

9,10-Dihydro-9-sila-10-heteroanthracenes as new radical-based reducing agents

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9,10-Dihydro-9-silaanthracenes **1** containing a heteroatom at the 10-position have been prepared and their reducing abilities for the reduction of some organic compounds under radical conditions have been investigated. Derivatives possessing a silicon, tin, oxygen or sulfur atom at the 10-position exhibited enhanced reactivities compared with the open-chain models. Among them, 9,10-dimethyl-9,10-dihydro-9,10-disilaanthracene **1a** proved to be the most effective reagent for AIBN-initiated dehalogenation of organic halides and deoxygenation of aliphatic alcohols via *O*-thiocarbonyl derivatives. The rate constants for hydrogen abstraction from the Si-H moiety of these silaanthracenes **1** were determined using the neophyl rearrangement as a free radical clock in order to estimate their reactivities.

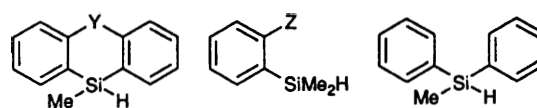
Introduction

Radical-based dehalogenation of organic halides¹ and deoxygenation of alcohols² play important roles in organic synthesis, especially for polyfunctionalized molecules like biologically active compounds. Although many synthetic reactions involving free radicals as intermediates have employed tributyltin hydride as a reducing agent,³ the replacement of such toxic and relatively expensive organotin compounds has been performed with other hydrogen donors containing the Si-H⁴ or P-H⁵ bond. Alkyl- and/or aryl-substituted silanes seem to be good alternatives to the stannanes, but these reagents require relatively drastic reaction conditions due to their lower hydrogen-donating abilities. Recently, some organosilanes with reduced Si-H bond strength were discovered.⁶ In particular, tris(trimethylsilyl)silane⁷ has proved to be an effective and versatile reducing agent, of which the Si-H bond is believed to be dramatically weakened by a hyperconjugation between a generated silyl radical and adjacent trimethylsilyl groups.⁸ However the compound is relatively expensive and, in addition, is unstable under aerobic conditions, yielding 1,1-bis(trimethylsiloxy)-2,2,2-trimethyldisilane.⁹ It has also been demonstrated that trialkylsilanes can reduce alkyl halides and xanthates under mild conditions, in which alkanethiols are used as polarity reversal catalysts.¹⁰

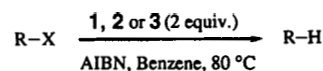
9,10-Dihydro-9,10-disilaanthracene derivatives are of interest both from chemical and theoretical points of view because they are considered to be the most probable precursors of the sila aromatics. To the best of our knowledge, there are only a few reports concerning their reactivities,¹¹ although several synthetic routes for the construction of the 9,10-dihydro-9,10-disilaanthracene frameworks have been developed.¹² As 9,10-dihydro-9,10-disilaanthracenes containing Si-H group(s) are regarded as a new type of reducing reagent, we examined their hydrogen-donating abilities in a radical-chain process.

In a preliminary communication,¹³ we reported the first examples of the dehalogenation reaction of organic halides and deoxygenation of aliphatic alcohols via *O*-thiocarbonyl derivatives with 9,10-dihydro-9,10-disilaanthracenes **1a-c** induced by azoisobutyronitrile (AIBN) at 80 °C.¹⁴

In these reactions, increasing reactivities of disilaanthracene derivatives, compared with those of their open-chain derivatives, were observed. As an extension of these studies, we would like to report the preparation of 9,10-dihydro-9-silaanthracenes **1** containing a heteroatom at the 10-position



- 1a**: Y = SiHMe
b: Y = SiHPh
c: Y = SiMe₂
d: Y = Si(Me)SiMe₃
e: Y = SnMe₂
f: Y = O
g: Y = S
h: Y = CH₂
- 2a**: Z = SiMe₃
b: Z = OMe
c: Z = SMe



X = Cl, Br, I, OCSNHPH, OCSNHAc, OCS₂Me, OCSOC₆H₄-4-F

and the reduction of some organic compounds by the silanes **1**, comparing their reactivities with their open-chain derivatives **2** and **3** under the radical conditions described in this paper. Furthermore, the rate constants for hydrogen abstraction from the Si-H moiety of these silaanthracenes were determined using the neophyl rearrangement as a free radical clock.

Results and discussion

9,10-Dihydro-9-sila-10-heteroanthracenes **1** were easily prepared by the reaction of the di-Grignard intermediate derived from (*o*-XC₆H₄)₂Y (X = Cl, Br; Y = O, S, SiHMe) with an appropriate metal dichloride involving a silicon or tin atom according to the procedure of Corey and co-workers.¹² Some of them are new compounds and showed satisfactory ¹H, ¹³C and ²⁹Si NMR and (HR)MS data (*vide infra*).

