

Homolytic Reactivity of Group 14 Organometallic Hydrides toward Nitroxides

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Received December 2, 1997

The spontaneous reactions of Et_3SiH , Ph_3GeH , Bu_3SnH , and $(\text{Me}_3\text{Si})_3\text{SiH}$ with 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) and related nitroxides have been investigated. Metal hydrides characterized by relatively weak metal–hydrogen bonds, like Ph_3GeH and Bu_3SnH , reduce TEMPO to the corresponding hydroxylamine while no reaction is observed with Et_3SiH and Ph_3SiH . Tris(trimethylsilyl)silane, on the other hand, is able to reduce the nitroxide to the corresponding hydroxylamine and amine in a ca. 1:1 ratio. By repeating the above reactions in the presence of thermal or photochemical radical initiators, deoxygenation of TEMPO was obtained in high yield with $(\text{Me}_3\text{Si})_3\text{SiH}$ and $(\text{Me}_3\text{Si})_2\text{Si}(\text{H})\text{Me}$, but not with other silanes, germanes, and stannanes. A mechanism for the reduction of TEMPO by the two trimethylsilyl-substituted silanes is proposed, and kinetic data for the various steps of the overall reaction are reported. In particular rate constants and activation parameters have been measured for the hydrogen transfer reaction from several silanes to the hindered aminyl radical 2,2,6,6-tetramethylpiperidinyl.

Introduction

Nitroxides represent the most important class of long-lived free radicals.¹ Strong persistency especially characterizes aliphatic nitroxides, R_2NO , having a radical center sterically hindered by the presence of bulky alkyl groups. Thus, 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) and several related derivatives have lifetimes of years when kept in the dark at ca. 0 °C. The persistency of hindered aliphatic nitroxides is essentially due to the fact that they cannot react with themselves by disproportionation, i.e., the reaction mainly responsible for the decay of these species. Nitroxides containing hydrogens β to the nitrogen atom have instead lifetimes of only few seconds at room temperature because of the ease by which they undergo disproportionation.

The behavior of nitroxide radicals has been extensively investigated over the last 40 years in different fields ranging from medicinal chemistry² to living free radical polymerization.³ The latter application is gaining a growing interest since it has been shown that the polymerization of styrene-based monomers, mediated by TEMPO, can be controlled to levels previously obtained only by using anionic or cationic procedures. The im-

portance of nitroxides has also increased enormously in the field of polymer stabilization⁴ since it became evident that the mechanism of inhibition of polymer photooxidation by hindered amine light stabilizers (HALS) involves oxidation of these compounds to nitroxide radicals. During polymer exposure to radiation, HALS give rise to nitroxides which can intercept alkyl radicals from the polymer to yield aminoethers or hydroxylamines which, in turn, react with peroxy radicals to regenerate nitroxides. The high effectiveness of hindered amines as polymer stabilizers is therefore essentially due to their ability to give rise to the cyclic regeneration of nitroxides. It is conceivable that the ability of HALS to protect polymers from photodegradation could be substantially increased if regeneration not only of the nitroxide but also of the amine, i.e., the other active species in the polymer stabilization process, could be achieved by using suitable additives.

In a recent paper it has been shown that regeneration of diarylamines, Ar_2NH , can take place at elevated temperatures (>120 °C) by thermal decomposition of the related aminoethers, Ar_2NOR , formed during the inhibition process of the autoxidation of hexadecane.⁵ Deoxygenation of hindered aliphatic nitroxides by thiophenols to give the corresponding amines has been also described.⁶

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Table 1. Conversions for the Spontaneous Reactions of TEMPO (0.2 M) with Organometallic Hydrides (0.4 M) and Yields of the Corresponding Hydroxylamine and Amine in Benzene at 80 °C

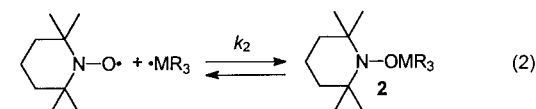
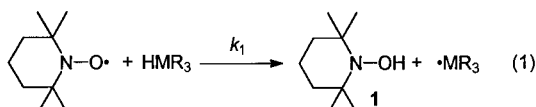
hydride	conversion (%)	time	yield of the hydroxylamine 1 (%)	yield of the amine 3 (%)
Et ₃ SiH	<3	3 h	—	—
Ph ₃ GeH	85	3 h	75.5	3
Bu ₃ SnH	98	10 m	96	3
(TMS) ₃ SiH	67	3 h	41	56

We have recently found that polyhydrosilanes, under free radical conditions in the absence of oxygen, are capable of reducing nitroxides to the corresponding amines.⁷ Given the importance of this reaction for its possible application in the above-mentioned field, we have undertaken an investigation on the reactivity of hindered aliphatic nitroxides in liquid solution toward simpler silanes, as well as other Group 14 organometallic compounds such as tin and germanium hydrides.

