

9,10-Dihydro-9,10-disilaanthracenes as a New Radical-based Reducing Agent: Importance of Transannular Interaction Between Silyl Radical and Silicon Atom

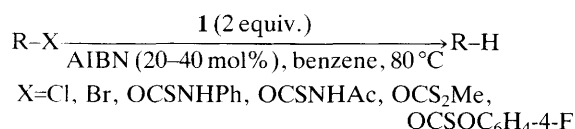
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9,10-Dihydro-9,10-disilaanthracenes containing Si–H moieties at 9,10-positions are effective reducing agents in AIBN-initiated dehalogenation and deoxygenation reactions, in which a transannular interaction between silyl radical and silicon atom is considered important.

Selective dehalogenation of organic halides¹ and deoxygenation of alcohols² are of considerable importance in organic synthesis. In these reactions, tributyltin hydride has been conveniently used as a reducing agent under radical conditions.³ Although organosilicon hydrides^{4,5} are considered to be preferable for ecological and toxicological reasons, these usually have too high a bond-dissociation energy for practical use. Several efforts have been made to produce compounds with reduced Si–H bond strength. One successful product is tris(trimethylsilyl)silane,⁶ in which the Si–H bond is dramatically weakened by an interaction between a generated silyl radical and adjacent silicon *d*-orbitals,⁷ although access to the compound is difficult due to low synthetic yields. Recently, attention has been focused on the chemical and theoretical properties of 9,10-dihydro-9,10-disilaanthracenes **1**. To the best of our knowledge, few reports concerning their reactivities exist.⁸ As **1** and **2** were regarded as a new type of reducing reagent, we examined their reactivities as part of our studies into the chemistry of organosilicon compounds. Described in this communication are the first examples of a dehalogenation reaction of organic halides and a deoxygenation of aliphatic alcohols *via* thioxocarbamate derivatives and **1** and **2** induced by AIBN at 80 °C. In these reactions, a transannular (*p*–*d*) π interaction between silicon atom and silyl radical is considered important.

9,10-Dihydro-9,10-disilaanthracenes **1a**–**c** were easily prepared from *o*-dihalobenzene and an appropriate dichlorosilane *via* two steps (more than 50% overall yields), according to Corey's procedure.⁹ A solution of 1-bromododecane (0.25 mmol), **1a** (2 equiv.) and AIBN (40 mol%) in benzene (0.5 ml) was heated at 80 °C under argon atmosphere for 1 h. Formation of dodecane in 90% yield (run 2) was observed by GLC analysis. The reaction was effectively inhibited by an addition of 2,6-di-*tert*-butyl-4-methylphenol as a radical scavenger. A similar reaction of **1c** with the bromide gave dodecane in 55% yield (run 3). On the other hand, **2** transformed the bromododecane into dodecane in a very low yield (less than 1%) under similar conditions (run 4). The remarkable difference of the reactivity between **1** and **2** can be rationalized by the natures of carbon and silicon at the opposite side of the ring. Similarly, reactions of the bromide with 1,2-bis(methylphenylsilyl)benzene (**3**, run 5) and triphenylsilane also gave trace amounts of dodecane. Coupled with the results from tris(trimethylsilyl)silane, these suggest that a contribution of a transannular (*p*–*d*) π interaction between silyl radical (9-position) and silicon atom (10-position) is important to generate silyl radical efficiently.



The distance between these atoms was calculated to be 0.327 nm using MNDO/PM3.¹⁰ Incidentally, it was shown by a reaction using deuterated **1a** (Si–D) that a hydrogen abstraction from Si–H(D) was included in a rate-determining step.[†]

As shown in Table 1, an application to secondary and tertiary bromides also afforded the corresponding products in 91 and 89% yields, respectively (runs 6 and 7). Only a trace

amount of dodecane was detected in a reaction of 1-chlorododecane with **1a** (run 1), probably due to the significant decrease in the rate of chlorine abstraction by the silyl radical. From the results, compound **1** was found to be comparable with tris(trimethylsilyl)silane in the reduction of organic halides, under milder conditions compared to other known hydrosilanes.

