Note

# Synthesis and characterization of 1-methyl-1-silaindane and 1-methyl-1-germaindane

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## Abstract

New synthetic routes to 1-methyl-1-silaindane (**1b**) and 1-methyl-1-germaindane (**1b**) were developed and the desired products were obtained in good isolated yield. Compounds **1a** and **1b** were fully characterized by mass spectroscopy, $^1$H and $^{13}$C{$^1$H} NMR, and infrared spectroscopy.
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## 1. Introduction

The importance of organosilicon and organogermanium compounds to molecular and materials chemistry cannot be understated. A variety of silanes have been developed for use in organic synthesis as protecting groups, as well as for C–C bond formation and functional group transfer reactions [1]. Optically active sila-pharmaceuticals have been prepared that display antimuscarinic properties [2]. Studies of Si–Si, Ge–Ge, and transition metal–Si/Ge bonding have lead to new structures with intriguing, non-classical bonding geometries and coordination environments [3–5]. Polysilanes and polygermanes represent materials with interesting electronic and physical properties due to the phenomenon of σ-conjugation associated with the polymer chain. These have been prepared catalytically via dehydrogenative and demethanative coupling [6]. Furthermore, organosilanes have been utilized to create hybrid organic–inorganic materials with applications in surface organometallic chemistry and catalysis [7].

In many cases, the desired organosilane or organogermane can be purchased or easily synthesized via salt metathesis beginning with a halide derivative. However, producing asymmetric cyclic compounds, such as those in Fig. 1, has proven to be more difficult. The bicyclic indane structure is particularly appealing for numerous applications alluded to above, and control over the R and R′ groups could tailor the system for the particular purpose. A few silaindanes have been reported, most of which are symmetrically substituted at Si [8–11]. The only germaindane reported is the symmetric 1,1-dimethyl-1-germaindane [12,13].

Early researchers in this field effected an intramolecular ring-closing of a pendant silyl group with an aryl chloride upon treatment with sodium in refluxing toluene [9]. This method of cyclization typically results in low yields of the desired silaindane. Recently, a catalytic dehydrogenative process was reported to cyclize pendant silyl groups via C–H activation of the aryl ring with good yields [8]. However, this process is not tolerant to chlorosilanes for further derivation and requires a Pt catalyst with harsh reaction conditions. Thus, a general one-step route to the synthesis of cyclic silanes and germanes with mild conditions is

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E = Si or Ge
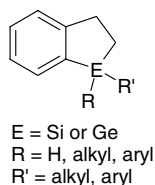R = H, alkyl, aryl
R' = alkyl, aryl

Fig. 1. Asymmetric sila- or germa-indanes.

welcome. Herein we report the synthesis and characterization of two novel compounds, 1-methyl-1-silaindane (**1a**) and 1-methyl-1-germaindane (**1b**). The compounds are prepared in good yields via single-step cyclizations at room temperature.

## 2. Experimental

### 2.1. General procedures

All manipulations were carried out in oven-dried glassware under an argon atmosphere using standard Schlenk techniques. Diethyl ether and THF were dried over potassium benzophenone ketyl and distilled under argon prior to use. Methylene chloride ($CH_2Cl_2$) and hexanes were dried over calcium hydride and distilled. Triphenyl phosphine, 2-bromophenethyl alcohol, methyltrichlorosilane, carbon tetrachloride, and magnesium turnings were purchased from Aldrich. Trichloromethylgermane was provided by Gelest, Inc. (Tulleytown, PA, USA). 1-Chloro-2-(2-bromoethyl)benzene [14] and 1-bromomagensio-2-(2-(chloromagensio)ethyl)benzene (**2**) [15] were prepared according to the literature procedure.