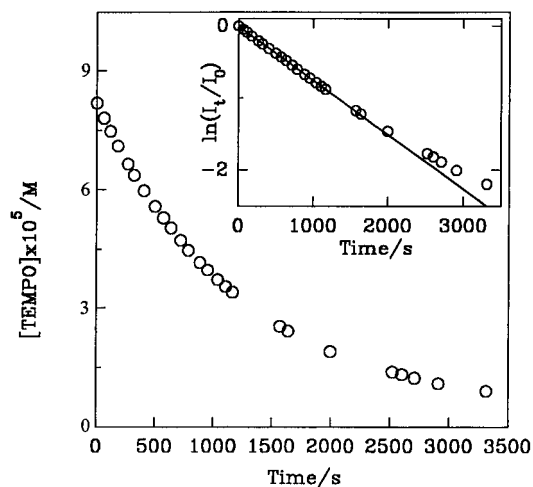
Results and Discussion

Spontaneous Reactions of TEMPO with Metal Hydrides. The room-temperature reaction of Group 14 metal hydrides with persistent nitroxides in oxygen free solutions afforded different results depending on the nature of the organometallic derivative employed. Thus, when using triethylsilane or triphenylsilane as the reducing agent, no appreciable reaction was observed even hours after mixing the reactants.

On the other hand, when reacting TEMPO with tributyltin hydride or triphenylgermanium hydride in deoxygenated benzene, the nitroxide concentration was observed to decrease gradually with time. GC/MS analyses (see Table 1) of the reaction mixtures showed that 2,2,6,6-tetramethyl-1-piperidinol (**1**) was the major product derived from the nitroxide together with a very small amount of 2,2,6,6-tetramethylpiperidine (**3**). This provides evidence that TEMPO reacts with the hydride by hydrogen transfer to give the corresponding hydroxylamine and tin or germyl radicals (eqs 1 and 2).



The yield of hydroxylamine based on nitroxide consumption was 96% with Bu₃SnH and 73% with Ph₃GeH. Although a 50% yield is expected on the basis of reactions 1 and 2, the excess of hydroxylamine obtained may be due to the reversibility at 80 °C of the reaction 2 giving back the tin or germyl radicals and the starting nitroxide. The latter may undergo hydrogen transfer from the unreacted metal hydride, and the Group 14 radicals will

**Figure 1.** Decay of TEMPO (8.2×10^{-5} M) in the presence of Bu₃SnH (0.017 M) at 60 °C. Insert: first-order plot of the experimental data.**Table 2. Rate Constants for the Reaction of TEMPO with Organometallic Hydrides**

hydride	<i>T</i> /K	[hydride]/M ^a	<i>k</i> ₁ /M ⁻¹ s ⁻¹
Bu ₃ SnH	333	0.034–0.062	2.5×10^{-2}
Ph ₃ GeH	333	0.38–0.68	1.8×10^{-4}
Et ₃ SiH	333	0.5	<i>b</i>

^a Range of concentrations employed. ^b Too low to be measurable.

give stable recombination products (eq 3), as suggested by the detection of hexabutylditin in the reaction mixture by GC/MS.

To determine the rate constants for hydrogen transfer *k*₁, the reactions of TEMPO with a large excess of an organometallic hydride were carried out inside an EPR tube by recording the EPR spectra of the mixture at different times. The time dependence of the TEMPO concentration showed clean first-order decays with both Bu₃SnH and Ph₃GeH in benzene at 60 °C (Figure 1). Deviation from first order was observed after ca. 80% of the nitroxide was consumed, and a small residual signal also remained at very long reaction times. The measured rate constants, *k*_{EPR}, were independent of the concentration of TEMPO and directly proportional to the concentration of the metal hydride, thus indicating that the reaction is a pseudo first-order process involving hydrogen atom abstraction from the hydride.

The bimolecular rate constants obtained from the *k*_{EPR} values determined in the initial part of the kinetics and from the hydride concentrations, in the assumption that each molecule of hydride traps two nitroxide radicals (see note 8), are listed in Table 2.

A still different behavior was observed when studying the reaction of TEMPO with tris(trimethylsilyl)silane (TMS)₃SiH since, in this case, no reproducible decay rates could be obtained. GC/MS analyses of the reaction mixtures provided evidence for the formation of another major product derived from TEMPO besides 2,2,6,6-tetramethyl-1-piperidinol. This was identified as 2,2,6,6-tetramethylpiperidine (**3**) (Table 1), similarly to what obtained in the reaction of nitroxides with polysilanes.⁷ This result prompted us to more thoroughly investigate the reduction of TEMPO by using several silanes and different reaction conditions.

