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Free radical chemistry associated with H(RSiH) "H

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Abstract

Polysilanes of the type $H(RSiH)_nH$, where R = n-hexyl or phenyl, have been used as radical-based reducing agents for organic halides. They rival the effectiveness of the other group 14 hydrides in reduction processes. The repetitive hydrogen transfer from the same molecule of $H(RSiH)_nH$ allows these compounds to be used in small quantities. Lower $(5 \times 10^4 M^{-1} s^{-1})$ and higher $(6 \times 10^5 M^{-1} s^{-1})$ limit values for the rate constant of the reaction of primary alkyl radicals with each SiH moiety of $H(PhSiH)_nH$ have been obtained by using unimolecular radical reactions as timing devices. The photochemical behavior of these polysilanes in the presence or absence of di-*tert*-butyl peroxide have been studied by EPR spectroscopy, and the -SiHR-SiR-SiHR radical (R = n-hexyl) has been identified as a transient species. Silyl radicals, obtained from $H(RSiH)_nH$ and thermally generated *tert*-butoxyl radicals, add to a variety of substrates containing double bonds to give the corresponding adducts for which EPR spectra have been recorded. © 1997 Elsevier Science S.A.

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1. Introduction

Silyl radicals play a strategic role in diverse areas of science [1]. For example, they are present as intermediates in the production of silicon-containing ceramics [2], in photodegradation [3,4] and functionalization [5,6] of polysilanes, and in radical reactions of interest to synthetic chemists [7].

Several reports have appeared in the literature describing the synthesis of poly(hydrosilane) [8–17]. The method for preparation was discovered by Harrod and coworkers in the mid 1980s and involves the dehydrogenative coupling of $RSiH_3$ in the presence of group 4 metallocenes (Eq. 1) [18]. However, little is known about their mode of action in free radical chemistry, or their importance in such processes [5,6,19,20].

Despite the large variety of reducing agents available

¹ On sabbatical leave. Permanent address: Dipartimento di Chimica Organica e Biologica, Università di Napoli 'Federico II', Via Mezzocannone 16, 80134 Napoli, Italy. for the removal of halogen substituents from organic halides [21], new non-toxic, economical, simple, and selective reducing systems are in constant demand. In the last few years, some of us have worked to develop new reducing systems under free radical conditions [7,22]. A feature associated with radical chain reactions under reducing conditions is hydrogen transfer from the reducing agent to a radical (Eq. 2) [23].

 $MH + R' \longrightarrow M' + RH$ (2)

The resulting M^{\cdot} radical undergoes further propagation step(s) to generate fresh R^{\cdot} radicals, thus completing the cycle of the chain reactions. In order to modulate the hydrogen donating abilities of this class of compounds, a considerable number of modified silanes has been introduced [24], (TMS)₃SiH being the most representative among them [25].

In this article we address some applications of polysilanes 1 and 2 in free radical chemistry. In particular, we describe the use of these polysilanes as reagents for reductive dehalogenation as well as their hydrogen donating abilities towards alkyl radicals. Furthermore, the reactions of silyl radicals, generated by hydrogen abstraction from the parent polysilanes, with a variety of

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Table 1 Reduction of organic halides with polysilanes 1 and 2^{*}

RX	polysilane 1 yield of AH, ^b %	polysilane 2 yield of RH, ^b %	RX	polysitme 1 yield of Rrt.11%.	polysilane 2 yield of RH, ^b so
CH3C(O)O(CH2)4-I	92		C ₈ H ₅ C(O)CH ₂ -Br	95	
ار			(CH3)3COC(O)CH2-Br	100	
	38	91	(CH3CH2OC(O)]2CH Br	92	
for of			CH ₃ O	Q3°	86
Xox jiino	95		CH ₃ O O O O	15 0	
N=C-CH2-I	96				
\sim			CH3OCH2CH2OCH2·CI	96	
СНа	88	99	020201	96	
C8H5CH2-Br	93	95	0	4	
C6F6CH2-8r	95		'allow	92"	98

^aBenzene- d_6 as solvent, AlBN (10-15 mol%), at 82-85°C, ^bNMR yields using (PhCH₂)₃O or PhCH₃ as the internal standard. ^cIsolated yield 90%, ^dReduction of benzylic moiety; isolated yield 87%.

substrates containing double bonds were studied by EPR spectroscopy.



