,4,6-triene (1,1-dimethylgermepin) (1c)

By analogy with preparation of silepin **1a** and stannepin **1b**, synthesis of C-unsubstituted germepin **1c** is expected to be accomplished by the reaction of germacyclohexadienyl anion **3c** with chlorocarbene. To date, no C-unsubstituted germacyclohexadiene **2c** has been reported, and only two examples with heteroatom substituents have been described [12–13]. Their conversion to the corresponding anion is difficult due to the nature of substituents on these germacyclohexadienes. Hence, a new synthetic method of C-unsubstituted germacyclohexadiene **2c** has to be explored. Since metal–metal exchange reaction between alkyl stannanes and chlorogermanes is known to occur at high temperature [14], germacyclohexadiene **2c** is expected to be prepared by the disproportionation reaction between **2b** and dichlorodimethylgermane. When a 1 : 1 mixture of the two was heated to 145–165°C for 26 h under argon, **2c** was obtained in 41% yield as the sole product after distillation under vacuum. To a solution of **2c** in ether was added 3.5 equiv. of BuLi at 0°C, and the solution turned yellow indicating the formation of germacyclohexadienyl anion **3c**. Then, 2.5 equiv. of CH_2Cl_2 was added to this solution at −78°C. The reaction mixture was allowed to warm to room temperature. After usual workup, the reaction mixture was submitted to TLC on silica gel to give **1c** as a colourless oil in 26% yield. The structure was determined on the basis of the ^1H NMR spectrum, in which **1c** shows an [AA'BB'CC'] pattern due to the six vinyl protons, *i.e.* the two GeMe signals appear at δ 0.22 ppm and three kinds of vinyl protons are observed at δ 5.83, 6.30 and 6.82 ppm (Fig. 1 and Table 1). ^{13}C NMR spectrum of **1c** shows three doublets due to the secondary olefinic carbons at δ 132.2, 132.6, and 138.7 ppm. A molecular ion peak corresponding to $C_8H_{12}{}^{74}Ge$ was obtained at m/z 182 on the FI mass spectrum of **1c**.

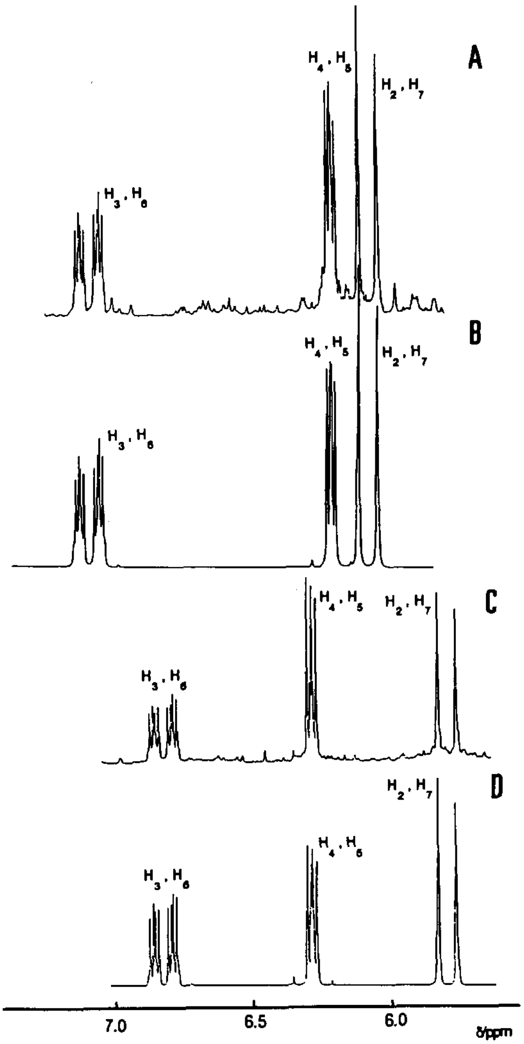


Fig. 1. Experimental and simulated ^1H NMR spectra of **1b** and **1c** (olefinic region). (A) and (C), observed spectra of **1b** and **1c**, respectively; (B) and (D) simulated spectra of **1b** and **1c**, respectively.

Structure of 1,1-di-n-butylstannepin (1b) and 1,1-dimethylgermepin (1c)

Both 1,1-di-n-butylstannepin (**1b**) and 1,1-dimethylgermepin (**1c**) show [AA′BB′CC′] spectral patterns in their ^1H NMR spectra, which are consistent with those obtained from spectral simulation as shown in Fig. 1. Spectral parameters are summarized in Table 1. The geometry of a heteropin is known to be closely related to the coupling constant $J_{3,4}$ in its ^1H NMR spectrum [15–16]. Dihedral angles α between the base plane [C(2), C(3), C(6), C(7)] and the stern plane [C(3), C(4), C(5), C(6)] are estimated to be around 27 and 26° for **1b** and **1c**, respectively, where $J_{3,4}$ values are obtained to be 6.13 and 5.17 Hz, respectively (*cf.* **1a**: $J_{3,4} = 6.30$ Hz, $\alpha = 25°$).