Thermally or Photochemically Initiated Reactions. The reactions of TEMPO with a variety of silanes

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Table 3. Reaction of TEMPO with Silicon Hydrides

entry	silane	initiator ^a	meth- od	conver- sion (%)	yield of amine 3 (%)
1	Et ₃ SiH (1:5) ^b	DBP	<i>c</i>	<5	—
2	PhSiH ₃ (1:5)	DBP	<i>c</i>	<5	—
3	Ph ₃ SiH (1:5)	DBP	<i>c</i>	<5	—
4	(TMS) ₃ SiH (1:2)	DBP	<i>c</i>	96	93
5	Et ₃ SiH (1:5)	TBPB	<i>c</i>	<5	—
6	PhSiH ₃ (1:5)	TBPB	<i>c</i>	<5	—
7	(TMS) ₃ SiH (1:2)	TBPB	<i>c</i>	97	85
8	(TMS) ₃ SiH (1:2)	AIBN	<i>d</i>	69	43
9	Et ₃ SiH (1:5)	TBHP	<i>e</i>	52	<5
10	Ph ₃ SiH (1:5)	TBHP	<i>e</i>	43	<5
11	(TMS) ₃ SiH (1:2)	TBHP	<i>e</i>	95	97
12	none	none	<i>f</i>	13	19
13	Et ₃ SiH (1:2)	TBP	<i>f</i>	48	24
14	Ph ₃ SiH (1:2)	TBP	<i>g</i>	47	33
15	(TMS) ₃ SiH (1:2)	TBP	<i>g</i>	100	98
16	(TMS) ₂ Si(H)Me (1:2)	TBP	<i>g</i>	57	74

^a TBHP ≡ di-*tert*-butyl hyponitrite, AIBN ≡ azobis(isobutyronitrile), DBP ≡ dibenzoyl peroxide, TBPB ≡ *tert*-butyl peroxybenzoate, TBP ≡ di-*tert*-butyl peroxide. ^b The ratios in parentheses indicate the molar ratio between TEMPO and the silicon hydride. ^c Toluene at 110 °C for 1 h (DBP 15% or TBPB 15%). ^d Benzene at 80 °C for 1 h (AIBN 15%). ^e Benzene at 60 °C for 1 h (TBHP 10%). ^f Toluene at 80 °C under UV irradiation for 2 h (TBP 10% if present). ^g Benzene at 80 °C under UV irradiation for 2 h (TBP 10%).

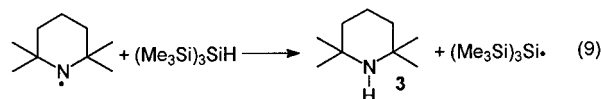
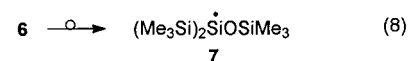
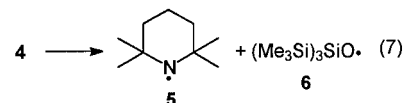
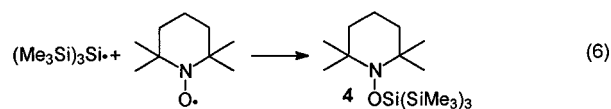
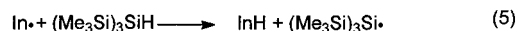
were carried out under nitrogen atmosphere for 1–2 h in benzene or toluene and in the presence of a thermal or a photochemical radical initiator. As thermal initiators we used di-*tert*-butyl hyponitrite (TBHP), azobis(isobutyronitrile) (AIBN), dibenzoyl peroxide (DBP) or *tert*-butyl peroxybenzoate (TBPB), and di-*tert*-butyl peroxide (TBP) as photochemical initiator. The reaction mixtures were analyzed by GC/MS using *tert*-butylbenzene as internal standard. The results of this study, collected in Table 3, can be summarized as follows; when the reaction was initiated thermally at 60 °C with TBHP, quantitative reduction of TEMPO to the corresponding amine **3** was achieved in the presence of (TMS)₃SiH (entry 11), while in the presence of Et₃SiH or Ph₃SiH less than 5% yield of amine was obtained (entries 9, 10). In all cases no hydroxylamine formation was detected by GC/MS.

In the case of the reaction of TEMPO with (TMS)₃SiH one of the major reaction products was identified as the siloxane (Me₂Si)₂(H)OSiMe₃ from its mass spectrum. When the reaction was photolytically initiated at 80 °C with TBP the formation of the amine was almost quantitative with (TMS)₃SiH (entry 15); with bis(trimethylsilyl)silane, (TMS)₂Si(H)Me, the nitroxide was also converted to the amine, but less efficiently (entry 16). With Et₃SiH or Ph₃SiH a ca. 30% yield of amine was obtained (entries 13 and 14), a value similar to the yield obtained by photolyzing the reaction mixture in the absence of the silane (entry 12).

