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Development of novel and efficient synthesis of group 14 element (Ge and Sn) catenates by use of samarium (II) diiodide

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Abstract

Group 14 element catenates such as di-, tri-, poly-germanes, and polystannanes are efficiently synthesized by use of the one-electron reducing agent SmI_2 under mild homogeneous conditions in good yields.

Keywords: Group 14 elements; Catenates; Samarium (II) diiodide

1. Introduction

Group 14 element (silicon, germanium, tin) backbone polymers have attracted considerable attention as a new class of soluble, film-forming polymers due to both their promising physical, chemical and optical properties and their potential technological utility [1–9]. Much attention is, therefore, being directed towards the development of synthetic routes. The most practical synthetic procedure for Group 14 element catenates is a Wurtz-type polycondensation of Group 14 element dihalides with an alkali metal (Kipping method). These reactions are usually carried out under vigorous conditions and often lead to low yields of the polymers because of their heterogeneous nature. Moreover, such reactions, in which moisture-sensitive alkali metals are used at elevated temperature, can be hazardous. Therefore, much milder, safer and more efficient methods are desirable. In this paper, we describe a new synthetic procedure for the formation of Group 14 element (Ge and Sn) catenates by use of samarium (II) diiodide (SmI_2). This reaction is particularly useful for the synthesis of polygermanes and polystannanes which are difficult to obtain in high yields by the Kipping method. SmI_2 is known to be a mild one-electron reducing agent and homogeneous nature, and it has been applied in a wide variety of carbon–carbon bond formation reactions [10].

2. Results and discussion

The formation of a germanium–germanium bond is first attempted by use of SmI_2. Digermanes are generally synthesized by treatment of halogermanes with an alkali metal [11]. However, the germanium–germanium bond formed by reductive coupling is easily cleaved under reductive conditions. Organodigermanes were cleaved with alkali metal to give the corresponding germyl anion species [12]. Therefore, it is significant that a mild reducing agent is chosen as a promoter of reductive formation of a germanium–germanium bond for control over

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cleavage of the formed bond. If the reductive potential of the reductant is too weak, the reductive coupling reaction of halogermanes can not proceed. SmI_2 has mild reduction potential ($Sm^{2+} = Sm^{3+} + e^-$; -1.55 V, $M = M^+ + e^-$; $-2.9 \sim -3.0$ V, M = alkali metals) and its reaction is carried out in a homogeneous system [10]. These facts prompted us to investigate the formation of a germanium–germanium bond by reductive coupling of halogermanes.

The reactions of various halogermanes used as substrates and coupling reactions of them with 2 equiv. of SmI_2 in THF–HMPA mixed solvents at room temperature were carried out. After stirring, this reaction mixture was passed through a short column of silica gel and eluted with ether. This ether eluate was evaporated and purified by silica gel (hexane only) to give digermanes as major products. Products were identified by comparing their IR, NMR, GC–MS spectra, and retention times on GC with those of authentic samples. The results are summarized in Table 1.

$$2R_3GeX \xrightarrow[\text{THF, HMPA, r.t.}]{2\ SmI_2} R_3GeGeR_3 \quad R = \text{alkyl, aryl}$$