In these heteropins, the relationship between dihedral angle α and J can be rationalized as follows [15,16]. The inner angle strain should increase with the

Table 1

Coupling constants (Hz) for **1a**, **1b**, and **1c** [a]

	1b	**1c**	**1a** [b]
$J_{2,3}$	13.88	13.18	14.31
$J_{3,4}$	5.71	6.13	6.30
$J_{4,5}$	13.52	12.74	12.70
$J_{2,4}$	0.39	0.55	0.61
$J_{2,5}$	0.38	0.74	0.70
$J_{2,6}$	−0.54	−0.39	−0.51
$J_{2,7}$	1.48	1.44	1.66
$J_{3,5}$	0.21	0.22	0.38
$J_{3,6}$	0.42	0.66	0.63

[a] Obtained by spectral simulation. [b] Ref. 1.

elongation of the carbon(C–2 and C–7)–metal bonds. The inner angle strain would be able to be released by the folding of the boat geometry. Hence the angle α should be the largest in stannepin **1b**.

These Group 14 element heteropins, **1a**, **1b**, and **1c** show absorption maxima at 281 nm (ϵ 2100), 279 nm (sh, ϵ 2100), and 279 nm (ϵ 2500), respectively, in their UV spectra in n-hexane. Since they adopt the folding boat geometry, the red shift of UV maximum of silepin **1a** compared with that of cycloheptatriene (261 nm) is ascribable to the possible cyclic σ–π conjugation involving one of the σ Si–Me bonds [1,17–20]. On the other hand, in the heavier element heteropins, **1b** and **1c**, the UV maxima are noted to show the small blue shift relative to that of **1a**. The following two possible explanations are conceivable, one is less effective orbital overlap between σ M–C bond (M = Ge and Sn) and π-orbitals of the triene, and the other is less effective orbital overlap among the triene π-orbitals due to the higher degree of folding of the triene part in **1b** and **1c** as estimated from comparisons of α values [21*].

Experimental section

^{1}H NMR spectra were recorded with Varian EM-390 and XL-200 spectrometers. ^{13}C NMR spectra were recorded with a JEOL FX-90Q spectrometer. Infrared spectra were obtained with a Hitachi EPI-G2 spectrophotometer. Mass spectra were measured on JMS-D 300 and Hitachi RMU-60 spectrometers. Ultraviolet spectra were recorded on a Hitachi 323 spectrophotometer. The ^{1}H NMR spectral simulation was achieved on the XL-200 spectrometer using the LAME which is the LAOCOON with magnetic equivalence added.

Materials

Di-n-butylstannane [22], dichlorodimethylgermane [23], and di-n-butyl-1-stannacyclohexa-2,5-diene (**2b**) [10–11] were prepared as described.

1,4-Pentadiyne

1,4-Pentadiyne was prepared by the modification of reported methods [11,24]. Ethynylmagnesium bromide was prepared in tetrahydrofuran (THF) (550 ml) from 13 g (0.53 mol) of Mg, 55 g (0.50 mol) of ethyl bromide and acetylene in a 1 l three-necked round-bottomed flask fitted with a reflux condenser, a dropping funnel and a mechanical stirrer. To the solution was added 1.0 g of freshly prepared copper(I) chloride under nitrogen and a solution of 42 g (0.35 mol) of propargyl bromide in THF (30 ml) dropwise at *ca.* 40°C over a period of 2 h. After addition, another portion of copper(I) chloride (0.35 g) was added and the mixture was stirred further for 3.5 h. The dark brown mixture was cooled to 0°C and hydrolyzed with 400 ml of water containing 10 ml of concentrated H_2SO_4. The organic layer was washed with aqueous NaCl until the volume was reduced to *ca.* 200 ml and dried over anhydrous Na_2SO_4. Flash distillation (120–130 Torr) on a water bath (30–40°C) into a receiver cooled by dry ice-MeOH gave 234 ml of a colourless distillate. ^{1}H NMR analysis of the distillate using C_6H_6 as an internal standard showed that the distillate contained 0.27 mol (77%) of 1,4-pentadiyne, together with a little water, which did not influence the subsequent hydrostannation.