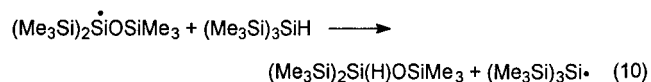
Initiators other than TBHP and TBP were also investigated. AIBN behaved as a less effective initiator (entry 8), due to the fact that the alkyl radicals resulting from its decomposition may react not only with the silane but also with TEMPO, while DBP and TBPB were both efficient initiators (entries 4, 7). When using Et₃SiH and Ph₃SiH no reaction was obtained with the last two initiators (entries 1–3 and 5, 6). These results indicate that the reaction of nitroxides with metal hydrides in a deoxygenated medium and in the presence of thermal initiators leads to the corresponding amines only when

the reducing agent is (TMS)₃SiH. When the reaction is initiated with UV light (entries 12–16), at least 20–25% of amine is formed even in the absence of metal hydrides and of radical initiators (entry 12). The amine is obtained in a high yield with (TMS)₃SiH, similarly to what was observed when using thermal initiation, and with (TMS)₂Si(H)Me.

Mechanism of Formation of the Amine. The formation of 2,2,6,6-tetramethylpiperidine (**3**) in the reactions of TEMPO with (TMS)₃SiH and (TMS)₂Si(H)Me can be explained as follows. If we consider the reaction with (TMS)₃SiH, the first step involves generation of tris(trimethyl)silyl radicals by hydrogen transfer to the initiating radicals followed by addition of (Me₃Si)₃Si to the oxygen atom of the nitroxide (eqs 4–6). The resulting adduct, **4**, will then fragment by cleavage of the nitrogen–oxygen bond to give an aminyl radical **5**, which by abstracting a hydrogen atom (eq 9) from the starting silane affords the amine **3**.



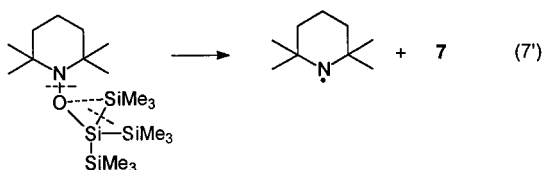
The apparently unexpected detection of the siloxane (Me₃Si)₂Si(H)OSiMe₃ can be accounted by two different reaction pathways, one implying the formation (eq 7) of the tris(trimethylsilyl)silyloxy radical (**6**) which has been reported to undergo easy migration of a Me₃Si group from silicon to oxygen⁸ to give (Me₃Si)₂Si(•)OSiMe₃ (**7**) (eq 8); this, under the present experimental conditions, may abstract a hydrogen atom from the starting silane affording the siloxane (Me₃Si)₂Si(H)OSiMe₃ (eq 10).



The other possibility is that the *N*-silyloxy amine adduct **4** will fragment in a concerted way to give the silyl radical **7** directly in addition to the aminyl radical **5** (eq 7').

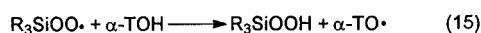
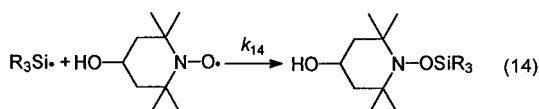
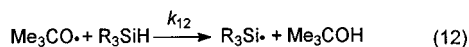
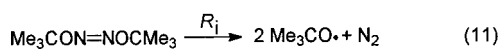
The various reaction steps will be discussed below in detail, and the experiments carried out to discriminate the two mechanisms will be described.

The initial steps of the reaction involve the formation of silyl radicals and their combination with nitroxides (eq 6) for which the rate constants are unknown. Since it has been shown that TEMPO reacts with several alkyl



radicals with a very high rate,⁹ it is also presumable that the rate constants for the combination of nitroxides with silyl radicals are large. To verify if this is the case, competitive kinetic studies for the reaction of triethylsilyl radicals, $\text{Et}_3\text{Si}\cdot$, with TEMPO and with molecular oxygen were carried out.

The experiments were performed by introducing into a thin EPR tube an air-saturated solution of the reaction mixture containing Et_3SiH (2 M), the thermal initiator *tert*-butyl hyponitrite (TBHP), the perdeuterated aliphatic nitroxide 2,2,6,6-tetramethyl-1-piperidinyloxy- d_{17} (TEMPO- d_{17}),¹¹ and a small amount of α -tocopherol (α -TOH, 1.510^{-3} M). The tube was then sealed and put into the EPR cavity kept at constant temperature (50 °C), and the spectra were recorded at constant time intervals. The reactions which take place in this system are exemplified below (eqs 11–16).



R=Et

Under the usual steady-state approximation for the concentration of the transient species, the kinetic equations describing the decay of oxygen and of the nitroxide (NOX) with time during the decomposition of TBHP can be worked out as in eqs 17 and 18.¹²

$$-\frac{d[\text{NOX}]}{dt} = R_i \frac{k_{14}[\text{NOX}]}{k_{14}[\text{NOX}] + k_{13}[\text{O}_2]} \quad (17)$$

$$-\frac{d[\text{O}_2]}{dt} = R_i \frac{k_{13}[\text{O}_2]}{k_{14}[\text{NOX}] + k_{13}[\text{O}_2]} \quad (18)$$

(9) *tert*-Butyl, benzyl and cumyl radicals react with TEMPO at 293 K with rate constants of 7.6×10^8 , 4.9×10^8 , and $1.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, respectively.¹⁰

(10) Chateaufeuf, J.; Luszyk J.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 1629. Beckwith, A. L. J.; Bowry, V. W.; Moad, G. *J. Org. Chem.* **1988**, *53*, 1632.