2. Results and discussion

2.1. Starting materials

Polysilane 1 and polysilane 2 were prepared by dehydropolymerization of the corresponding silane monomer and Cp_2ZrMe_2 catalyst, generated in situ from Cp_2ZrCl_2 and MeLi, following the literature procedure [26]. After work-up, the polymeric materials gave the expected ¹H NMR, IR and UV-visible spectra. Analysis by gel permeation chromatography (GPC; polystyrene standards) revealed that polymer 1 ($M_w =$ 2440, $M_w/M_n = 1.89$) obtained from phenylsilane had a bimodal molecular weight distribution with linear and cyclic portions of 86 and 14%, respectively. On the other hand, *n*-hexylsilane afforded polymer 2 ($M_w =$ 1310, $M_w/M_n = 1.08$) with monomodal GP chromatograms and with a narrow distribution under identical experimental conditions.

2.2. Reductive dehalogenation

The reduction of a variety of organic halides was carried out using the above described poly(phenylsilane). A benzene- d_6 solution (2-4 ml) containing the halogen derivative (0.1-0.2 M), the poly(phenylsilane) (0.1 equiv)³ and a radical initiator was heated at 82-85°C. ¹H NMR analysis allowed for the determination of the reaction yields (Table 1). The disappearance of the starting material (observed by NMR) corresponded to ca. 50% replacement of SiH with SiX as expected from the reaction stoichiometry³. A similar percentage of SiH replacement with SiX was estimated by comparing the intensities of IR stretching frequencies of the ν_{Si-H} and the $\nu_{C=C}$ ⁴ In a few cases, the isolation of the reduced product was readily obtained by adding n-pentane and filtering off the polymeric material which precipitated from the crude mixture (see Table 1).

By replacing polysilane 1 with polysilane 2, the reduction of halides was still efficient. However, in

³ Taking into consideration the statistical number of hydrogens (n = 23), 0.1 equiv. of poly(phenylsilane) corresponds to 2.3 equiv. of SiH moieties.

⁴ In the starting poly(phenylsilane) the intensity ratio of the ν_{Si-H} (2108 cm⁻¹) and one of the three $\nu_{C=C}$ (1812, 1879 and 1950 cm⁻¹) is ca. 10. When the reaction is over, the $\nu_{C=C}$ intensities remained unchanged, whereas the ν_{Si-H} intensity was reduced ca. 60%.

these reactions 0.4-0.5 equiv. of polysilane 2 was necessary in accordance with the lower molecular weight obtained by GPC. Some examples are reported in Table 1.

Evidence of a free radical chain mechanism, in which the two propagation steps are the H atom abstraction from the poly(phenylsilane) by an alkyl radical (Eq. 3) and the X atom abstraction from alkyl halide by the silyl radical (Eq. 4), was provided by the observations that the reactions: (1) started only in the presence of radical initiators such as AIBN and dibenzoyl peroxide, (2) were retarded by 2,6-di-*tert*-butyl-4-methylphenol and duroquinone, which are expected to interfere with the propagation steps 3 and 4 [1], respectively, and (3) were inhibited by nitroxides such as TEMPO.

$$R' + - \stackrel{Ph}{\underset{H}{si-}} \qquad RH + - \stackrel{Ph}{\underset{Si-}{si-}} (3)$$

$$-\overset{Ph}{\underset{\dot{s}i}{=}} + RX \xrightarrow{Ph} -\overset{Ph}{\underset{\dot{s}}{=}} + R.$$
(4)