1,1-Di-n-butyl-1-stannacyclohepta-2,4,6-triene (1,1-di-n-butyl-stannepin) (1b)

Into a 30 ml two-necked round-bottomed flask fitted with a magnetic stirring bar, a reflux condenser and a serum cap were placed 236 mg (2.33 mmol, 1.4 equiv.) of diisopropylamine and 7 ml of absolute ether under argon. To the stirred solution cooled to -78°C was added 1.6 ml (2.32 mmol, 1.4 equiv.) of 1.45 *N* BuLi in ether with a syringe. The LDA solution formed was then warmed to 0°C and a solution of 504 mg (1.69 mmol) of **2b** in ether (1 ml) added. The colour of the solution, yellow, changed gradually to green. After 1 h, the solution was cooled to -78°C and 4.7 ml (6.8 mmol, 4.0 equiv.) of 1.45 *N* BuLi in ether, and then 0.33 ml (5.15 ml, 3.0 equiv.) of CH_2Cl_2 was added. The mixture was allowed to warm to room temperature gradually, and the colour changed to brown with precipitation of salt. The resulting mixture was hydrolyzed and extracted with ether. The organic layer was washed with ether and subsequently with aqueous NaCl and dried over anhydrous Na_2SO_4. After evaporation of the solvent *in vacuo*, the residue was subjected to TLC on silica gel to give **1b** (171 mg, 0.550 mmol, 33%). **1b**: colourless oil; ^{1}H NMR ($CDCl_3$) δ 0.8–1.6 (m, 18H, Bu), 6.08 (br d, 2H, H-2,7), 6.21 (m, 2H, H-4,5), 7.07 (m, 2H, H-3,6); ^{13}C NMR ($CDCl_3$) δ 10.1 (t), 13.6 (q), 17.0 (t), 29.1 (t), 132.5 (d), 133.4 (d), 142.0 (d); UV (n-hexane) λ(sh) 279 nm (ϵ 2100); MS m/z (%) 255 ($M^+ -$ Bu based on ^{120}Sn, 46) 177 (39), 78 (100); high resolution MS Found: 255.0201, $C_{10}H_{15}{}^{120}Sn$ ($M^+ -$ Bu) calcd.: 255.0196.

1,1-Dimethyl-1-germacyclohexa-2,5-diene (2c)

Into a 10 ml one-necked round bottomed flask equipped with a reflux condenser were placed 3.47 g (11.6 mmol) of **2b** and 1.60 g (9.22 mmol) of dichlorodimethylgermane under argon. First the mixture was heated at 145°C. After 18 h, 20–30% of the starting materials had reacted and the mixture was heated at 160°C for a further 8 h. GLC of the reaction mixture showed that the starting materials disappeared completely. Vacuum distillation of the mixture gave 637 mg (3.77 mmol, 41%) of **2c**. **2c**: colourless oil; b.p. 80°C/80 Torr; ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 6H, GeMe), 2.94 (tt, 2H, $J_{2,4} = J_{4,6} = 2.0$ Hz, $J_{3,4} = J_{4,5} = 3.8$ Hz, H-4), 6.02 (dt, 2H, $J_{2,3} = J_{5,6} = 13.9$ Hz, $J_{2,4} = J_{4,6} = 2.0$ Hz, H-2,6), 6.55 (dt, 2H, $J_{2,3} = J_{5,6} = 13.9$ Hz, $J_{3,4} = J_{4,5} = 3.8$ Hz, H-3,5); ^{13}C NMR ($CDCl_3$) δ -1.2 (q), 33.2 (t), 126.6 (d), 142.0 (d); MS *m/z* (%) 170 (M^+ based on ^{74}Ge, 4), 155 (100), 89 (47); high resolution MS Found: 170.0163, $C_7H_{12}{}^{74}Ge$ calcd.: 170.0151.

1,1-Dimethyl-1-germacyclohepta-2,4,6-triene (1,1-dimethylgermepin) (1c)

Into a two-necked round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser and a dropping funnel were placed 616 mg (3.65 mmol) of **2c** and 15 ml of absolute ether under argon. To the stirred solution was added dropwise 8.8 ml (13 mmol, 3.5 equiv.) of 1.45 *N* BuLi in ether at 0°C. The resulting yellow solution was cooled to -78°C and then a solution of 780 mg (9.18 mmol, 2.5 equiv.) of CH_2Cl_2 in ether (3 ml) was added. The reaction mixture was allowed to warm gradually to room temperature. After hydrolysis, followed by extraction with ether, the organic layer was washed with water and then with aqueous NaCl and dried over anhydrous Na_2SO_4. After careful evaporation of the solvent followed by bulb to bulb distillation, the distillate was subjected to TLC on silica gel (developing solvent: n-hexane, eluent: ether) to afford 134 mg (0.741 mmol, 20%) of **1c** containing a trace of C_6H_6. **1c**: colourless oil; ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 6H, GeMe), 5.83 (br d, 2H, H-2,7), 6.30 (m, 2H, H–4,5), 6.82 (m, 2H, H-3,6); ^{13}C NMR ($CDCl_3$) δ -3.46 (q), 132.2 (d), 132.6 (d), 138.7 (d); UV (n-hexane) λ(max) 279 nm (ϵ 2500); FI-MS *m/z* (%) 182 (M^+ based on ^{74}Ge, 62), 180 (M^+ based on ^{72}Ge, 30), 178 (M^+ based on ^{70}Ge, 28), 78 (100); high resolution MS Found: 182.0162, $C_8H_{12}{}^{74}Ge$ calcd.: 182.0151.

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