(11) Perdeuterated TEMPO was used since the contribution to the line width from unresolved proton hyperfine splitting is negligible.

(12) α -Tocopherol has been added to the solution as scavenger of the $\text{R}_3\text{SiOO}\cdot$ peroxy radicals. The reaction of *tert*-butoxyl radicals with α -TOH (whose rate constant is $3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)¹³ has been neglected since the ratio between the concentrations of Et_3SiH and α -TOH is 1330 while the ratio between the rate constants for the hydrogen abstraction from α -TOH and the silane ($k_{12}^{323} = 8.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$)¹⁴ is only 350.

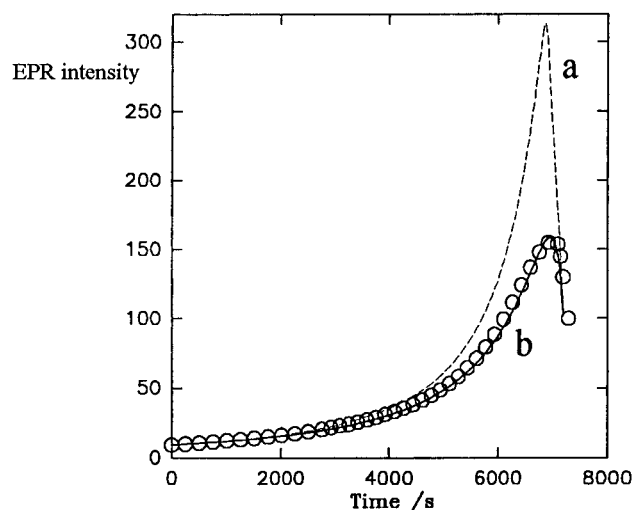


Figure 2. The circles show the experimental time dependence of the height of the central line of the EPR spectrum of TEMPO- d_{17} observed during the decomposition of TBHP (43 mM) at 50 °C in benzene in the presence of Et_3SiH (2.0 M), TEMPO- d_{17} (0.150 mM) and α -tocopherol (1.5 mM). Lines a and b are the corresponding simulations using k_{13}/k_{14} ratios of 32 and 6.1, respectively.

The change of both nitroxide and oxygen concentration during the course of the reaction within the closed tube was determined by following the evolution of the three lines EPR spectrum of the nitroxide. The integrated intensity of these signals is proportional to the nitroxide concentration while their width is related to the concentration of oxygen since the effect of the latter on the EPR spectra of radicals is that of producing a strong broadening of the spectral lines due to Heisenberg spin exchange.^{15,16} In oxygen-containing media the measured line width can be expressed as the sum of two terms (eq 19) one (W_{int}) being the intrinsic width and the other the oxygen-induced broadening. The latter one is proportional to the oxygen concentration through a constant b which is a function of the interaction radius between oxygen and the radical and of the diffusion coefficient of oxygen in solution.¹⁷

$$W = W_{\text{int}} + b[\text{O}_2] \quad (19)$$

An other spectral parameter, sensitive to the oxygen concentration, but much easier to measure than the width, is the peak to peak height of the EPR line, I . This is proportional to both the radical concentration and the reciprocal of W .² In the present case where the radical is a nitroxide, the EPR signal height is expressed by eq 20 indicating that, when carrying out the reaction in a closed system, I depends not only on the nitroxide concentration but also on the amount of oxygen dissolved in solution.

As a typical example, Figure 2 shows the dependence on time of the intensity of the central line of TEMPO- d_{17} (2.6×10^{-5} M). At the beginning of the reaction the

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(14) Chatgililoglu, C.; Ingold, K. U.; Luszyk, J.; Nazran, A. S.; Scaiano, J. C. *Organometallics* **1983**, *2*, 1332.

(15) Eastman, M. P.; Kooster, R. G.; Das M. P.; Freed, J. H. *J. Chem. Phys.* **1969**, *51*, 2690.

(16) Backer, J. M.; Budker, V. G.; Eremenko S. I.; Molin, Yu. N. *Biochim. Biophys. Acta* **1977**, *460*, 152.

$$I \propto \frac{[\text{NOX}]}{(W_{\text{int}} + b[\text{O}_2])^2} \quad (20)$$

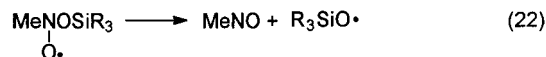
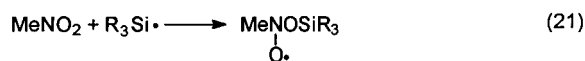
intensity of the EPR lines increases since the silyl radicals produced in reaction 12 react with oxygen rather than with the nitroxide. While oxygen is consumed in the reaction vessel, the width of the EPR lines decreases and their height increases. Only when most of the oxygen has been consumed do the silyl radicals begin to react with TEMPOL-*d*₁₇ (eq 14) and the EPR signals of the latter start to decrease.