Chlorotriethylgermane (Et_3GeCl) was treated with 2 equiv. of SmI_2 in THF/hexamethylphosphoric triamide (HMPA) at room temperature for 24 h to give hexaethyldigermane ($Et_3GeGeEt_3$) in 69% isolated yield (Entry 1). This reaction progressed without HMPA, but the reaction mixtures should be stirred for long reaction periods (>100 h) to give $Et_3GeGeEt_3$ in good yield. Therefore, HMPA was necessary for this reductive coupling of Et_3GeCl at the point of practical protocols. When more reactive bromotriethylgermane (Et_3GeBr) was used as a substrate, the reaction mixture was stirred at room temperature for 15 h to afford $Et_3GeGeEt_3$ in good yield (73%) (Entry 2). Sterically hindered digermanes could be synthesized by reductive coupling of halogermanes by use of SmI_2. Hexabutyl- and hexa-*i*-propyl-digermanes could be obtained in good yields, when the corresponding chlorogermanes or bromogermanes were treated with SmI_2 (Entries 3–6). In all cases, the reductive coupling of bromogermanes by use of SmI_2 gave efficiently the corresponding digermanes compared with those of chlorogermanes. Phenyl-substituted digermanes also could be given by this method under similar reductive conditions. Diphenylmethylhalogermanes were used as substrates to give the corresponding tetraphenyl-substituted digermanes in excellent yields (Entries 7 and 8). In contrast to alkyl-substituted halogermanes, phenyl-substituted halogermanes were easily reduced to afford the corresponding digermanes (Entries 1 vs. 7 and 2 vs. 8). These results led to synthesize asymmetric digermanes by the combination of chlorogermane and bromogermane. Anticipated reductive coupling of the corresponding halogermanes occurred and 1,1,1-triethyl-2,2,2-triphenyldigermane or 1,1,1-tributyl-2,2,2-trimethyldigermane were obtained in good to excellent yields (Entries 9 and 10). These types of compounds could not be produced in good yields by treatment of halogermanes with an alkali metal.

Table 1
The formation of Ge–Ge Bond by use of SmI_2[a]

Entry	Substrates	Time (h)	Yield[b] (%)
1	Et_3GeCl	24	69
2	Et_3GeBr	15	73
3	*n*-Bu_3GeCl	24	62
4	*n*-Bu_3GeBr	15	66
5	*i*-Pr_3GeCl	24	39
6	*i*-Pr_3GeBr	15	45
7	$Ph_2MeGeCl$	12	95
8	$Ph_2MeGeBr$	1	98
9[c]	$Et_3GeCl + Ph_3GeBr$	1	96
10[d]	*n*-$Bu_3GeCl + Me_3GeBr$	15	59

[a] THF solution of SmI_2 (0.1 mol/dm^3) and HMPA (8% V/V) were used.
[b] Isolated yield.
[c] Et_3GeCl/Ph_3GeBr = 1/1.
[d] *n*-Bu_3GeBr/Me_3GeBr = 1/1.

As shown in Table 1 SmI_2 is a useful reagent for the formation of germanium–germanium bonds from halogermanes. This result suggested that other Group 14 element catenates could be synthesized by SmI_2. Therefore, we tried to investigate applications of this method for various catenate compounds.

Organotrigermanes are mostly prepared by two methods: (1) the reaction of dihalogermanes and two equiv of halogermanes with alkali metals, and (2) by treatment of halogermanes and monohalodigermanes with alkali metals [11]. These procedures are multiple-step reactions and the corresponding trigermanes were produced in low yields. It is obviously unfavorable as a practical procedure for organotrigermanes. As mentioned above, SmI_2 was useful for the synthesis of Group 14 element catenates. Therefore, synthesis of various trigermanes and analogues using SmI_2 was examined.

Reaction conditions for the formation of trigermanes were optimized using Et_3GeCl and dibromophenylgermane (Ph_2GeBr_2) as model substrates. 1,1,1,3,3,3-hexaethyl-2,2-diphenyltrigermane ($(Et_3Ge)_2GePh_2$) was identified by the IR, NMR, and GC–MS spectra, and retention times on GC with those of authentic samples.

$$2\ Et_3GeCl + Ph_2GeBr_2 \xrightarrow[\text{THF, HMPA, r.t.}]{\text{excess } SmI_2} Et_3Ge-\underset{\displaystyle Ph}{\overset{\displaystyle Ph}{\underset{|}{\overset{|}{Ge}}}}-GeEt_3$$

As shown in Table 2, THF solution of SmI_2 was added to the mixture of Et_3GeCl and Ph_2GeBr_2 in HMPA to give trigermane $(Et_3Ge)_2GePh_2$ in 63%

Table 2
Synthesis of $(Et_3Ge)_2GePh_2$ by use of SmI_2[a]