The $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded at 400 MHz and 100 MHz, respectively, on a JEOL Eclipse+400 spectrometer at room temperature in chloroform-*d* (Aldrich) or acetone-*d*$_6$ (Acros). $^1$H NMR chemical shifts are reported relative to tetramethylsilane ($\delta = 0.00$ ppm), and $^{13}$C NMR shifts are reported relative to chloroform-*d*, ($\delta = 77.0$ ppm). IR spectra were obtained on a Mattson FT-IR spectrometer on NaCl plates. A Fisons Instruments GC8030 was used in tandem with a Fisons MD800 mass spectrometer; the gas-chromatograph employed an Alltech ECONO-CAP Faster Fatty Acid Phase column, with phase SE-54, and dimensions 30 m × 0.25 mm ID × 0.25 μm. UV–Vis absorbance spectra of **1** and **2** were obtained in dilute THF solution using a Chem 2000 spectrometer.

### 2.2. Synthesis

#### 2.2.1. 1-Bromo-2-(2-chloroethyl)benzene

A solution of triphenyl phosphine (7.18 g, 27.4 mmol) in $CH_2Cl_2$ (25 mL) was added dropwise (10 min) to a solution of 2-bromophenethyl alcohol (5.00 g, 24.9 mmol) and carbon tetrachloride (4.00 mL, mmol) in $CH_2Cl_2$ (50 mL) at 0 °C. After 15 min the ice bath was removed and the reaction was refluxed for 4 h. Additional $CCl_4$ was added (1 mL) and the reaction was refluxed for an additional

3 h then stirred at room temperature overnight. The solvent was evaporated under vacuum to yield a yellow oil, which was triturated with hexanes and filtered through Celite. This solution was concentrated under vacuum and the desired product eluted first through a column of silica gel with hexanes as the eluent. Removal of the solvent yielded a colorless oil (4.8 g, 88% yield). $^1$H NMR ($CDCl_3$): $\delta$ 7.55 (d, 1H, aryl, $^3J_{H–H} = 8.1$ Hz), 7.26 (m, 2H, aryl), 7.13 (m, 1H, aryl), 3.74 (t, 2H, Cl–C$H_2$, $^3J_{H–H} = 7.3$ Hz), 3.20 (t, 2H, aryl-C$H_2$, $^3J_{H–H} = 7.3$ Hz).

#### 2.2.2. 1-Methyl-1-silaindane (1a)

A solution of **2** in THF was prepared *in situ* from 1-bromo-2-(2-chloroethyl)benzene (1.00 g, 4.56 mmol). The solution was added dropwise over 20 min via filter cannula to a stirred solution of trichloromethylsilane (0.54 mL, 4.56 mmol) in THF (10 mL) at −78 °C. The stirred solution was allowed to warm to room temperature overnight. The reaction mixture was then added dropwise (10 min) via cannula to a stirred suspension of lithium aluminum hydride (0.26 g, 6.85 mmol) in THF (10 mL) at 0 °C. After 30 min, the reaction was allowed to warm to room temperature while stirring an additional 5 h. The reaction flask was then immersed in an ice bath and a 10% aqueous ammonium chloride solution (30 mL) was added dropwise to destroy the excess lithium aluminum hydride. The solution was then filtered and 25 mL of diethyl ether were added. The filtrate was washed with a 10% aqueous ammonium chloride solution (3 × 30 mL), and then the organic layer was dried over magnesium sulfate. The solution was filtered and the solvent was removed *in vacuo* yielding a yellow oil (73% crude yield). Integration of the gas-chromatograph peaks shows that the crude product is >98% pure. Vacuum distillation affords 0.340 g of a colorless oil, (50% isolated yield, bp 27 °C, 0.001 mmHg). Anal. Calc. for $C_9H_{12}Si$: C, 72.90; H, 8.16. Found: C, 72.57; H, 8.38%. $^1$H NMR (acetone-*d*$_6$): $\delta$ 7.59 (d, 1H, $^3J_{H–H} = 7.3$ Hz, aryl), 7.27 (m, 2H, aryl), 7.18 (t, 1H, $^3J_{H–H} = 7.2$ Hz, aryl), 4.66 (q, 1H, $^3J_{H–H} = 3.5$ Hz, Si–*H*), 3.08 (m, 2H, Ar-C$H_2$), 1.24 (m, 1H, Si–C*H*), 0.95 (m, 1H, Si–C*H*), 0.36 (d, 3H, $^3J_{H–H} = 3.7$ Hz, Si–C$H_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 153.6 (s, C9), 136.8 (s, C4), 132.6 (s, C5), 129.5 (s, C8), 125.7 (s, C6), 125.6 (s, C7), 32.3 (s, C1), 8.7 (s, C2), −4.4 (s, C3). IR (neat, cm$^{-1}$): 3056, 2956, 2910, 2118 (Si–H), 1588, 1441. MS [*m/z*]: 148 (M$^+$), 147 (M−H$^+$), 133 (M−CH$_3^+$), 132 (M−CH$_4^+$), 120 (M−CH$_2$CH$_2^+$), 105 (M−CH$_3$–CH$_2$CH$_2^+$). UV–Vis (THF): $\lambda$ (nm) 268 (630 cm$^{-1}$ M$^{-1}$), 275 (560 cm$^{-1}$ M$^{-1}$).