Simulation of the time dependence of the intensity of the EPR spectrum of TEMPOL-*d*₁₇ during the course of the reaction provides the ratio of the rate constants for the combination of silyl radicals with oxygen and with the nitroxide k_{13}/k_{14} . Numerical integration¹⁸ of the simultaneous differential eqs 17 and 18 gave the best fit to the experimental points by using $k_{13}/k_{14} = 6.1$, i.e., the Et₃Si radicals react with oxygen six times faster than with the nitroxide. The absolute value of k_{13} has not been measured in solution but only in the gas phase (ca. $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$)¹⁹ for the reaction of Me₃Si radicals with O₂. By assuming this value also in benzene, k_{14} is estimated to be ca. $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, thus implying that the reaction of silyl radicals with nitroxides is so fast that, in the absence of oxygen, all other reactions of silyl radicals can be safely disregarded.

The following step in the proposed reaction mechanism for the deoxygenation of the nitroxide to give the amine (eqs 4–9) is represented by the cleavage of the nitrogen–oxygen bond of the silylaminoether to give an aminyl radical via either a two-step pathway implying the formation of a silanoxyl radical (**6**) which undergoes fast rearrangement to **7** (eqs 7, 8) or a concerted path leading directly to **7** (eq 7). In the case of the reaction with (TMS)₃SiH the two mechanisms cannot be differentiated since the final products are identical. On the other hand, the fact that neither amine, nor silanol (Et₃SiOH or Ph₃SiOH), formation was observed when reacting TEMPO with Et₃SiH or Ph₃SiH suggests that the tris(trimethylsilyl)silyl adduct to TEMPO (**4**) undergoes a concerted fragmentation. It would be hard to justify why cleavage of the nitrogen–oxygen bond to give aminyl and silyloxy radicals (eq 7) should occur only in the case of **4** and not in that of the Et₃Si or Ph₃Si adducts.

To further investigate this point the silane was reacted, under free radical conditions, with nitromethane, MeNO₂. In this case the silyl radicals are known⁸ to add to MeNO₂ to give the corresponding silyloxy-nitroxides (eq 21) which decay by fragmentation at the N–O bond (eq 22) to afford MeN=O and R₃SiO. The latter radical is expected to abstract a hydrogen atom from the starting silane, thus giving the silanols Et₃SiOH and Ph₃SiOH (eq 23) for R = Et and Ph, or to undergo reactions 8 and 10 to afford the siloxane (Me₃Si)₂Si(H)OSiMe₃ for R = Me₃Si.

GC/MS analysis of the final mixtures of the reactions of nitromethane with the three silanes revealed, in all cases, the major products as those resulting from nitrogen–oxygen cleavage of the intermediate silyloxy nitroxides, i.e., Et₃SiOH, Ph₃SiOH, and (Me₃Si)₂Si(H)OSiMe₃.



In another experiment the triethylsilyl adduct to TEMPO was prepared by reacting the nitroxide with Et₃Si radicals in triethylsilane containing an equimolecular amount of the TBHP initiator at 50 °C. This adduct (identified by its mass spectrum) was kept at 80 °C for 12 h without observing any appreciable decomposition.

On this basis it can be concluded that only the adducts of the polysilanes, (TMS)₃SiH and (TMS)₂Si(H)Me, fragment at the oxygen–nitrogen bond via a concerted mechanism to afford aminyl radicals which give the observed amine. This reaction can take place only if the hydrogen transfer from the (TMS)₃SiH or (TMS)₂Si(H)Me to the aminyl radical (eq 9) is characterized by a rate constant large enough to compete with other possible pathways for the decay of the aminyl radical. Despite the great number of rate constants for the reaction of simple alkyl radicals with different substrates,²⁰ kinetic data for nitrogen-centered radicals are substantially more limited. Newcomb and co-workers²¹ have measured rate constants for the bimolecular reactions of thiols and tin hydride with dialkylaminyl radical and Roberts and Ingold²² have found that the 2,2,6,6-tetramethylpiperidyl radical decays, following pseudo first-order kinetics, by abstracting a hydrogen atom from most of the solvents used.

