The Selective Lithiation and *In Situ* Trimethylsilylation of Benzyldiphenylchlorosilane and its Methoxy Analog. Compounds Which Could Conceivably Lead to Stable Si=C Species on Pyrolysis

K. G. RUTHERFORD[1] AND R. J. SEIDEWAND[2]

Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4

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The selective lithiation and *in situ* trimethylsilylation of benzyldiphenylchlorosilane and its methoxy analog to give (α-trimethylsilylbenzyl)diphenylchlorosilane and (α-trimethylsilylbenzyl)diphenylmethoxysilane in excellent yields is reported. These compounds exhibit much greater stability on pyrolysis than β-halocarbosilanes. A stable Si=C species was not obtained on pyrolysis of the compounds synthesized.

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On rapporte la lithiation sélective et la triméthylsilylation *in situ* du benzyldiphénylchlorosilane et de son analogue méthoxylé; ces réactions qui se produisent avec d'excellents rendements conduisent au (α-triméthylsilylbenzyl)diphénylchlorosilane et au (α-triméthylsilylbenzyl)diphénylméthoxysilane. Ces composés, comparés aux β-halocarbosilanes, sont beaucoup plus stables vis-à-vis de la pyrolyse. On n'a pu obtenir d'espèces Si=C par pyrolyse des composés synthétisés.

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Introduction

The exceptional thermal instability of β-haloalkylsilanes (1, 2) has been known for some time. A few representative compounds shown in Fig. 1 decomposed (3, 4) upon attempted distillation to produce a silyl halide and an olefin.

$$Et_3SiCH_2CH_2Cl \xrightarrow{80\,^{\circ}C} Et_3SiCl + CH_2{=}CH_2$$

$$Me_3SiCH_2CHBrCH_3 \xrightarrow{40\,^{\circ}C} Me_3SiBr + CH_2{=}CHCH_3$$

$$Me_3SiCH_2CHClCH_3 \xrightarrow{90\,^{\circ}C} Me_3SiCl + CH_2{=}CHCH_3$$

FIG. 1. Thermal cleavage of β-haloalkylsilanes.

These elimination reactions have been postulated to proceed through a four-centered activated complex (Fig. 2), promoted by overlap of the lone pair of electrons on the β-heteroatom with the vacant d orbitals of silicon (2).

In addition to halogen substituents, the cleavage reaction also occurs when there is a β-oxygen atom capable of being transferred, presumably in a *cis*-like manner, to silicon via a similar four-centered transition state.

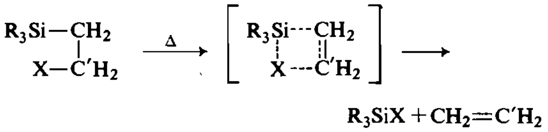

FIG. 2. Proposed mechanism for β-haloalkylsilane cleavage.

The intriguing ramifications of this mechanism involve the carbon atom C′. If C′ were to be replaced by a silicon atom and if appropriate groups were to be attached to the Si and C atoms which could allow for resonance and/or steric stabilization, the possibility of generating a stable silico-olefin may be realized on pyrolysis. Incorporation of a sufficient molecular weight may also add to the stability of the resultant Si=C species. The transient existence of molecules containing (p–p)π bonded silicon and germanium has been well documented in the literature over the past few years (5), however, stable systems have not as yet been synthesized. Model compounds[3] aimed at providing stable systems were thus synthesized for pyrolytic studies.

Results and Discussion

Benzyldiphenylchlorosilane (**1**) was readily

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[1] To whom all inquiries should be directed.

[2] Present address: Dwight P. Joyce Research Center, Glidden-Durkee, Division of SCM Corporation, Strongsville, Ohio 44136.

[3] Previous compounds synthesized and pyrolyzed are reported in ref. 6.

obtained from the reaction of benzylmagnesium chloride and diphenyldichlorosilane. Benzyldiphenylmethoxysilane (**2**) was obtained from the methanolysis of **1**.