Reduction of some organic compounds by silaanthracene derivatives **1**

In order to acquire the reducing abilities of the silaanthracene derivatives **1**, a reduction of 1-bromododecane with the silane **1** was examined and the results are listed in Table 1. When a benzene solution (0.5 mol dm⁻³) of 1-bromododecane (0.25 mmol) and 2 equiv. of the silane **1a** in the presence of AIBN (40 mol%) was heated at 80 °C under argon atmosphere for 1 h, a direct GC analysis of the reaction mixture using tridecane as an internal standard showed the formation of dodecane in 90%

Table 1 Reduction of 1-bromododecane and CCl₄ by silanes

Reducing agent	Yield (%)	
	1-Bromododecane ^a	CCl ₄ ^b
1a ^c	90	100
1c	80	89
1d ^d	80	87
1e	14	71
1f	18	76
1g	77	81
1h	Trace	4
2a	10	2
2b	7	39
2c	3	12
3	Trace	23

^a Determined by GC. ^b Determined by ¹H NMR spectroscopy. ^c A 6:4 mixture of *trans* and *cis* isomers. ^d A 9:1 mixture of isomers.

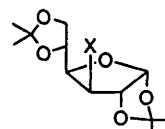
yield. Similar treatments of the silanes **1c** and **1d** with the bromide gave dodecane in 80% yields, respectively, whereas the methylene analogue **1h** and diphenylmethylsilane **3** transformed 1-bromododecane into dodecane only in a very low yield (less than 1%) under similar conditions. Moreover, the reduction of the bromide by (2'-trimethylsilylphenyl)dimethylsilane **2a**, the open-chain model for **1c**, resulted in dodecane in 10% yield. The remarkable difference in the reactivity among the silanes **1a**, **1c**, **1d**, **1h**, **2a** and **3** can be rationalized by the hypothesis that two silicon atoms are present in a conformationally restricted cyclic structure. The planar disilaanthracene frameworks and/or a transannular interaction between the silicon atoms may be responsible for the efficient generation of the silyl radical. Incidentally, the distance between these atoms was calculated to be 0.327 nm using MNDO/PM3,¹⁵ which is substantially shorter than the sum of the van der Waal's radius of silicon atoms (0.42 nm). In order to throw some light on this, the compounds **1e–g**, containing tin, oxygen or sulfur at the 10-position, were prepared and their reactivities towards 1-bromododecane were also examined. While the reactivity of the sulfur analogue **1g** towards 1-bromododecane was comparable to that of **1c**, affording 77% yield of dodecane, reduction with the tin and oxygen analogue **1e** and **1f** gave dodecane only in 14 and 18% yields, respectively. Coupled with the fact that (2'-methylsulfanylphenyl)dimethylsilane **2c**, the open chain model for **1g**, is a less effective reductant giving dodecane only in 3% yield, it is likely that the cyclic structure of **1g** was also important to accelerate the reaction. Relatively lower yields obtained from the reaction with **1e** and **1f** may be attributed to some conformational change in the central ring due to the differences of atomic size and bond lengths in respect of tin and oxygen. It was pointed out by Corey and co-workers^{12a} that a replacement of one silicon atom of 9,10-dihydro-9,10-disilaanthracene derivatives by tin or the methylene group resulted in a smaller butterfly angle (*i.e.* a less planar framework).

Similar observations are also shown in Table 1, as the results obtained from the reactions of the silanes **1**, **2** or **3** with carbon tetrachloride (CCl₄). When a mixture of **1c**, CCl₄ (2 equiv.) and AIBN (10 mol%) was heated at 80 °C for 1 h, the direct analysis of the reaction mixture by ¹H NMR spectroscopy exhibited the production of the corresponding chlorosilane in 89% yield. The reduction product of the CCl₄, chloroform, was also detected by GC analysis. Other silaanthracenes **1d–g** containing silicon, tin, oxygen or sulfur at the 10-position were also reactive, affording the corresponding chlorosilanes in moderate to good yields. Compounds **1h** and **3** were less effective giving the corresponding chlorosilanes in 4 and 23% yields, respectively, which also suggests the importance of the cyclic structure with both silicon and a heteroatom. Compared with the reactivities of **1c** and **1g**, those of the open-chain derivatives **2a** and **2c** are remarkably lower giving the corresponding chlorosilanes in 2

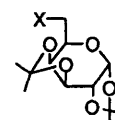
and 12% yields, respectively. However, the reactivity of **2b**, compared with **1f**, was not so significantly lowered. The phenomena observed in the reaction of oxygen analogues **1f** and **2b** suggest that the through-bond interaction between oxygen and the silyl radical would not be ruled out for the enhancement of their reactivity compared with non-functionalized silanes.