To measure the rate constants for hydrogen abstraction from silanes by hindered aminyl radicals, 2,2,6,6-tetramethylpiperidine was reacted in the EPR cavity with *tert*-butoxy radicals, photolytically produced from di-*tert*-butyl peroxide in deoxygenated benzene or *tert*-butylbenzene, in the presence of a given silane. UV irradiation of the solutions resulted in the immediate formation of a radical whose EPR spectrum showed nitrogen and proton splittings and a *g*-value (a_{N} 14.66 G, a_{H} (18H) 0.82 G, *g* 2.0046) characteristic of the 2,2,6,6-tetramethylpiperidyl radical (**5**). When the light was shut off, the EPR signals disappeared following good pseudo first-order kinetics with decay times dependent on the nature and concentration of the silane present in the system. In the case of (TMS)₃SiH also the EPR spectrum of the corresponding silyl radical was visible; however, its decay was much faster than that of the aminyl radical.

The room-temperature rate constants, reported in Table 4, were obtained from the measured k_{EPR} values and the concentration of the silanes in the assumption that each molecule of silane traps two aminyl radicals. The Arrhenius parameters for reaction 9 are also listed in Table 4 while the corresponding plots are shown in Figure 3.

A remarkable feature of the data in Table 4 is the unusually low values of log *A* which for hydrogen abstraction reactions are normally in the range 8.5–9.0.²⁴

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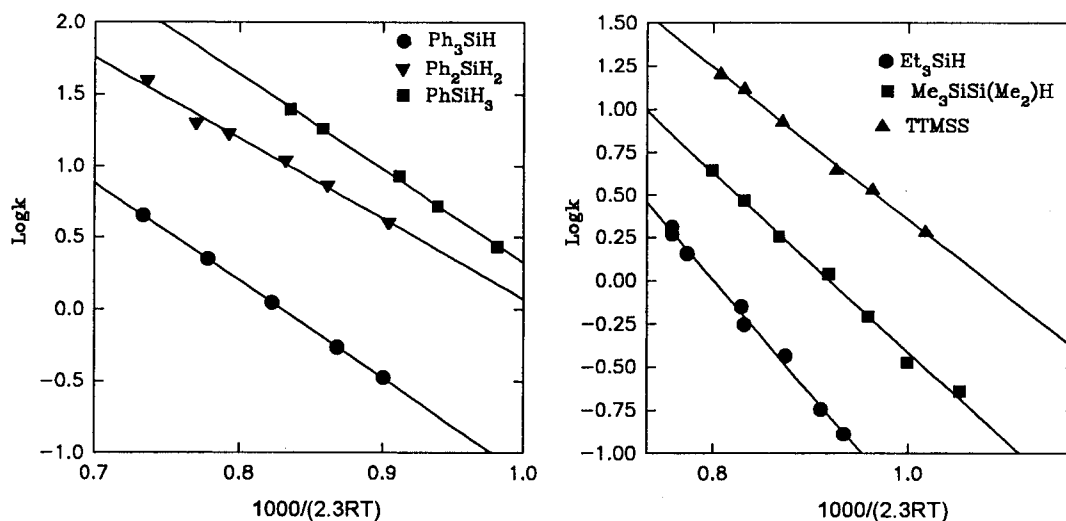


Figure 3. Arrhenius plots for the reaction of the aminyl radical **5** with silicon hydrides in *tert*-butylbenzene solutions.

Table 4. Kinetic Parameters for the Reaction of the 2,2,6,6-TetramethylpiperidinyI Radical with Silicon Hydrides

hydride	$\log A/$ $M^{-1} s^{-1}$	$E_a/$ $kcal mol^{-1}$	$k_H^{298}(R_2N\bullet)/$ $M^{-1} s^{-1}$	$k_H^a(RCH_2\bullet)/$ $M^{-1} s^{-1}$
Et ₃ SiH	5.2	6.5	2.7	6.4×10^2 (298 K)
Ph ₃ SiH	5.7	6.7	5.3	4.6×10^4 (413 K)
Ph ₂ SiH ₂	5.8	5.8	32.1	5.6×10^4 (413 K)
PhSiH ₃	6.9	6.6	119.2	2.9×10^4 (413 K)
(TMS) ₃ SiH	4.8	4.4	34.4	1.4×10^5 (298 K)
TMSSi(H)Me ₂	4.8	5.2	10.0	3.5×10^3 (298 K)

^a $k_H(RCH_2\bullet)$ is the rate constant for hydrogen abstraction from the silane by primary alkyl radicals.²³

These low values can be explained in terms of the high steric demand for a reaction in which both the radical center in the abstracting aminyl radical and the hydrogen-silicon bond in the silane are sterically hindered.²⁵ Due to the importance of steric factors in these reactions, the order of reactivity does not follow the strength of the metal-hydrogen bond as for the reactions of silanes with alkyl radicals (see the last column of Table 4) or other nonhindered radicals.²³