In 1971, West (7) reported that the methyl group of trimethylsilyl derivatives can be metalated by the strongly hindered base, *tert*-butyllithium. Trimethylchlorosilane (**3**), for example, can be metalated and then trapped by excess chlorosilane. We found that the addition of *tert*-butyllithium to a *mixture* of **1** and **3** proved to be an excellent procedure for the synthesis of (α-trimethylsilylbenzyl)diphenylchlorosilane (**4**). An analogous selective lithiation reaction with a mixture of **2** and **3** conveniently afforded (α-trimethylsilylbenzyl)diphenylmethoxysilane (**5**). The above reactions (crude yields ≥75%) are summarized in Fig. 3. Both compounds **4** and **5** now provided us with the desired 1,4-juxtaposition of silicon and a heteroatom substituent (Fig. 2).

Attempted pyrolytic elimination (6) of **3** from **4** at temperatures up to 470 °C resulted essentially only in recovery of starting material. The pyrolysis of **5** in the temperature range 300–470 °C did result in decomposition but led to a complex mixture, as shown by i.r. and n.m.r. analysis, as well as furnishing trimethylmethoxysilane **6**, $(CH_3)_3SiOCH_3$, in a 50% yield. None of the desired Si=C compound was obtained.

The nature of the route leading to **6** can only be speculated, but if it does involve the formation of $Ph_2Si{=}CHPh$, the high temperatures employed probably favor intermolecular processes leading to a complex high molecular weight residue.

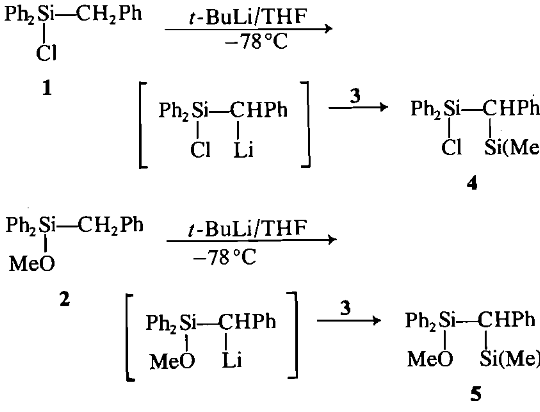

FIG. 3. Selective lithiation by *tert*-butyllithium and *in situ* trapping by trimethylchlorosilane.

The reason for the stability of **4**, when under the same conditions **5** completely decomposes, remains rather obscure at this point.

Experimental

Infrared spectra were recorded on a Beckman IR-12 spectrometer in chloroform. Nuclear magnetic resonance spectra were obtained with a Jeolco C-60 HL spectrometer in deuteriochloroform with methylene chloride as an internal standard (τ 4.70). Gas–liquid chromatography (g.l.c.) was performed on Hewlett Packard 720 and 5750 instruments. Columns utilized were as follows: 6 ft × ¼ in. 10% SE 30 on 60–80 Chromosorb W, 8 ft × ¼ in. 20% SE 30 on 60–80 Chromosorb W and 6 ft × ¼ in. 10% Dexsil 300 on 60-80 Chromosorb W. All reactions were run in dried apparatus under an atmosphere of nitrogen and the silyl chlorides were purified prior to use. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Benzyldiphenylchlorosilane (1)

Benzylmagnesium chloride (200 mmol) in 150 ml of ether and diphenyldichlorosilane (53.2 g, 210 mmol) in 125 ml of ether were stirred for 15 min at 0 °C and then refluxed 2 h. Upon cooling, the solution was filtered through Super Cel under an atmosphere of N_2 with the aid of an additional 150 ml of ether and the filtrate was concentrated. Methylene chloride (50 ml) was added and the solution was refiltered and concentrated to a pale yellow liquid. Short path distillation gave 40.9 g (66%) of **1**: b.p. 147–150 °C (0.003 Torr); m.p. 52–57 °C; n_D^{25} 1.6085; i.r. 7.0, 8.97, and 19.0 (SiCl) μ; n.m.r. τ 2.7 (m, 15) and 7.2 (s, 2).