The reduction of other organic compounds by the silaanthracenes **1**, mainly **1a**, has also been investigated and the results are compiled in Table 2. While the reactions of secondary, tertiary and phenacyl bromides with the silane **1a** afforded the expected hydrocarbons in high yields (runs 5, 14 and 17), only trace amounts of the reduction products were detected in the reactions with the corresponding chlorides (runs 1 and 16), probably due to the significant decrease in the rate of chlorine abstraction by the silyl radical. Unexpectedly, only a low yield of dodecane was obtained in the reaction with 1-iodododecane (run 3) presumably due to the generation of some inhibitors such as iodine during the reaction course. In fact, a reduction of 1-bromododecane by the silane **1a** in the presence of the iodide gave dodecane only in 11% yield.

We previously reported a radical deoxygenation and a deuteration of aliphatic alcohols *via* thioxocarbamate derivatives using various silanes,¹⁶ and it was found that the reaction with Et₃SiH or Ph₃SiH proceeded only at higher temperatures (~140 °C). Obviously milder conditions would be preferable for the deoxygenation of polyfunctionalized molecules. Therefore we examined the deoxygenation of aliphatic alcohols using the disilaanthracenes **1**. The results on the deoxygenation reactions are also summarized in Table 2. Typically, a benzene solution (0.05 mol dm⁻³) of cyclododecyl *N*-phenylthioxocarbamate (0.5 mmol), the silane **1a** (2 equiv.) and AIBN (20 mol%) was refluxed for 2 h under argon atmosphere and the progress of the reaction was monitored by TLC and GC. The crude mixture was subjected to flash chromatography on silica gel to afford an expected cyclododecane in 96% yield (run 6). Other disilaanthracenes **1b** and **1c** were also considered as reducing agents (runs 7 and 8) and **1b**, containing two Si–H groups as well as **1a**, was found to be more effective than **1c**. However, the silanes **2a** and **3** gave no deoxygenated products at all (runs 9 and 10). Similar treatment of other *O*-thiocarbonyl derivatives using the silane **1a** was investigated. Although the deoxygenation of cyclododecyl *N*-acetylthioxocarbamate¹⁷ and 4-fluorophenylthiocarbonate^{4a} occurred to afford cyclododecane in 100 and 87% yields, respectively (runs 11 and 12), xanthate¹⁸ gave the products in a somewhat lower yield (19%, run 13). In order to apply this reaction to other alcohols, we tried to examine the deoxygenation of *N*-phenylthioxocarbamates derived from primary and tertiary alcohols and the corresponding hydrocarbons were isolated in 64 and 85% yields, respectively (runs 4 and 15). Furthermore, a reduction of the thioxocarbamates **4a** and **5a** obtained from furanose and pyranose derivatives were similarly carried out and afforded the corresponding deoxysugars **4b** and **5b** in 87 and 40% yields, respectively (runs 18 and 19).



4a X = OCSNHPh
4b X = H



5a X = OCSNHPh
5b X = H

Kinetic study of the reaction of silaanthracenes **1** with the neophyl radical

An absolute rate constant for hydrogen abstraction from a silane by a primary alkyl radical can be obtained by competition

Table 2 Reduction of some organic compounds by silanes

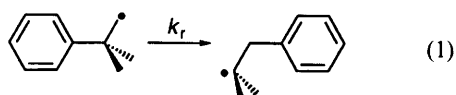
Run	R	X	Silane	Time/h	Yield (%)
1	1-Dodecyl	Cl	1a	1	Trace
2		Br	1a	1	90 ^c
3		I	1a	1	5 ^c
4		OCSNHPH	1a	2	64 ^c
5	2-Dodecyl	Br	1a	1	91 ^c
6	Cyclododecyl	OCSNHPH	1a ^d	2	96
7			1b ^b	2	88
8			1c	2	5
9			2a	2	0
10			3	2	0
11		OCSNHAc	1a	4	100
12		OCSOC ₆ H ₄ -4-F	1a	4	87
13		OCS ₂ Me	1a	4	19
14	1-Adamantyl	Br	1a	2	89 ^c
15		OCSNHPH	1a	2	85
16	PhCOCH ₂	Cl	1a	1	5 ^c
17		Br	1a	1	81 ^c
18		4a	1a	3	87
19		5a	1a	3	40

^a A 6:4 mixture of *trans* and *cis* isomers. ^b A 6:4 mixture of isomers. ^c Determined by GC.