2.3. Kinetic studies

In order to quantify the observed reactivity of poly(phenylsilane) towards primary alkyl radicals we first attempted the free-radical clock methodology [23] by means of a 5-hexenyl radical cyclization. Thus, 6-bromo-1-hexene was allowed to react with poly(phenvlsilane) under normal conditions, and the products were analyzed by GC and ¹H NMR. To our surprise the volatile products, i.e., 1-hexene, methylcyclopentane and cyclohexane, accounted for only 40 to 70% of the 6-bromo-1-hexene consumption, depending on the experimental conditions. The [1-hexene]/[methylcyclopentane] ratio decreased upon increasing the initial concentration of silane, thus suggesting the consumption of 1-hexene during the reaction. Furthermore, the NMR spectra of the solid residue showed broad signals corresponding to alkyl protons. On this basis, we attribute the lower than expected amount of 1-hexene to the hydrosilylation of the olefins by the polysilane [5,6]. It is worth pointing out that these results are in contrast with the well known reactivity of Et_3Si^{-5} and $(TMS)_3Si^{-1}$ [29] radicals, where the bromide is at least 100 times more reactive than the alkene.

To verify if the silyl radical from poly(phenylsilane) showed a different reactivity, we performed competition experiments between $CH_2 = CHR$ and $BrCH_2CH_2R$

(where $R = C_8 H_{17}$). The obtained results indicate that the bromide is only 2.9 times more reactive than the alkene. ⁶ A behavior similar to that of poly(phenylsilane) has been observed for (MeS)₃SiH [31] and an explanation based on the different nucleophilicity of the silyl radicals was advanced.

By performing experiments with 6-bromo-1-hexene under second order kinetics and low conversions we estimated a higher limit for the rate constant of primary alkyl radical with H(PhSiH)_nH, i.e., $k_{\rm H} < 6 \times 10^5 \text{ M}^{-1}$ s^{-1} per H atom. We were also able to obtain a lower limit for the rate constant using the neophyl rearrangement as a free-radical clock [23]. A benzene- d_6 solution containing neophyl bromide (0.2 M) and poly(phenylsilane) (0.02 M) was allowed to react at 85°C. 'H NMR of the crude reaction mixture and GC analysis of volatile products showed the formation of tert-butylbenzene. No evidence for isobutylbenzene (the expected rearrangement product) was obtained. Therefore, we estimate the rate constant of primary alkyl radical with H(PhSiH), H to be larger than $10^6 \text{ M}^{-1} \text{ s}^{-1}$, i.e., the rate constant for the rearrangement of neophyl radical is 2.2×10^4 s⁻¹ at 85°C [32], multiplied by at least 50 (from the limit of detection of the GC analysis). Taking into account the statistical number of hydrogens abstracted (n = 23), we calculated $k_{\rm H} > 5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ per H atom. These lower and higher limit values (referring to rate constant per H atom) are in satisfactory agreement with the rate constant of 1.0×10^5 M⁻¹ s⁻¹ for the reaction of the neophyl radical with (Me₃Si)₂Si(H)Me at 80°C [33].

2.4. EPR studies

The spectrum obtained upon ultraviolet irradiation of a mixture of polysilane 2 and di-tert-butyl peroxide in cyclohexane at room temperature is shown in Fig. 1a.⁷ When irradiation was cut off, the remaining signals (g ca. 2.0057) persisted for several hours (Fig. 1b) and correspond to the superimposition of signals from at least two persistent paramagnetic species. An EPR spectrum similar to that in Fig. 1b was produced by irradiation of a sample without peroxide. The spectrum in Fig. 1c, obtained by subtracting spectrum (b) from spectrum (a), is characterized by the coupling of the unpaired electron with two hydrogens (7.10 G) and a g-factor of 2.0047. In an independent experiment and in the presence of 2-methyl-2-bromopropane, all signals in Fig. 1a were completely replaced by that of the tert-butyl radical.

This behavior and the spectral parameters [1,34,35], allow us to identify the transient species as the silvl

⁵ Rate constants for the reaction of triethylsilyl radicals with $CH_2 = CH(CH_2)_3CH_3$ [27] and $CH_3(CH_2)_4Br$ [28] are 4.8×10^6 and 5.4×10^8 M⁻¹ s⁻¹, respectively at 300 K.