Anal. Calcd. for $C_{19}H_{17}ClSi$: C, 73.87; H, 5.54;, Cl, 11.47. Found: C, 73.76; H, 5.58; Cl, 11.38.

(α-Trimethylsilylbenzyl)diphenylchlorosilane (4)

To 4 g (13 mmol) of **1** and 1.65 ml (13 mmol) of **3** in 25 ml of THF at −78 °C was added dropwise 6.2 ml (14 mmol) of 2.26 *M* *tert*-butyllithium in pentane in 25 ml of pentane. The resulting clear orange solution was stirred at −78 °C for 2 h. After addition of 0.3 ml (2 mmol) of **3** the solution was allowed to warm to room temperature and then stirred for an additional 2 h. Lithium chloride was removed by filtration under nitrogen using Super Cel and the colorless filtrate was concentrated. Methylene chloride (20 ml) was added and the solution was refiltered, concentrated, and distilled (short path) to give 3.0 g of a colorless viscous oil: b.p. 154–155.5 °C (0.003 Torr); n_D^{25} 1.5877. Gas–liquid chromatography and subsequent i.r. and n.m.r. analyses revealed **4** (94%), **1** plus a lower retention component (1%), and an unidentified high retention time component (5%). Preparative g.l.c. afforded pure **4**: i.r. 7.0, 9.03, 11.7, and 19.4 μ; n.m.r. τ 2.6 (m, 15), 7.52 (s, 1, CH), and 10.1 (CH_3Si).

Anal. Calcd. for $C_{22}H_{25}ClSi_2$: C, 69.34; H, 6.61; Cl, 9.30. Found: C, 69.23; H, 6.89; Cl, 9.35.

Benzyldiphenylmethoxysilane (2)

Benzyldiphenylchlorosilane (**1**) (5.17 g) was converted by the method of Sauer (9) into **2** (3.9 g, 76%); b.p. 142–144 °C (0.005 Torr); n_D^{25} 1.5923; i.r. 3.52, 7.0, 8.93, and 9.17 μ; n.m.r. τ 2.7 (m, 15), 6.42 (s, 3), and 7.24 (s, 2).

Anal. Calcd. for $C_{20}H_{20}OSi$: C, 78.89; H, 6.62; Si, 9.22. Found: C, 78.55; H, 6.78; Si, 8.90.

(α-Trimethylsilylbenzyl)diphenylmethoxysilane (5)

To 3.96 g (13 mmol) of **2** and 1.65 ml (13 mmol) of **3** in 25 ml of THF at −78 °C was added dropwise 6.2 ml (14 mmol) of 2.26 *M tert*-butyllithium in pentane in 20 ml of pentane. The resulting yellow solution was stirred at −78 °C for 2 h. After addition of 0.3 ml (2 mmol) of **3** the solution was allowed to warm to room temperature and then stirred for an additional 2 h. Lithium chloride was removed by filtration under nitrogen using Super Cel and the colorless filtrate was concentrated. Methylene chloride (20 ml) was added and the solution was refiltered, concentrated, and distilled (short path) to give 3.8 g of a colorless viscous oil; b.p. 151–153 °C (0.005 Torr); n_D^{25} 1.5757. Gas–liquid chromatography and subsequent i.r. and n.m.r. analysis revealed **5** (88%) and an unresolved peak (12%) at the same retention time as **2**. Preparative g.l.c. gave pure **5**: i.r. 3.53, 7.0, 8.98, 9.18, 11.7, and 19.2 μ; n.m.r. τ 2.6 (m, 15), 6.45 (s, 3, OCH_3), 7.75 (s, 1, CH), and 10.05 (s, 9, CH_3Si).

Anal. Calcd. for $C_{23}H_{28}OSi_2$: C, 73.34; H, 7.49; Si, 14.91. Found: C, 73.39; H, 7.51; Si, 14.61.

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