Table 3 Hydrogen abstraction rates for various silanes

Compound	[Silane]/mol dm ⁻³	Conversion (%)	(<i>k_r</i> / <i>k_H</i>)/mol dm ⁻³	Correlation	<i>k_H</i> ³⁵³ /10 ⁴ dm ³ mol ⁻¹ s ⁻¹
1c	1.01–2.08	76–100	0.367	0.992	4.5
1d	1.01–1.89	76–100	0.374	0.999	4.0
1e	1.12–1.64	62–74	0.987	0.999	1.7
1f	1.14–2.04	44–64	0.740	0.995	2.2
1g	1.14–2.27	73–98	0.191	0.985	8.7
2b	1.71–2.16	4–5	1.52	0.999	1.1
3	1.22–1.66	3–13	2.06	0.999	0.8

between this process and the rearrangement of the radical with a known rate constant. Recently, this indirect procedure, a free-radical clock method,¹⁹ was skillfully utilized for a kinetic study of the reaction of various silanes by Chatgililoglu and co-workers.^{6b,20} We chose the neophyl rearrangement [reaction (1)] as the timing device, because its Arrhenius expression [eqn. (2)], where $\nu = 2.3RT$ kcal mol⁻¹,[†] has been shown by Franz *et al.*²¹



$$\log(k_r/s^{-1}) = (11.55 \pm 0.32) - (11.82 \pm 0.48)/\nu \quad (2)$$

If a large excess of the silane is used in order to prevent a significant change in its concentration during the reaction, then the relation as shown in the eqn. (3) holds, where *k_H* is the

$$[\text{Silane}] = \frac{k_r}{k_H} \frac{[\text{PhCMe}_3]}{[\text{PhCH}_2\text{CHMe}_2]} \quad (3)$$

rate constant for hydrogen abstraction from the silane. Thus, the mean value of $k_r/k_H = 0.367$ mol dm⁻³ was obtained by measuring the relative ratios of *tert*-butylbenzene and isobutylbenzene at various concentrations of 9,10-dihydro-9,9,10-trimethyl-9,10-disilaanthracene **1c** according to eqn. (3). By taking $k_r = 1.66 \times 10^4$ s⁻¹ at 353 K obtained from eqn. (2), we calculate $k_H = 4.5 \times 10^4$ dm³ mol⁻¹ s⁻¹. The rate constants for H atom abstraction of other silanes were measured by a similar treatment and the results are summarized in Table 3. With the silanes **1h**, **2a** and **2c**, the yields of the butylbenzenes were too low to quantify their relative yields due

to the shorter chain lengths. From these results, the values of *k_H* for the silaanthracenes **1c–g** were found to be faster than those for the corresponding open-chain analogues, in particular **1c**, **1d** and **1g** are 6, 5 and 11 times more reactive than diphenylmethylsilane **3**,²² respectively. Regarding compound **1d** containing an Si–Si bond which possesses a higher hyperconjugative ability,⁸ an increase in the reactivity was not observed compared with the silane **1c**. Furthermore, we measured the rate constant for the reaction of the neophyl radical with deuteriated **1c** (Si–D) to investigate the primary isotope effect of the reaction and found it to be $k_D = 1.39 \times 10^4$ dm³ mol⁻¹ s⁻¹. The deuterium content for *tert*-butylbenzene was determined to be 95% by GC–MS spectrometry using selected ion monitoring (SIM) mode. In accordance with the method of Chatgililoglu *et al.*,^{20b} we calculated $k_{\text{SiD}} = 1.3 \times 10^4$ dm³ mol⁻¹ s⁻¹ and $k_{\text{Me}} = 7.0 \times 10^2$ dm³ mol⁻¹ s⁻¹ by taking $k_D = k_{\text{SiD}} + k_{\text{Me}} = 1.39 \times 10^4$ dm³ mol⁻¹ s⁻¹ and $k_{\text{SiD}}/k_{\text{Me}} = 95/5$, where k_{SiD} and k_{Me} are the rate constants for deuterium atom abstraction and hydrogen abstraction from the methyl group, respectively. Similarly, taking $k_H = k_{\text{SiH}} + k_{\text{Me}} = 4.5 \times 10^4$ dm³ mol⁻¹ s⁻¹ we calculated $k_{\text{SiH}} = 4.4 \times 10^4$ dm³ mol⁻¹ s⁻¹, where k_{SiH} is the rate constant for H atom abstraction from the Si–H group. These values allow us to calculate $k_{\text{SiH}}/k_{\text{SiD}} = 3.4$.

