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Reactions of Tris(trimethylsilyl)silyl Radicals with Nitroalkanes. EPR, Kinetic, and Product Studies

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The radical-initiated reaction of tris(trimethylsilyl)silane with a variety of aliphatic nitro derivatives has been investigated. This silane, which for many applications is a valid alternative to tributyltin hydride, is unable to reduce tertiary nitroalkanes to the corresponding hydrocarbons. EPR results, as well as kinetic and products studies, have shown that this "anomalous" behavior is due to the fact that the nitroxide adducts formed by addition of tris(trimethylsilyl)silyl radicals to the nitro compounds fragment preferentially at the nitrogen–oxygen bond rather than at the carbon–nitrogen bond as in the analogous tributyltin adducts. The resulting silyloxy radical, $(Me_3Si)_3SiO^\bullet$, undergoes a fast rearrangement ($k \geq 10^7$ s^{-1} at room temperature) with migration of a Me_3Si group from silicon to oxygen to give $(Me_3Si)_2\dot{S}iOSiMe_3$ which adds to the nitro compound affording a secondary nitroxide adduct. The kinetics of the decay of both primary and secondary adducts to nitromethane has been studied over a wide range of temperatures. With tertiary nitroalkanes persistent aminyl radicals, $R\dot{N}OSi(SiMe_3)_3$, have also been detected.

Reduction of tertiary or resonance-stabilized nitroalkanes with tributyltin hydride, under free-radical conditions, results in the cleavage of the carbon–nitrogen bond yielding the corresponding hydrocarbons.[1] During the last decade this reaction has been extensively used to successfully reduce various tertiary nitro compounds.[2,3] Mechanistic studies based on spectroscopic,[4] kinetic,[5] and electrochemical[5] data are consistent with a free-radical chain reaction where the key propagation steps are the addition of $Bu_3Sn^\bullet$ to the nitro group and the subsequent elimination of an alkyl radical (eqs 2 and 3).[6] It is

$$R^\bullet + Bu_3SnH \rightarrow RH + Bu_3Sn^\bullet \qquad (1)$$

$$Bu_3Sn^\bullet + RNO_2 \rightarrow RN(O^\bullet)OSnBu_3 \qquad (2)$$

$$RN(O^\bullet)OSnBu_3 \rightarrow R^\bullet + Bu_3SnONO \qquad (3)$$

worthwhile to point out that the cleavage at the carbon–nitrogen bond is peculiar to tin adducts of nitro compounds, since fragmentation takes place preferentially at the nitrogen–oxygen bond in the analogous adducts of carbon-centered radicals.[7] For instance, the latter process is more than 2 orders of magnitude faster than alkyl elimination in the $Me_3CN(O^\bullet)OCMe_3$ nitroxide at room temperature.[7,8]

In recent studies by some of us on tris(trimethylsilyl)silane (TTMSS) as a reducing agent,[9–11] this material was found to be an attractive alternative to tributyltin hydride for several methodologies in radical-based syntheses.[3,12,13] However, attempts to replace the nitro group with hydrogen were unsuccessful when reacting 4-nitro-2,2,4-trimethylpentane or *p*-cyano-α-nitrocumene with TTMSS.[10] Since it has been shown by laser flash photolysis[10] and EPR spectroscopy[14] that the addition of $(Me_3Si)_3Si^\bullet$ radicals to Me_3CNO_2 is a fast process ($k^{298} = 1.16 \times 10^7$ M^{-1} s^{-1}) leading to the formation of the corresponding silyloxy nitroxide, it might be the evolution of the latter one which follows a route different from that outlined in eq 3 for the tin adduct. To get a better insight on this unexpected behavior, we have undertaken a detailed study of the radical initiated reaction of TTMSS with the nitroalkanes **1a–f**.