⁶ The relative rate constant was calculated from the loss of starting materials by using the method of [30].

⁷ Attempts to observe satellite lines failed, due to the low intensity of the signals.

radical 3 obtained by hydrogen abstraction by *tert*butoxyl radical from the starting poly(*n*-hexylsilane). The EPR spectrum showed with decreasing temperature, an alternating line-width effect which is usually observed when the difference in frequency between the coupling constants is comparable to the frequency of conformational interconversion. This is indicative of restricted rotational motion about the C-Si bond between the radical center and the alkyl substituent. An analogous effect was previously reported by McKinley and coworkers [34,35] for the analogous silyl radicals obtained by UV irradiation of a solution containing poly(di-n-alkylsilane)s.



The nature of the persistent species is still unclear even if the g-factors are consistent only with silyl radicals carrying three silyl groups (4). Mechanistic schemes for their formation could be suggested based on the addition of transient silyl radicals to the appropriate disilenes generated photolytically [34-36].

UV irradiation of a solution containing polysilane 1 in the presence or absence of di-*tert*-butyl peroxide led only to the formation of the persistent paramagnetic



Fig. 1. (a) ESR spectrum obtained by photolyzing a solution of polysilane 2 and di-*tert*-butyl peroxide in cyclohexane; (b) Spectrum observed when irradiation was discontinued; (c) Spectrum obtained by subtracting spectrum (b) from spectrum (a).

species 4 (cf. Fig. 1b). The lack of formation of the transient silyl radical in the presence of peroxide is probably due to the high reactivity of the silyl radicals toward aromatic substitution [1].

In order to avoid the formation of the persistent radicals due to the UV irradiation, we tried to generate the silyl radical by thermal decomposition of di-*tert*-butyl hyponitrite at 323 K. No EPR spectra of the above species was observed, instead a radical showing splitting from two different nitrogens ($a_{N1} = 3.55$ G, $a_{N2} = 14.09$ G) and characterized by a g-factor of 2.00425, was observed. On the basis of the observed spectroscopic parameters we identified this species as the adduct of silyl radicals to the nitrogen-nitrogen double bond of hyponitrite (6) [37].

Taking advantage of the above experiment, we were able to obtain the EPR spectra of silyl radical adducts derived from polysilanes 1 and 2 with a variety of unsaturated substrates. Thus, silv! radicals 3 and 5 were generated by thermal decomposition of di-tert-butyl hyponitrite and the corresponding polysilane in the presence of an appropriate substrate at 320-340 K inside the EPR cavity. The EPR parameters for the radical adducts are summarized in Table 2. A comparison of the measured hyperfine splitting constants of the 3 and 5 radical adducts with those of the corresponding trialkyl- or triarylsilyl adducts [37] indicates very small variations of the spin density distribution, despite the substantial difference in the silvl group. The lines in the recorded spectra are generally broad and show more pronounced asymmetric line-width effects than in the radical adducts of monosilanes. This observation can be attributed to the presence of a very bulky silyl group which causes slow tumbling and therefore incomplete averaging of the anisotropy of the hyperfine splitting and g-tensors.

Radicals 3 and 5 add readily to the carbonyl moiety. The EPR parameters for some adducts are reported in Table 2 (entries 1–6). The EPR spectrum obtained by reacting duroquinone with silyl radical 3 is reported in Fig. 2 as an example (entry 5). The reaction of silyl radicals with 2,6-di-*tert*-butyl-*para*-benzoquinone afforded the adducts resulting from the addition to the less hindered carbonyl oxygen (entry 4). The addition of silyl radicals to 9,10-phenanthroquinone gave rise to adducts characterized by the magnetic equivalence of the two aromatic rings (entry 6). This means that the intramolecular migration of the silyl group between the two oxygens is fast in the EPR time scale (Scheme 1).