In conclusion, we have demonstrated that 9,10-dihydro-9-silaanthracenes carrying a heteroatom such as silicon, tin, oxygen or sulfur at the 10-position are estimated to be more reactive as radical-based reducing agents than the corresponding open-chain derivatives and 9,10-dihydro-9-silaanthracene itself. In particular disilaanthracene **1a** was found to be a practical reagent for dehalogenation of organic halides and deoxygenation of aliphatic alcohols *via* *O*-thiocarbonyl derivatives. The reason for the enhanced reactivities of the cyclic silanes is still not clear, however the planarity of the radical centre induced by ring closure is the main contribution to the extra stabilization of the silyl radical.

[†] 1 cal = 4.184 J.

Experimental

General

GC measurements were performed on a Ohkura GC-103C and a GL Sciences GC-380 gas chromatograph using a 50 m × 0.25 mm methyl silicone capillary column (Quadrex). TLC was carried out on Merck silica gel 60 F₂₅₄. Flash column chromatography was performed on Merck silica gel 60 (230–400 mesh). IR spectra were recorded on a Perkin-Elmer 1600 IR spectrometer. ¹H, ¹³C and ²⁹Si NMR spectra were measured in CDCl₃ solution on a Varian UNITY-400 spectrometer. All chemical shifts are reported as δ values (ppm) relative to residual chloroform (δ_H 7.26), the central peak of deuteriochloroform (δ_C 77.0) or tetramethylsilane (δ_{Si} 0.0). *J* values are given in Hz. Mass spectra (EI) were obtained on a JEOL JMS-AX-500 spectrometer with DA7000 data system. GC-MS was measured with the direct combination of GC (Hewlett-Packard GC 5890 Series II with a 25 m × 0.25 mm methyl silicone capillary column) and a JEOL JMS-AX-500 spectrometer. Selected ion monitoring (SIM) method was used to determine isotopic distribution in the deuteriated products, focusing on M⁺ and (M + 1)⁺ ions.

Materials

Most of the starting materials and reagents were commercial products and were used as received. Bis(*o*-chlorophenyl)methylsilane,^{12a} bis(2-bromophenyl) ether,²³ bis(2-bromophenyl)sulfide,²⁴ bis(2-chlorophenyl)methane,²⁵ (2'-chlorophenyl)trimethylsilane²⁶ and neophyl bromide²⁷ were prepared according to the literature. Preparation of *N*-phenyl- and *N*-acetyl-thioxocarbamates have previously been reported.^{16b,17} *O*-Cyclododecyl *S*-methyl dithiocarbonate¹⁸ and cyclododecyl 4-fluorophenylthiocarbonate^{4a} were prepared according to the Barton's procedure. Solvents were distilled over sodium in the presence of benzophenone.

Preparation of 9,10-dihydro-9-sila-10-heteroanthracenes 1

For example, the preparation of 9,10-dihydro-9,9,10-trimethyl-9,10-disilaanthracene **1c** is described as follows. To Mg turnings (2.43 g, 100 mmol) in tetrahydrofuran (THF) (25 cm³) was added 1,2-dibromoethane (16.90 g, 90 mmol) in THF (75 cm³), and the mixture was refluxed under argon atmosphere for 1 h. After the solution was cooled to room temperature, K (5.85 g, 150 mmol), KI (5.81 g, 35 mmol) and THF (100 cm³) were added and refluxed for 2 h. Then, bis(*o*-chlorophenyl)dimethylsilane (5.34 g, 20 mmol) was added to the resulting black suspension of activated Mg and the mixture was heated to reflux for 3 h, after which dichlorodimethylsilane (3 cm³) was added at room temperature. After being stirred at room temperature overnight, the reaction mixture was quenched with aqueous NH₄Cl and extracted with diethyl ether. The crude product was purified by flash chromatography on silica gel to give disilaanthracene **1c** (4.34 g, 85%) and the structure was confirmed by comparison with the reported spectral data,^{12a} $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3052, 2956, 2109, 1424, 1407, 1262, 1247 and 1125; δ_{H} 0.45 (3 H, s), 0.53 (3 H, s), 0.62 (3 H, d, *J* 3.9), 4.94 (1 H, q, *J* 3.9), 7.42 (4 H, m) and 7.70 (4 H, m); δ_{Si} -17.0 and -32.6; *m/z* 254 (M⁺).

Other 9,10-dihydro-9-silaanthracene derivatives of **1** were similarly prepared from the corresponding dihalides and the appropriate metal dichlorides, and their spectral data are as follows.