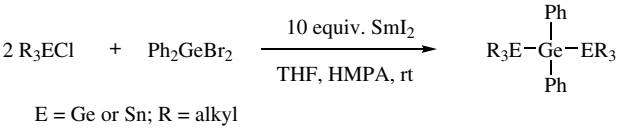
Method	Additional reagent	Mother liquor	Yield[b] (%)
A	SmI_2 in THF	Et_3GeCl/Ph_2GeBr_2 in HMPA	63
B	Et_3GeCl	Ph_2GeBr_2/SmI_2 in THF/HMPA	0
C	Ph_2GeBr_2	Et_3GeCl/SmI_2 in THF/HMPA	38
D	Et_3GeCl/Ph_2GeBr_2 in THF	SmI_2 in THF/HMPA	77

[a] THF solution of SmI_2 (0.1 mol/dm^3) and HMPA (8% V/V) were used.
[b] Isolated yield.

isolated yield (method A). In contrast, a mixture of this reducing reagent and Ph_2GeBr_2 in THF/HMPA was added to Et_3GeCl. Many by-products were formed and the desired $(Et_3Ge)_2GePh_2$ could not obtained (method B). Furthermore, Ph_2GeBr_2 was added to the solution of Et_3GeCl and SmI_2. The trigermane was formed in low yield (method C). When the THF solution of Et_3GeCl and Ph_2GeBr_2 was slowly added to the THF/HMPA solution of SmI_2, the corresponding trigermane was given in the highest yield (method D).

Optimized reaction conditions of the formation of trigermanes were further examined by use of method D. An increasing in the concentration of SmI_2 relative to Et_3GeCl (from 5.0 to 10 equiv.) improved the yield of $(Et_3Ge)_2GePh_2$ (86%). Extending the dropping time from 30 min to 2 h at room temperature improved the yield of $(Et_3Ge)_2GePh_2$ (86–94%). Lowering the reaction temperature from room temperature to 0 °C resulted in lower yields of $(Et_3Ge)_2GePh_2$ (94–74%), while raising the temperature to 100 °C showed a slight decrease, affording $(Et_3Ge)_2GePh_2$ in 85% yield. A decreasing in the concentration of THF solution of Et_3GeCl and 2 equiv. of Ph_2GeBr_2 afforded $(Et_3Ge)_2GePh_2$ quantitatively. If concentrated solutions of substrates were added to SmI_2, $(Et_3Ge)_2GePh_2$ was produced together with a tetragermane, $Et_3Ge(Ph_2Ge)_2GeEt_3$, as a by-product.

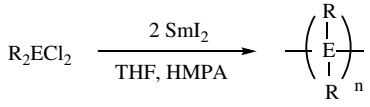
At the next stage, applications of this reaction for the preparation of various trigermanes and analogues by the reaction of trialkyl-substituted Group 14 element chlorides (R_3ECl, E = Ge, Sn; R = alkyl) with Ph_2GeBr_2 were investigated. All products were identified by their IR, NMR, and GC–MS spectra. These results are summarized in Table 3.



E = Ge or Sn; R = alkyl

Trigermanes having sterically hindered substituents such as *i*-propyl group could be synthesized by this method (Entry 2). Furthermore, Sn–Ge–Sn bond was formed by the use of SmI_2 (Entry 4). These types of compounds are important because they can be used as precursors for the formation of Sn–Ge bond containing polymers, and a few synthetic methods have been reported [13]. Therefore, SmI_2-promoted reactions are significant for efficient synthesis of these compounds in the field of polymers containing Group 14 elements.

In the synthesis of trigermanes, the reaction of Et_3GeCl, Ph_2GeBr_2, and SmI_2 gave tetragermane, $Et_3Ge(Ph_2Ge)_2GeEt_3$, as a by-product. This result prompted us to apply SmI_2 to the formation of polymers containing Ge–Ge and Sn–Sn backbone bonds.