Fig. 2. EPR spectrum obtained by addition of silyl radicals generated by hydrogen abstraction from polysilane 2 with duroquinone.

This behavior is in contrast with that found for the benzil adducts of Et_3Si , Ph_3Si , and $(TMS)_3Si$ which at room temperature are characterized by the magnetic



unequivalence of the aromatic rings [38] but is, however, similar to that found for the benzil adduct of Ph₃Sn [39]. Since it seems from previous data that the rate of fluxional motion depends on the strength (in-

Table 2

EPR	parameters of	adducts	obtained	by	addition of	of sily	I radical	5	ano 3 to	various	substrates
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Entry	Silyl Radical	Adduct	T/K	g-factor	Hyperfine splittings / Gauss
1	5	ox	330	2.0029	0.75 (2H), 0.84 (2H), 3.41 (2H), 3.73 (2H)
	3		330	2.0029	0.76 (2H), 0.82 (2H), 3.43 (2H), 3.75 (2H)
2	5	çx	330	2.0029	1,24 (4H), 3.16 (4H), 3.52 (2H)
	3		330	2.0029	1.22 (4H), 3.12 (4H), 3.54 (2H)
3	5	ox	340	2.0029	1.56 (2H), 4.77 (2H), 5.69 (H), 15.11 (3H)
	3	CH	335	2.0029	1.52 (2H), 4.81 (2H), 5.68 (H), 15.15 (3H)
4	5	X	320	2.0047	1.14 (2H)
	3	ò-∕≻ox	315	2.0047	1.12 (2H)
5	5	\searrow	330	2.0048	5.78 (6H), 1.42 (6H)
	3	o-∕_>-ox	315	2.0048	5.79 (6H), 1.38 (6H)
6	5	o ox	313	2.0035	0.47 (4H), 2.04 (4H)
	3	$\langle \mathcal{P} \rangle$	313	2.0036	0.44 (4H), 1.91 (4H)
7	5	CH ₂ X	330	2.0026	1.33 (4H), 3.01 (4H), 3.23 (2H), 10.84 (2H)
	3	0.0	325	2.0026	1.27 (4H), 3.03 (4H), 3.24 (2H), 10.63 (2H)
8	5	0.	320	2.0035	0.86 (4H), 2.72 (2H), 3.12 (2H), 8.56 (2H)
	3	CH ₂ X	320	2.0034	0.92 (4H), 2.91 (2H), 3.07 (2H), 8.27 (2H)
9	5	N N-Y	335	2.0033	0.28 (2H), 5.69 (2H), 5.13 (N), 7.19 (N)
	3	``/`` ^	350	2.0033	0.27 (2H), 5.53 (2H), 5.33 (N), 7.34 (N)
10	5	1	330	2.0052	29.38 (N)
	3	[⊥] "`0 − X	312	2.0052	29.22 (N)
1)	5	ò	325	2.0052	29.02 (N), 8.65 (3H)
	3	H ₃ C-N O-X	320	2.0052	23.81 (N), 8.64 (3H)

versely proportional) of the oxygen-metal bond, the observed behavior suggests that the O-Si bond strength in the polysilane adducts is lower than in the corresponding monosilyl adducts.

Silyl radicals from 3 and 5 readily add to 1,1-diphenylethylene; the ESR spectral parameters of the resulting adducts are also reported in Table 2 (entry 7) and are similar to those of the triarylsilyl adducts [40]. An additional point worthy of comment is the behavior of 9-methylenanthrone when reacted with silyl radicals. Due to the presence of two reactive sites, i.e., the exocyclic C=C and C=O double bonds, attack may, in principle, occur at either of these. However when reacting these radicals with 9-methylenanthrone from 320 to 350 K, only adducts arising from attack at the methylene carbon are observed (entry 8). The preferential formation of carbon adducts with respect to the thermodynamically more stable oxygen adducts indicates that the addition of this type of silicon radicals to methylenanthrone is kinetically controlled. This behavior is similar to that found for the Ph₃Si adduct [41].