RNO_2

1a: R = Me **1d**: R = Me_3C
1b: R = Et **1e**: R = $Me_3CCH_2CMe_2$
1c: R = Me_2CH **1f**: R = *p*-$CNC_6H_4CMe_2$

Results and Discussion

EPR and Kinetic Studies. Nitromethane (1a). $MeNO_2$ was reacted at room temperature within the EPR cavity with $(Me_3Si)_3Si^\bullet$ radicals photolytically produced from TTMSS and di-*tert*-butyl peroxide in benzene or *tert*-butylbenzene solutions freed of oxygen. When starting to irradiate, an EPR spectrum (see Figure 1) consisting of the superimposition of spectra due to two radical species characterized by very similar hyperfine splittings and *g* factors (see Table I) was observed. From the magnitude of the nitrogen coupling constants (ca. 29 G), both species could be identified as oxy nitroxides, $MeN(O^\bullet)OX$.[15] The

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Table I. ESR Spectral Parameters of the Nitroxides RN(O•)X (2–6) and Aminyls R$\dot{N}$X (7) Observed in the Photolytic Reaction of $(Me_3Si)_3SiH$ with RNO_2

R	X	radical	a_N	a(R)	a_{other}	g
Me	$OSi(SiMe_3)_3$	**2a**	29.02	8.97 (3 H)	1.32 ($3^{29}Si$)	2.0053_8
	$OSi(SiMe_3)_2OSiMe_3$	**3a**	28.27	8.92 (3 H)		2.0053_0
	$OCMe_3$	**4a**	26.40	8.67 (3 H)		2.0055
Et	$OSi(SiMe_3)_3$	**2b**	28.87	8.26 (2 H), 0.33 (3 H)	1.30 ($3^{29}Si$)	2.0054
	$OSi(SiMe_3)_2OSiMe_3$	**3b**	28.20	8.22 (2 H), 0.30 (3 H)		2.0054
	OCMe	**4b**	26.48	7.77 (2 H)		2.0056
Me_2CH	$OSi(SiMe_3)_3$	**2c**	29.10	5.26 (1 H), 0.22 (6 H)		2.0052
	$OSi(SiMe_3)_2OSiMe_3$	**3c**	28.54	5.05 (1 H), 0.20 (6 H)		2.0052
	$OCMe_3$	**4c**	26.62	3.80 (1 H)		2.0056
	$Si(SiMe_3)_3$	**5c**	10.63	1.49 (1 H)		2.0070
	Me_2CH	**6c**	14.90	4.44 (1 H)		2.0060
Me_3C	$OSi(SiMe_3)_3$	**2d**	29.10			2.0055
	$OSi(SiMe_3)_2OSiMe_3$	**3d**	28.80			2.0054
	$OCMe_3$	**4d**	27.18			2.0056
	$Si(SiMe_3)_3$	**5d**	10.87		6.70 ($1^{29}Si$) 4.38 ($3^{29}Si$)	2.0070
	Me_3C	**6d**	15.83			2.0060
	$OSi(SiMe_3)_3$	**7d**	14.88		7.69 ($1^{29}Si$) 9.70 ($1^{13}C$)	2.0051
Me_2YC[a]	$OSiR_3$[b]	**2e,3e**	29.84			2.0053
	$Si(SiMe_3)_3$	**5e**	11.23			2.0068
	$OSi(SiMe_3)_3$	**7e**	14.63		7.65 ($1^{29}Si$) 9.70 ($1^{13}C$)	2.0051
Me_2YC[a,d]	$OSiR_3$[b,d]	**2f,3f**	29.17			2.0053
	YMe_2C	**6f**	14.59			2.0060
	$OSi(SiMe_3)_3$	**7f**	14.27			2.0052

[a] Y = CH_2CMe_3. [b] The superimposed spectra of **2e** and **3e** (and of **2f** and **3f**) could not be resolved. [c] Y = p-CNC_6H_4. [d] A fourth unidentified radical (a_N 16.2 G, g 2.0048) was also detected.