1a:^{12a} $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3052, 2115, 1427, 1261 and 1127; *m/z* 240 (M⁺); major isomer δ_{H} 0.58 (3 H, d, *J* 3.9), 4.95 (1 H, q, *J* 3.9), 7.42 (4 H, m) and 7.72 (4 H, m); δ_{Si} -30.8; minor isomer δ_{H} 0.63 (3 H, d, *J* 3.9), 4.92 (1 H, q, *J* 3.9), 7.43 (4 H, m) and 7.71 (4 H, m); δ_{Si} -32.4.

1b: $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3049, 2119, 1427, 1260 and 1125 (Found: M⁺, 302.0974. C₁₉H₁₈Si₂ requires *M*, 302.0948); major isomer δ_{H} 0.64 (3 H, d, *J* 3.9), 4.24 (1 H, q, *J* 3.9), 5.47 (1 H, s) and 7.33–

7.77 (13 H, m); δ_{C} -4.3, 128.1, 128.7, 128.9, 129.8, 134.3, 135.6, 135.7, 135.8, 140.2 and 142.3; δ_{Si} -30.0 and -31.2; minor isomer δ_{H} 0.52 (3 H, d, *J* 3.9), 4.97 (1 H, q, *J* 3.9), 5.45 (1 H, s) and 7.33–7.77 (13 H, m); δ_{C} -3.7, 128.1, 128.7, 128.9, 129.8, 134.4, 135.6, 135.7, 135.8, 140.1 and 142.4; δ_{Si} -30.6 and -30.8.

1d: $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3048, 2955, 2096, 1426, 1261, 1242 and 1113 (Found: M⁺, 312.1145. C₁₇H₂₄Si₃ requires *M*, 312.1186); major isomer δ_{H} 0.03 (9 H, s), 0.68 (3 H, s), 0.72 (3 H, d, *J* 3.8), 4.84 (1 H, q, *J* 3.8), 7.40 (4 H, m), 7.60 (2 H, m) and 7.68 (2 H, m); δ_{C} -5.7, -4.9, -2.0, 127.8, 128.5, 133.7, 134.0, 140.5 and 144.7; δ_{Si} -35.2, -33.0 and -17.1; minor isomer δ_{H} 0.00 (9 H, s), 0.44 (3 H, d, *J* 4.4), 0.63 (3 H, s), 4.98 (1 H, q, *J* 4.0), 7.40 (4 H, m), 7.60 (2 H, m) and 7.68 (2 H, m); δ_{C} -3.7, -2.2, -1.3, 127.8, 128.5, 134.1, 134.7, 144.0 and 144.6; δ_{Si} -32.7, -29.0 and -18.9.

1e: $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3045, 2970, 2119, 1423, 1260, 1247, 1122 and 1098; δ_{H} 0.50 (3 H, s), 0.52 (3 H, s), 0.61 (3 H, d, *J* 3.9), 4.93 (1 H, q, *J* 3.9), 7.35 (4 H, m), 7.59 (2 H, m) and 7.71 (2 H, m); δ_{C} -9.0, -8.7, -3.7, 128.0, 128.7, 134.3, 136.0, 144.2 and 149.4; δ_{Si} -27.9 (Found: M⁺, 346.0176. C₁₉H₁₈SiSn requires *M*, 346.0200).

1f:²³ $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3065, 3004, 2958, 2124, 1592, 1573, 1462, 1424, 1303, 1268, 1221 and 1130; δ_{H} 0.57 (3 H, d, *J* 3.6), 5.03 (1 H, q, *J* 3.5), 7.15 (4 H, m), 7.43 (2 H, m) and 7.53 (2 H, m); δ_{Si} -44.2; *m/z* 212 (M⁺).

1g: $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3053, 2125, 1575, 1422, 1260, 1133 and 1047; δ_{H} 0.66 (3 H, d, *J* 3.7), 4.80 (1 H, q, *J* 3.7), 7.31 (4 H, m), 7.54 (2 H, m) and 7.63 (2 H, m); δ_{C} -7.5, 126.2, 127.9, 129.5, 132.4, 134.3 and 142.5; δ_{Si} -33.1 (Found: M⁺, 228.0389. C₁₃H₁₂SiS requires *M*, 228.0429).

1h:²⁸ $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3055, 2997, 2111, 1587, 1564, 1462, 1436, 1253, 1133 and 1078; δ_{H} 0.65 (3 H, d, *J* 3.8), 4.08 and 4.14 (2 H, ABq, *J* 17.0), 4.85 (1 H, q, *J* 3.8), 7.28 (2 H, m), 7.35 (4 H, m) and 7.64 (2 H, m); δ_{Si} -35.3; *m/z* 210 (M⁺).