R = Me, Et; E = Ge
R = Me, Et, Bu, Hex; E = Sn

Polymerization of R_2ECl_2 (R = alkyl; E = Ge, Sn) by use of SmI_2 under various conditions was examined. Results of polymerization of R_2ECl_2 by use of 2 equiv. of SmI_2 are summarized in Table 4. First, we investigated polymerization of Bu_2GeCl_2 by treatment of SmI_2 in THF/HMPA at room temperature for 24 h. The

Table 3
Synthesis of trigermanes and analogues by use of SmI_2[a]

Entry	R_3Ecl	Ph_2GeBr_2	Product	Yield[b] (%)
1	Me_3GeCl	Ph_2GeBr_2	$(Me_3Ge)_2GePh_2$	87
2	*i*-Pr_3GeCl	Ph_2GeBr_2	(*i*-$Pr_3Ge)_2GePh_2$	30
3	Et_3SnCl	Ph_2GeBr_2	$(Et_3Sn)_2GePh_2$	39

[a] THF solution of SmI_2 (0.1 mol/dm^3) and HMPA (8%V/V) were used.
[b] Isolated yield.

Table 4
Polymerization of R_2ECl_2 by use of SmI_2[a]

Entry	E	R	Temperature (°C)	Time (h)	λ_{max} (nm)	M_w[a]	M_n[a]	M_w/M_n	Yield[b] (%)
1	Ge	Me	reflux	1	327	4200	3700	1.14	9
2	Ge	Et	rt	24	289	2380	2030	1.17	19
3	Ge	Et	reflux	1	325	4890	4330	1.13	25
4	Sn	Me	rt	24	285	1120	750	1.49	19
5	Sn	Et	rt	24	368	4820	3980	1.21	74
6	Sn	Et	reflux	5	367	4100	3570	1.15	76
7	Sn	Bu	rt	65	289	2100	2030	1.04	17
8	Sn	Hex	rt	65	305	2770	2340	1.18	6

[a] Determined by GPC based on polystyrene standard.
[b] Isolated yield.

poly(diethylgermane)s, $(Et_2Ge)_n$, produced using SmI_2 had a narrow molecular weight distribution, but relatively low in molecular weight ($M_w = 2380$, $M_w/M_n = 1.17$, Entry 2). Raising the reaction temperature from 23 to 65 °C resulted in higher molecular weight of $(Et_2Ge)_n$ with a narrow M_w/M_n and higher ($M_w = 4890$, $M_w/M_n = 1.13$, Entry 3). The yields of $(Et_2Ge)_n$ were also increased (19–25%). The $(Et_2Ge)_n$ prepared by Wurtz-type coupling of dichlorogermanes with sodium metal in dispersion at elevated temperature showed a distinctly bimodal broad M_w/M_n and molecular weight in excess of about $(3–4) \times 10^5$ were obtained [7.8.9f]. Therefore, polymerization of dichlorogermanes using SmI_2 is much milder, safer, and more efficient methods.

Polymerization of Et_2SnCl_2 by treatment of SmI_2 in THF/HMPA at room temperature for 24 h and reflux temperature for 1 h was examined (Entries 5, 6). The poly(diethylstannane)s, $(Et_2Sn)_n$, showed a narrow molecular weight distribution ($M_w/M_n = 1.15–1.21$) and molecular weights in $(4.1–4.9) \times 10^3$ were obtained. Raising the reaction temperature from 23 to 65 °C scarcely improved the molecular weight of $(Et_2Sn)_n$. Polymerization of other dichlorostannanes by using SmI_2 in THF/HMPA at room temperature were also examined (Entries 4, 7, 8). Polystannanes were difficult to synthesize in good yields by the Kipping method [13]. The tin-tin bond formed by reductive coupling is easily cleaved under reductive conditions due to its weak bond strength. This method by using SmI_2 can be applied for the formation of various polystannanes under mild conditions.

3. Conclusion

In this paper, we have described the synthesis of useful various Group 14 element catenates, such as digermanes, trigermanes (and analogues), polygermanes, and polystannanes by treatment of Group 14 element halides with SmI_2 which is well-known as a mild one-electron reducing reagent under homogeneous conditions. Particularly, syntheses of asymmetric digermane, trigermane analogues having Sn–Ge–Sn bonds, and polystannanes are very important in the field of Group 14 elements because they have so far been difficult to be formed by practical methods. We believe that this convenient method would be generally applicable to a wide range of Group 14 element catenates and related compounds.