Radicals 3 and 5 also react with pyrazine and nitoalkanes. In the former case, the adducts were identified by EPR as those resulting from attack at the heterocyclic nitrogen (Table 2, entry 9). With nitro derivatives all radical species could be identified as silyloxyl nitroxides from the magnitude of the nitrogen coupling constants (entries 10 and 11). With 2-methylnitropropane, a second spectrum corresponding to the di-tert-butyl nitroxide which developed over time was observed. The detection of di-tert-butyl nitroxide during the reaction, suggests the following reaction sequence: (1) the decay of silvloxyl nitroxide BuN(O')OSiR, takes place by cleavage of the nitrogen-oxygen bond and affords t-BuN=O; (2) photocleavage of t-BuN=O gives tert-butyl radical, and (3) the addition of tert-butyl radical to the nitroso compound.

It is interesting to point out that the behavior of polysilanes 1 and 2 is similar to that of tris(trimethyl-silyl)silane [42], which is unable to reduce nitroalkanes since the nitroxide adducts fragment upon cleavage of the nitrogen-oxygen bond. ⁸

3. Experimental details

3.1. General procedure for reduction of organic halides

A sealed vial containing benzene- d_6 solution (2-4 ml) of the halogen derivative (0.1-0.2 M), the poly(phenylsilane) (0.1 equiv) and α, α' -azoisobutyronitrile (AIBN; 10-15 mol%) as initiator was heated

at 82-85°C for 1-3 h. The reactions were analyzed by ¹H NMR and IR. Yields were quantified by ¹H NMR analysis, using dibcnzyl ether or toluene as the internal standard and authentic samples as references.

3.2. Competition experiments between 1-decene and n-decyl bromide

A benzene- d_6 solution containing equimolar amounts (0.13 M) of *n*-decyl bromide, 1-decene and poly(phenylsilane) together with AIBN (20%) was heated at 80°C. An aliquot of the reaction was analyzed at different times (10, 20, 30 and 40 min) by ¹H NMR following the disappearance of starting bromide and alkene [30]. Dit___zyl ether was used as the internal standard.

3.3. General procedure for kinetic measurements

A benzene- d_6 solution containing either 6-bromo-1hexene or neophyl bromide, the appropriate amount of poly(phenylsilane) and AIBN (10 mol%) were allowed to react at 85°C. ¹H NMR spectra of the crude reaction mixtures and GC analysis of volatile products were recorded by using dibenzyl ether and undecane as the internal standards, respectively.

3.4. EPR measurements

EPR spectra were recorded on a Bruker ESP300 spectrometer equipped with an NMR gaussmeter for field calibration and a Hewlett Packard 5350B microwave frequency counter for the determination of the *g*-factors which were corrected with respect to that of the perylene radical cation in concentrated H_2SO_4 (g = 2.00258). Digitized EPR spectra were transmitted to an AT-486 PC in order to analyze complex spectra by means of autocorrelation [44] or cepstral [45] techniques. Photolysis was carried out by focusing the unfiltered light from a 500 W high-pressure mercury lamp on the EPR cavity.

4. Conclusions

Poly(hydrosilane)s have been shown to rival the efficiency and effectiveness of the other group 14 hydrides in dehalogenation reactions. Therefore, the prospects for $H(RSiH)_nH$ as widely used radical-based reducing agents are very promising considering the practical, economical and environmental possibilities of these materials. EPR studies provided information on the structural characteristics of silyl radicals, generated from poly(hydrosilane)s by hydrogen abstraction, and on their chemical reactivities in addition to multibonds. These results could lead to the planning of new methodologies in organic synthesis as well as to the preparation of a

⁸ Cleavage at the carbon-nitrogen bond is, instead, peculiar to tin adducts of nitro compounds. See [43] and references cited therein.

variety of functionalized polysilanes. A partial elucidation of the photochemical behavior of poly(hydrosilane)s has also been achieved. Further work on the free-radical chemistry of poly(hydrosilane)s is in progress in our laboratories.

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