These results led us to examine a deoxygenation of aliphatic alcohols *via* thioxocarbamates and thioxocarbonates using **1**. Previously, we reported a radical deoxygenation and a deuteration of aliphatic alcohols *via* thioxocarbamate derivatives using triethylsilane and deuteriotriethylsilane,¹¹ and the reactions proceeded only at high temperature (~140 °C). It became obvious that milder conditions would be preferable to introduce D atom stereoselectively into organic molecule. In a typical procedure, a mixture of cyclododecyl *N*-phenylthioxocarbamate (0.5 mmol), **1a** (2 equiv.) and AIBN (20 mol%) in benzene (10 ml) was refluxed for 2 h under argon atmosphere until no further change was observed. It was checked at intervals by TLC and GLC. After purification of the crude products by flash chromatography on silica gel, the expected cyclododecane was obtained in 96% yield (run 9). Similarly, other 9,10-dihydro-9,10-disilaanthracenes (**1b** and **1c**) were tried as reducing agents. Consequently, it was found that **1b**, as well as **1a**, containing two Si–H moieties at 9,10-positions was effective (run 10), and **1c** was less effective (run 11). On

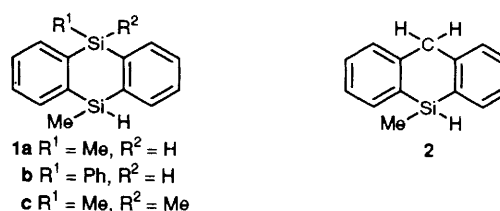


Table 1 Yields of dehalogenation and deoxygenation reactions

Run	R	X	Reducing Agent	t/h	Yield (%)
1	1-Dodecyl	Cl	1a ^a	1	Trace
2		Br	1a	1	90 ^c
3			1c	1	55 ^c
4			2	1	Trace
5			3	1	Trace
6	2-Dodecyl	Br	1a	1	91 ^c
7	1-Adamantyl	Br	1a	2	89 ^c
8	1-Dodecyl	OCSNHPH	1a	2	64 ^c
9	Cyclododecyl	OCSNHPH	1a	2	96
10			1b ^b	2	88
11			1c	2	5
12			2	2	0
13		OCSNHAc	1a	4	100
14		OCS ₂ Me	1a	4	19
15		OCSO-4-F-C ₆ H ₄	1a	4	87
16	1-Adamantyl	OCSNHPH	1a	2	85

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

the other hand, **2** was not effective (run 12). Triphenylsilane gave no deoxygenated product. The transannular interaction described above is also supposed to be important in these reactions. Other *O*-thiocarbonyl derivatives were examined and some of them were expectedly converted into hydrocarbons. For example, cyclododecyl *N*-acetylthiocarbamate¹² and 4-fluorophenylthiocarbonate⁴ afforded cyclododecane in 100 and 87% yields, respectively (runs 13 and 15), though they needed slightly prolonged reaction time (4 h). However, xanthate¹³ gave the product in unsatisfactory yield (19%), probably due to low radicophilicity of thiocarbonyl group (run 14). In order to investigate the applicability of the reaction, we tried to examine the deoxygenation of primary and tertiary alcohols and the corresponding hydrocarbons were obtained in 64 and 85% yields, respectively (runs 8 and 16). Currently we are exploring the possibility of stereoselective radical reduction using **1**.

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Footnotes

† The value of k_H/k_D was estimated to be approximately 4.

‡ Compound **1b** is new compound and the spectral data are as follows.

¹H NMR spectra in CDCl₃ at 400 MHz: major isomer δ 0.64 (d, 3 H, *J* = 3.9 Hz), 4.24 (q, 1 H, *J* = 3.9 Hz), 5.47 (s, 1 H), 7.33–7.77 (m, 13

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H): minor isomer δ 0.52 (d, 3 H, *J* = 3.9 Hz), 4.97 (q, 1 H, *J* = 3.9 Hz), 5.45 (s, 1 H), 7.33–7.77 (m, 13 H). ²⁹Si NMR spectra in CDCl₃ at 79.5 MHz: major isomer δ -31.2, -30.0; minor isomer δ -30.8, -30.6. HRMS (EI): *m/z* 302.0974 (*M*⁺, C₁₉H₁₈Si₂ requires 302.0948).

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