#### 2.2.3. 1-Methyl-1-germaindane (1b)

A THF solution of **2** was prepared from 1-bromo-2-(2-chloroethyl)benzene (2.0 g, 9.11 mmol) and transferred dropwise over 20 min to a solution of trichloromethylgermane (1.77 g, 9.11 mmol) in THF (20 mL) at −78 °C. The stirred solution was allowed to warm to room temperature overnight. The contents of this reaction were added dropwise over 20 min to a suspension of lithium aluminum

hydride (0.80 g, 21.1 mmol) in THF (15 mL) at 0 °C. After 30 min, the ice bath was removed and the solution was stirred overnight at room temperature. The solution was filtered via cannula, rinsed with dry diethyl ether (3 × 10 mL), and the solvent was removed *in vacuo*, yielding 1.35 g of a faint yellow oil (77% crude yield). Integration of the GC shows that the crude product is >95% pure. Vacuum distillation yields 0.880 g of a colorless oil (50% isolated yield, bp 29 °C, 0.001 mmHg). Anal. Calc. for $C_9H_{12}Ge$: C, 56.07; H, 6.27. Found: C, 55.98; H, 6.39%. $^1H$ NMR (acetone-$d_6$): $\delta$ 7.58 (d, 1H, $^3J_{H-H} = 7.3$ Hz, aryl), 7.23 (m, 2H, aryl), 7.16 (dt, 1H, aryl, $^4J_{H-H} = 2.3$ Hz, $^3J_{H-H} = 6.7$ Hz), 4.79 (m, 1H, Ge–*H*), 3.12 (m, 2H, Ar-C*H₂*), 1.45 (m, 1H, Ge–C*H*), 1.12 (m, 1H, Ge–C*H*), 0.52 (d, 3H, $^3J_{H-H} = 3.3$ Hz, Ge–C*H₃*). $^{13}C\{^1H\}$ NMR (CDCl₃): $\delta$ 151.5 (s, C9), 138.9 (s, C4), 132.8 (s, C5), 128.7 (s, C8), 125.8 (s, C6), 125.7 (s, C7), 33.8 (s, C1), 10.0 (s, C2), −4.4 (s, C3). IR (neat, cm$^{-1}$): 3055, 2967, 2913, 2034 (Ge–H), 1589, 1441. MS [*m/z*]: 193 (M$^+$), 192 (M−H$^+$), 178 (M−CH₃$^+$), 177 (M−CH₄$^+$), 164 (M−H−CH₂CH₂$^+$), 149 (M−H−CH₃-CH₂CH₂$^+$). UV–Vis (THF): $\lambda$ (nm) 262 (1133 M$^{-1}$ cm$^{-1}$), 269 (1076 M$^{-1}$ cm$^{-1}$).