4. Experimental

^1H- and ^{13}C NMR spectra were recorded in $CDCl_3$ with tetramethysilane (TMS) as an internal standard on Varian Unity Inova-400. GC–MS were measured with JEOL JMS-DX 303 mass spectrometer. The UV and UV–Vis spectra were recorded with a Shimadzu UV 2200 spectrometer. IR spectra were recorded on Shimadzu FT IR 4200 spectrometer. GPC was performed with JAI LC-908 and Jasco UVDEC-100-IV. Gas chromatographic analyses were performed with Shimadzu GC-8A equipped with 1 m 20% SE30. Column chromatography was performed with silica gel (Wako Pure Chemical Industries, Ltd., Wakogel C-300). Thin-layer chromatography was performed on 0.25 mm E. Merck silica gel plates (60F-254).

4.1. Materials

Sodium metal, lithium metal, magnesium and samarium metal were commercially available products. Diethylether and THF were distilled from sodium benzophenone ketyl under nitrogen before use. Dibutylether was dried over sodium wire and distilled before use. HMPA was dried over calcium hydride and purified by distillation under argon atmosphere. MeOH and toluene were purified by distillation prior to use. All solvents of column chromatography and the other commercial reagents were used without purification. Compounds Et_3GeCl [14], Et_3GeBr [14], $i\text{-}Pr_3GeCl$ [15], $i\text{-}Pr_3GeBr$ [15], $n\text{-}Bu_3GeCl$ [16], $n\text{-}Bu_3GeBr$ [16], $Ph_2MeGeCl$ [17], $Ph_2MeGeBr$ [17], Ph_3GeBr [18],

Me_3GeBr [19], Ph_2GeBr_2 [20], $(Et_3Ge)_2$ [21], $(n\text{-}Bu_3Ge)_2$ [21], $(i\text{-}Pr_3Ge)_2$ [22], $(Ph_2MeGe)_2$ [23], $Me_3GeGeBu_3$ [21], $Et_3GeGePh_3$ [24], Me_2GeCl_2 [25], Et_2GeCl_2 [26], Me_2SnCl_2 [27], Et_2SnCl_2 [28], Bu_2SnCl_2 [29], Hex_2SnCl_2 [30], $(Me_3Ge)_2GePh_2$ [31], $(Et_3Sn)_2GePh_2$ [32], $(Et_2Ge)_n$ [9f], and $(Et_2Sn)_n$ [13] were prepared in accordance with reported procedures. THF solution of SmI_2 (0.1 mol/dm^3) was prepared according to the literature [33]. All reactions were carried out under argon or nitrogen atmosphere.

4.2. Preparation of organodigermanes

As a representative example, the preparation of hexaethyldigermane ($(Et_3Ge)_2$) is described. A THF solution of SmI_2 (3.0 mL, 0.30 mmol) was added to an HMPA (0.24 mL) solution of Et_3GeBr (36.0 mg, 0.15 mmol). After stirring for 15 h at room temperature, this reaction mixture was passed through a short column of silica gel and eluted with ether. This ether eluate was evaporated and purified by silica gel (hexane only) to give compound $Et_3GeGeEt_3$ (17.5 mg, 73%). This digermane was identified by comparison with an authentic compound (GC–MS and ^{1}H NMR) which was described in the literature [22].