9,10-Dihydro-9,9,10-trimethyl-9,10-[10-²H]disilaanthracene

A solution of silane **1c** (3.04 g, 11.9 mmol) and benzoyl peroxide (BPO) (0.286 g, 1.18 mmol) in CCl₄ (18.17 g, 118 mmol) was refluxed for 2 h. After removal of the solvent, the residual chlorosilane was dissolved in dry diethyl ether and was added dropwise to a suspension of LiAlD₄ (0.50 g, 12.1 mmol) in diethyl ether. Usual work-up followed by flash column chromatography afforded the corresponding deuteriosilane (2.44 g, 81%), $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3052, 2956, 1534, 1423, 1261, 1247 and 1124; δ_{H} 0.45 (3 H, s), 0.53 (3 H, s), 0.61 (3 H, s), 7.42 (4 H, m) and 7.70 (4 H, m) (Found: M⁺, 255.1027. C₁₅H₁₇DSi₂ requires *M*, 255.1010).

(2'-Trimethylsilylphenyl)dimethylsilane 2a

To a suspension of activated Mg prepared as described above was added dropwise (2'-chlorophenyl)trimethylsilane (5.52 g, 30.0 mmol) followed by dimethylchlorosilane (3.09 g, 33 mmol). After usual work-up, fractional distillation gave the title compound **2a** (3.86 g, 62%), bp 90 °C/3 mmHg (lit.,²⁹ 75–76 °C/2.5 mmHg); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2956, 2159, 1412, 1248 and 1121; δ_{H} 0.33 (6 H, d, *J* 3.7), 0.35 (9 H, s), 4.76 (1 H, hep, *J* 3.7), 7.34 (2 H, m) and 7.58 (2 H, m); δ_{Si} -3.7 and -20.6; *m/z* 208 (M⁺).

(2'-Methoxyphenyl)dimethylsilane 2b

To a solution of 2-methoxyphenyl magnesium bromide prepared from 2-bromoanisole (5.61 g, 30 mmol) and Mg (0.88 g, 36 mmol) in diethyl ether (30 cm³) was added dimethylchlorosilane (3.41 g, 36 mmol), and the mixture was stirred at room temperature for 1 h. Then, the reaction mixture was treated with aqueous NH₄Cl, and the crude product was distilled under reduced pressure to yield 4.29 g (86%) of title compound **2b**, bp 94 °C/20 mmHg; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2957, 2119, 1588, 1460, 1429 and 1237; δ_{H} 0.33 (6 H, d, *J* 3.6), 3.82 (3 H, s),

4.40 (1 H, hep, J 3.6), 6.84 (1 H, m), 6.96 (1 H, m), 7.37 (1 H, m) and 7.43 (1 H, m); δ_{C} -3.8, 55.1, 109.6, 120.6, 125.6, 131.2, 135.8 and 164.4; δ_{Si} -18.9 (Found: M^+ , 166.0839. $\text{C}_9\text{H}_{14}\text{OSi}$ requires M , 166.0814).

(2'-Methylsulfonylphenyl)dimethylsilane 2c

To a mixture of Mg turnings (1.29 g, 53 mmol) in diethyl ether was added a solution of 2-bromothioanisole (9.02 g, 44 mmol) in diethyl ether (44 cm^3) followed by dimethylchlorosilane (5.01 g, 53 mmol). Usual work-up and distillation gave pure **2c** (5.71 g, 71%), bp 115 °C/20 mmHg; ν_{max} (neat)/ cm^{-1} 2957, 2124, 1574, 1422 and 1248; δ_{H} 0.42 (6 H, d, J 3.8), 2.48 (3 H, s), 4.56 (1 H, m, J 3.8), 7.16 (1 H, m), 7.34 (2 H, m) and 7.47 (1 H, m); δ_{C} -3.4, 17.7, 125.2, 127.6, 130.2, 135.3, 138.2 and 144.9; δ_{Si} -18.7 (Found: M^+ , 182.0537. $\text{C}_9\text{H}_{14}\text{SSi}$ requires M , 182.0586).

Reduction of 1-bromododecane with silanes

Typically, a solution of 1-bromododecane (62.3 mg, 0.25 mmol), 9,10-dihydro-9,10-dimethyl-9,10-disilaanthracene **1a** (0.12 g, 0.50 mmol) and AIBN (16.4 mg, 0.10 mmol) in dry benzene (0.5 cm^3) was kept at 80 °C under an argon atmosphere for 1 h. The crude product was analysed by GC, dodecane (90% yield) being quantified using tridecane as an internal standard.

Under the same conditions as above, other silanes were also studied and the results are listed in Table 1.