Conclusions

TEMPO reacts spontaneously at 80 °C with Bu₃SnH and Ph₃GeH by hydrogen atom abstraction from the hydride to give the corresponding hydroxylamine characterized by an O-H bond dissociation energy (BDE) of 69 kcal mol⁻¹ in benzene.²⁶ Bu₃SnH, BDE (Me₃Sn-H) = 77 kcal mol⁻¹,²⁷ reacts faster than Ph₃GeH, BDE (Bu₃Ge-H) = 82.6 kcal mol⁻¹,²⁸ while Et₃SiH and Ph₃SiH do not react at 333 K due to the large endothermicity of this reaction, BDE (Me₃Si-H) = 95 kcal mol⁻¹.²³ When using tris(trimethylsilyl)silane, BDE ((TMS)₃Si-H) = 83 kcal mol⁻¹,²³ as metal hydride the spontaneous reaction with TEMPO follows a different path since, in addition

to the hydroxylamine, a major amount of amine is formed. When the same reaction is carried out in the presence of radical initiators the reduction of TEMPO to the corresponding amine occurs with an almost quantitative yield with (TMS)₃SiH, and with a lower although conspicuous yield with (TMS)₂Si(H)Me. Under the same conditions, i.e., in the presence of radicals able to abstract a hydrogen atom from the metal hydride, Et₃SiH and Ph₃SiH afford the silyl adducts to the nitroxide and no amine or hydroxylamine are obtained. Therefore, only polysilanes seem to be able to perform the deoxygenation of nitroxides. This has been interpreted by suggesting that this reaction takes place by a concerted fragmentation of the aminosilyl ether formed by addition of the silyl radical from (TMS)₃SiH and (TMS)₂Si(H)Me to the oxygen atom of the nitroxide. The driving force of this reaction appears to be in the initial stage the formation of a strong oxygen-silicon bond at the expense of the much weaker nitrogen-oxygen and silicon-silicon bonds.²⁹ Once the fragmentation has occurred, recombination of the silyl radical **7** with the aminyl **5** does not take place because of the steric crowding around the radical centers of both species, so that evolution to the amine and to the siloxane (Me₃Si)₂Si(H)OSiMe₃ is preferred.

Finally, a noteworthy point is the formation under UV irradiation in benzene of ca. 20% amine from the nitroxide in the absence of any other reactants. Although nitroxides have been reported to react photochemically with aliphatic solvents³² by hydrogen abstraction to afford hydroxylamines and aminoethers, it seems difficult to envisage a reasonable reaction path leading to its deoxygenation.³³

Experimental Section

Materials. Bis(trimethylsilyl)methylsilane (TMS)₂Si(H)Me,³⁴ pentamethyldisilane,³⁴ and *tert*-butyl hyponitrite³⁵ were pre-

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pared following literature procedure. All other materials were commercially available.

General Procedure for the Reaction of TEMPO with Silanes. A solution of TEMPO (0.1 M), the silane (0.1–0.5 M), a radical initiator, and an internal GC standard, in benzene or toluene, was degassed and sealed under argon in Pyrex ampules. The reaction mixture was thermolyzed or photolyzed in the temperature range 333–373 K. The products of the reactions were analyzed by a HP GC5890 Series II chromatograph coupled to an HP mass selective detector Model 5971 using a 30 m \times 0.25 mm HP-5MS cross-linked 5% phenylsilicone capillary column with temperature programming from 50 to 250 °C. The products of interest were identified by comparison of their retention times with authentic materials.

Kinetic Studies for the Reaction of Triethylsilyl Radical with TEMPOL- d_{17} and Molecular Oxygen. A solution of triethylsilane (2.0 M), *tert*-butyl hyponitrite (0.1 M), 2,2,6,6-tetramethyl-1-piperidinyloxy- d_{17} (1.5×10^{-4} M), and a small amount of α -tocopherol (1.5×10^{-3} M) in benzene was air-

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saturated at room temperature and introduced (ca. 200 L) into a capillary tube with the internal diameter of ca. 1.85 mm. A second capillary tube (external diameter of 1.60 mm) sealed at one end was introduced into the sample tube so as to leave very little dead volume space. The decrease of the nitroxide concentration and the oxygen uptake was followed by EPR spectroscopy as described in the paper.

EPR Measurements. The EPR spectra were recorded on a Bruker ESP300 spectrometer equipped with an NMR gaussmeter for field calibration, a Bruker ER033M field-frequency lock, and a Hewlett-Packard 5350B microwave frequency counter for the determination of the *g*-factors, which were corrected with respect to that of perylene radical cation in concentrated H₂SO₄ (*g* 2.00258). Photolysis was carried out by focusing the unfiltered light from a 500 W high-pressure mercury lamp on the EPR cavity. Digitized decay traces of the EPR signals necessary for kinetic measurements were acquired by means of a dedicated computer and were transferred to an AT-486 (33 MHz) personal computer in order to be analyzed. The temperature was controlled with a standard variable temperature accessory and was monitored before and after each run with a copper–constantan thermocouple.

Acknowledgment. Financial support from MURST and CNR is gratefully acknowledged. We also thank Dr. S. Bernardoni for assistance in some kinetic measurements.

JO972178I