## 3. Results and discussion

While a variety of substituted 1-silaindanes are known (*e.g.* 1,1-dimethyl and 1,1-diphenyl) the parent, 1-silaindane, has not been reported. The only reported 1-silaindane in which there is one hydrogen on the silicon is 1-phenyl-1-silaindane [9]. Compound **1a** was initially prepared in order to determine an appropriate route for the synthesis of **1b**. The key step in the synthesis of the desired bicyclic structures was forming the correct Grignard reagent to close the five-membered ring. Three methods were investigated for producing compound **1a**. The first method involved an attempt to form the di-Grignard of 1-bromo-2-(2-bromoethyl)benzene [9]. While this di-Grignard reacts with dichlorodiphenylsilane to produce 1,1-diphenyl-1-silaindane [9], compound **1a** was not the major product in the reaction of the di-Grignard with trichloromethylsilane followed by treatment with lithium aluminum hydride.

The second method examined for the preparation of **1a** was the metalation of 1-chloro-2-(2-bromoethyl)benzene. In diethyl ether, metalation of the ethyl-bromide was the primary product, although some di-Grignard and intramolecular coupling to yield 1,4-di-(2-chlorophenyl)butane also occurred. Since there was significant formation of the mono-Grignard, the addition of a terminal –SiHCH₃Cl group was performed and confirmed by GC–MS. Unfortunately, the subsequent conversion of the product to a Grignard followed by ring-closing was consistently unsuccessful, leaving only the unreacted starting material. Cyclization of the product was also attempted using lithium aluminum hydride to convert the –SiHCH₃Cl group into a –SiH₂CH₃group followed by refluxing with sodium in toluene to close the ring [9]. While the desired product was verified by GC–MS, the yield was quite low.

The third and most successful method of preparing **1a** (Scheme 1) was from a di-Grignard reagent, **2**, that was recently reported in the literature [15]. It was prepared from 1-bromo-2-(2-chloroethyl)benzene, which is not commercially available. A new synthetic route to 1-bromo-2-(2-chloroethyl)benzene was developed with yields similar to other routes that have been reported [15,16]. In preparing the di-Grignard, the magnesium was activated with 1,2-dibromoethane, and upon addition of 1-bromo-2-(2-chloroethyl)benzene, yielded **2** which was not isolated. Compound **2** reacted with trichloromethylsilane to generate **3a** *in situ* which was then reduced with lithium aluminum hydride, giving **1a** in good yield. Upon successful synthesis of **1a**, the germanium analogue, **1b**, was prepared using a similar series of reactions and trichloromethylgermane. The products were purified via careful vacuum distillation and the isolated yield was 50% for each.

Compounds **1a** and **1b** were initially characterized using gas chromatography–mass spectroscopy. For both compounds, there were five easily assignable peaks in the mass spectrum: the molecular ion peak, loss of a hydrogen, loss of the methyl, loss of the ethylene bridge, and loss of the methyl and ethylene groups. Infrared spectra of the compounds were also obtained. In addition to the distinctive aryl bands, intense peaks in the characteristic regions for Si–H ($v = 2105$–$2165$ cm$^{-1}$) and Ge–H ($v = 2020$–$2060$ cm$^{-1}$) stretches assured the presence of the E–H bond in each sample [17]. UV–Vis spectra were also obtained, and the peaks were in the typical range for aryl $\pi$–$\pi^*$ transitions.