4.3. Preparation of trigermanes and analogues

As a representative example, the preparation of 1,1,1,3,3,3-hexaethyl-2,2-diphenyltrigermane ($(Et_3Ge)_2GePh_2$) is described. A THF solution (40 mL) of Et_3GeCl (25.7 mg, 0.13 mmol) and Ph_2GeBr_2 (23.3 mg, 0.06 mmol) was added dropwise to a THF–HMPA (12:1) solution of SmI_2 (6.0 mL, 0.60 mmol) for 2 h at room temperature. After being stirred for 1 h, the reaction mixture was passed through a short column of silica gel and eluted with ether. The evaporated ether eluate was purified by silica gel (hexane only) to give compound $(Et_3Ge)_2GePh_2$ (30.8 mg, 94%). Tetragermane, $Et_3Ge(Ph_2Ge)_2GeEt_3$, was also detected. 1,1,1,3,3,3-Hexaethyl-2,2-diphenyltrigermane: IR (neat, NaCl) 3067, 3052, 3021, 3009, 2950, 2928, 2905, 2870, 2826, 1562, 1482, 1429, 1378, 1080, 1011, 968, 731, 698, 565 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.46–7.26 (m, 10H), 0.98 (m, 30H); ^{13}C NMR (δ, $CDCl_3$) 140.2, 135.5, 127.8, 127.3, 9.9, 6.1. MS *m*/*z* (relative intensity): 546 (M^+, 30), 517 (25), 461 (20), 431 (20), 381 (80), 310 (100), 280 (40), 151 (50), 103 (25). 1,1,1,4,4,4-Hexaethyl-2,2,3,3-tetraphenyltetragermane: ^{1}H NMR (δ, $CDCl_3$) 7.42–7.21 (m, 20H), 0.79 (s, 30H). MS *m*/*z* (relative intensity): 774 (M^+, 10), 536 (100), 359 (20), 301 (10), 257 (5), 209 (3), 151 (3). 2,2-Diphenyl-1,1,1,3,3,3-hexa-*i*-propyltrigermane: a white solid; 156–177 °C (decomp.); IR (KBr) 3096, 2967, 2942, 2917, 2882, 2962, 1462, 1431, 1221, 1078, 1001, 876, 729, 700, 523 cm^{-1}; ^{1}H NMR (δ, $CDCl_3$) 7.64–7.25 (m, 10H), 1.65 (sept, 6H, J = 7.50 Hz), 1.09 (d, 36H, J = 7.50 Hz); ^{13}C NMR (δ, $CDCl_3$) 141.7, 136.3, 136.3, 127.5, 21.1, 17.7. MS *m*/*z* (relative intensity): 630 (M^+, 30), 587 (90), 545 (60), 427 (70), 385 (75), 352 (100), 301 (20), 203 (50), 161 (30). Found: C, 57.42; H, 8.52%. Calcd for $C_{30}H_{52}Ge_3$: C, 57.16; H, 8.32%.

4.4. Polymerization of R_2ECl_2 by use of SmI_2

As a representative example, the preparation of poly(diethylgermane) $(Et_2Ge)_n$ was described. A THF solution of SmI_2 (16.0 mL, 1.60 mmol) was dropped to HMPA solution of Et_2GeCl_2 (161 mg, 0.80 mmol). This mixture was stirred for 1 h at reflux temperature. After removing the solvent in vacuo, $(Et_2Ge)_n$ was given by recrystallization from MeOH (26.2 mg, 25%). $(Et_2Ge)_n$: ^{1}H NMR (δ, $CDCl_3$) 1.17 (br, m); IR (cm^{-1}, neat) 2900, 2850, 1450, 1420, 1370, 1220, 1200, 1010, 940, 790, 670. $(Me_2Ge)_n$: ^{1}H NMR (δ, $CDCl_3$) 0.20–0.47 (m); IR (cm^{-1}, neat) 2900, 2870, 1400, 1220, 820, 745. $(Me_2Sn)_n$: ^{1}H NMR (δ, $CDCl_3$) 1.15–1.36 (m); IR (cm^{-1}, KBr) 2860, 1470, 1380, 990, 720. $(Et_2Sn)_n$: ^{1}H NMR (δ, $CDCl_3$) 1.25–1.66 (m); IR (cm^{-1}, KBr) 2960, 1450, 1430, 1190, 940, 670, 570. $(Bu_2Sn)_n$: ^{1}H NMR (δ, $CDCl_3$) 1.49–1.87 (m); IR (cm^{-1}, KBr) 2980, 1635, 1465, 1070, 860, 670, 565. $(Hex_2Sn)_n$: ^{1}H NMR (δ, $CDCl_3$) 0.62–1.88 (m); IR (cm^{-1}, KBr) 960, 2400, 1640, 1155, 1100, 950, 680, 600.

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