Reaction of silanes with carbon tetrachloride

A reaction of 9,10-dihydro-9,9,10-trimethyl-9,10-disilaanthracene **1c** with CCl_4 was representative. When a mixture of silane **1c** (0.12 g, 0.48 mmol) and CCl_4 (0.17 g, 1.1 mmol) in the presence of AIBN (8.7 mg, 0.053 mmol) was heated at 80 °C for 1 h, the direct analysis of the reaction mixture by ^1H NMR spectroscopy showed the production of the corresponding chlorosilane in 89% yield along with chloroform which was also detected by GC analysis. The authentic chlorosilane was obtained by refluxing silane **1c** and BPO (10 mol%) in CCl_4 (2 equiv.) for 1 h. δ_{H} 0.51 (3 H, s), 0.52 (3 H, s), 0.92 (3 H, s), 7.49 (4 H, m), 7.71 (2 H, m) and 7.87 (2 H, m) (Found: M^+ , 288.0550. $\text{C}_{15}\text{H}_{17}^{35}\text{ClSi}$ requires M , 288.0557).

Other silanes were similarly treated and the yields of the corresponding chlorosilanes are also compiled in Table 1.

Reduction of *N*-phenylthiocarbamates

A typical procedure is described for deoxygenation of cyclododecyl *N*-phenylthiocarbamate using 9,10-dihydro-9,10-dimethyl-9,10-disilaanthracene **1a**. A solution of the thiocarbamate (0.16 g, 0.5 mmol), silane **1a** (0.24 g, 1.0 mmol) and AIBN (16.4 mg, 0.1 mmol) in benzene (10 cm^3) was refluxed under an argon atmosphere for 2 h. The progress of the reaction was monitored by GC and TLC analyses. The crude product obtained after removal of the solvent was purified by flash chromatography affording pure cyclododecane (80.5 mg, 96%) as a colourless solid. The structure was confirmed by comparison with an authentic sample using GC and GC-MS analyses.

Other *N*-phenylthiocarbamates were deoxygenated under analogous conditions and the yields are shown in Table 2.

3-Deoxy-1,2:5,6-di-*O*-isopropylidene- α -D-glucofuranose 4b

A solution of the corresponding 3-*O*-(*N*-phenyl)thiocarbamate **4a** (0.198 g, 0.5 mmol), silane **1a** (0.24 g, 1.0 mmol) and AIBN (16.4 mg, 0.1 mmol) in benzene (10 cm^3) was refluxed under an argon atmosphere for 3 h and the crude product was purified by flash chromatography on SiO_2 to afford the 3-deoxysugar **4b** (106 mg, 87%). The structure was confirmed by comparison with the reported ^1H NMR and mass spectra in the literature.^{16b} δ_{H} 1.32 (3 H, s), 1.36 (3 H, s), 1.43 (3 H, s), 1.51 (3 H, s), 1.77 (1 H, ddd, J 13.5, 10.2 and 4.8), 2.18 (1 H, dd, J 13.5

and 4.4), 3.79–3.85 (1 H, m), 4.08–4.19 (3 H, m), 4.76 (1 H, dd, J 4.8 and 3.7) and 5.82 (1 H, d, J 3.7) (Found: M^+ - Me, 229.1054. $\text{C}_{11}\text{H}_{17}\text{O}_5$ requires M , 229.1076).

6-Deoxy-1,2:3,4-di-*O*-isopropylidene- α -D-galactopyranose 5b

Deoxygenation of the corresponding 6-*O*-(*N*-phenyl)thiocarbamate **5a** (0.198 g, 0.5 mmol) was carried out as described above and a similar work-up gave the 6-deoxysugar **5b**^{16b} (49.1 mg, 40%). δ_{H} 1.26 (3 H, d, J 6.6), 1.33 (3 H, s), 1.35 (3 H, s), 1.47 (3 H, s), 1.52 (3 H, s), 3.92 (1 H, dq, J 1.9 and 6.6), 4.08 (1 H, dd, J 7.9 and 1.9), 4.29 (1 H, dd, J 5.1 and 2.4), 4.59 (1 H, dd, J 7.9 and 2.4) and 5.52 (1 H, d, J 5.1) (Found: M^+ - Me, 229.1044. $\text{C}_{11}\text{H}_{17}\text{O}_5$ requires M , 229.1076).

General procedure for kinetic measurement

To a solution of neophyl bromide in benzene was added silane (ca. 6 equiv.) at concentrations between 1.0 and 2.3 mol dm^{-3} as shown in Table 3. Then, the reaction mixture was heated at 80 °C in a sealed tube using AIBN as an initiator. The relative yields of *tert*-butylbenzene and isobutylbenzene were obtained by GC and the conversion, the sum of the chemical yields of butylbenzenes, was quantified using dodecane as a GC standard.

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