In order to further characterize **1a** and **1b** extensive NMR experiments were performed. Acetone-$d_6$ and chloroform-$d$ were the solvents used for $^1H$ and $^{13}C\{^1H\}$ NMR spectra, respectively, to avoid overlap of solvent peaks with sample peaks. In the $^1H$ spectra, both compounds displayed an upfield doublet corresponding to the methyl group; the chemical shift and coupling constants for **1a** and **1b** are similar to ethylmethylphenylsilane [18] and (4-trifluorotolyl)dimethylgermane [19], respectively. While the Si–H in **1a** was a well resolved quartet, the corresponding Ge–H in **1b** was not. This was not unexpected
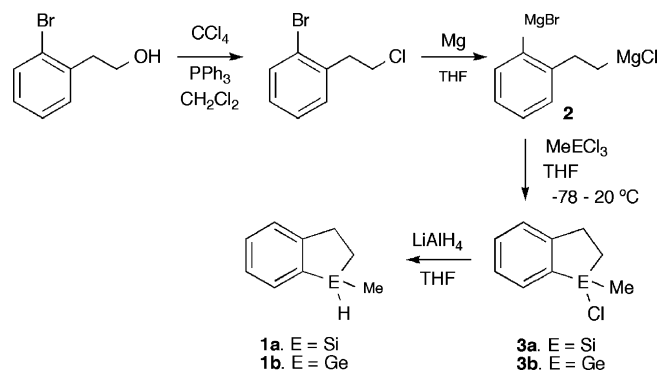


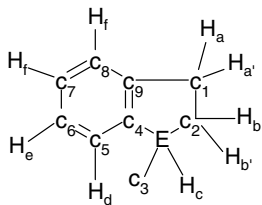Scheme 1. Synthetic route to compounds **1a** and **1b**.

Fig. 2. Atom labeling assignments for **1a** and **1b**.

as the Ge–H signal for (4-trifluorotolyl)dimethylgermane was not well resolved [19].

The $^{13}$C{$^1$H} and the remaining signals in the $^1$H spectra were assigned (Fig. 2) using DEPT, $^1$H–$^{13}$C HETCOR and $^1$H–$^1$H COSY experiments. The two less intense aromatic peaks had no matching peaks in the DEPT spectrum, corresponding to quaternary carbons. Based on similar compounds [18], the quaternary carbon bonded to the heteroatom in **1a** and **1b** can be assigned as the peak further upfield (C4). Two of the three upfield peaks inverted, indicative of methylene groups while the most upfield peak remained unchanged, indicative of the methyl carbon (C3).

Since the Si/Ge atom is a stereocenter, the protons on C1 and C2 are diastereotopic. Three sets of multiplets were observed between $\delta$ 0.9 and 3.5 ppm in the $^1$H NMR spectrum. Integration of the three multiplets found that the relative intensities of the peaks were 2:1:1. The protons on C2 were anticipated to resonate upfield of those on C1 [18]. The protons on C2 are closer to the stereocenter thus giving a greater difference between $H_b$ and $H_{b'}$ than $H_a$ and $H_{a'}$. In addition, the $^1$H–$^1$H COSY spectrum revealed that there was no coupling between $H_c$ and the two proton multiplet for $H_a$/$H_{a'}$. Finally, the $^1$H–$^{13}$C HETCOR spectrum confirmed the coupling between $H_a$/$H_{a'}$ and C1 and $H_b$/$H_{b'}$ and C2.

In similar aromatic silanes, the aromatic protons *ortho* to the silicon atom are the furthest downfield and have chemical shifts near 7.50 ppm [18], which allows for assignment of $H_d$ and the $^1$H–$^{13}$C HETCOR spectrum indicates that this proton is bound to C5. In addition, the $^1$H–$^1$H COSY spectrum reveals coupling between $H_d$ and the most upfield aromatic peak which was assigned as $H_e$. The $^1$H-$^{13}$C HETCOR spectrum was then used to assign C6. The $H_f$ protons were coincidentally equivalent. The remaining carbon atoms were assigned by comparison to related compounds [18]; carbon atoms *para* to a silyl group tend to be more downfield than those *ortho* to an ethyl group.

## 4. Summary

The reaction of the di-Grignard, **2**, with either trichloromethylsilane or trichloromethylgermane followed by subsequent treatment with lithium aluminum hydride yields **1a** or **1b**, respectively. The cyclization reaction proceeds with high selectivity, and the products are obtained in good yield after vacuum distillation. Both **1a** and **1b** were fully characterized and the $^1$H and $^{13}$C peaks were assigned.

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