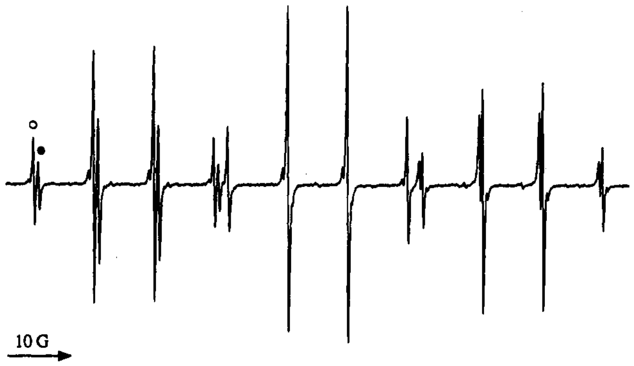
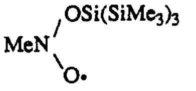


Figure 1. Room-temperature EPR spectrum detected under continuous photolysis of a benzene solution of $MeNO_2$ (0.1 M), $(Me_3Si)_3SiH$ (0.1 M), and di-*tert*-butyl peroxide (1 M). Marks indicate the low field signals due to nitroxides **2a** (○) and **3a** (●).

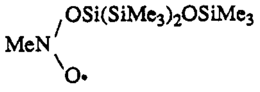
spectrum of one of them shows on the wings of each peak two satellite lines, 1.32 G apart, whose intensity is ca. 8% of that of the main line. Since this is the intensity expected for three equivalent ^{29}Si nuclei ($I = {}^1/_2$, relative abundance 4.70%), we assigned this spectrum to the adduct of $(Me_3Si)_3Si^•$ radicals to nitromethane, **2a**.

The spectral parameters did not allow us to identify the second radical; however, the following observations indicating that the two nitroxides were strictly connected allowed us to assign structure **3a** to this species. In fact, by carrying out experiments under continuous photolysis, i.e., in the conditions where the nitroxides were formed and decayed with the same rate, (i) the relative amounts of **2a** and **3a** were found to be independent of the irradiation time and of the silane concentration within the range 0.005–0.1 M, (ii) at constant light intensity, the ratio [**2a**]/[**3a**] decreased with increasing temperature, the change being reversible; (iii) by keeping the temperature constant, the ratio [**2a**]/[**3a**] was proportional to the square root of the light intensity, I, and to the square root of the peroxide concentration.



$MeN(O^•)OSi(SiMe_3)_3$

2a



$MeN(O^•)OSi(SiMe_3)_2OSiMe_3$

3a

We also studied the disappearance of the EPR signals of the two nitroxides when stopping the irradiation; at room temperature, radical **2a** decayed with first-order kinetics while the decay curve of **3a** was initially rather complex but then followed good second-order kinetics.

For concentrations of the silane ca. 0.01 M or less, a third nitroxide was observed (**4a**) which on the basis of the spectral parameters was identified as $MeN(O^•)OCMe_3$.[16] This nitroxide might originate from the attack of $Me_3C^•$ radicals to nitromethane or from the addition of $Me_3CO^•$ radicals to nitrosomethane. Since the presence of *tert*-butyl radicals seems unlikely in our experimental system, we conclude that some nitrosomethane is formed, i.e., that the first order decay of radical **2a** is due to the cleavage of the nitrogen–oxygen bond thus affording MeN=O and $(Me_3Si)_3SiO^•$ (vide infra). The [tris(trimethylsilyl)silyl]oxy radical might, in principle, give the usual reactions of alkoxy radicals (hydrogen abstraction, radical combination); in that case, however, it is hard to justify the observation of radical **3a**. A more likely explanation is that $(Me_3Si)_3SiO^•$ undergoes a facile migration of a Me_3Si group from silicon to oxygen to give $(Me_3Si)_2\dot{S}iOSiMe_3$. This reaction is in fact predicted to be exoergonic by at least 45 kcal/mol, on the basis of the known values of the bond dissociation energies for Me_3Si–$SiMe_3$, 80.5 kcal/mol, and for Me_3Si–OH, 128 kcal/mol.[17] In fact, a similar rear-

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[16] The structure of **4a** was confirmed by producing the authentic nitroxide by reaction of nitromethane with $Me_3C^•$ radicals generated by photolysis of di-*tert*-butyl ketone.

rangement has recently been observed by some of us (vide infra).[18] Moreover, an analogous 1,2-shift of silyl groups from silicon to sulfur is well documented.[19] The rearranged silicon-centered radical may now attack nitromethane affording **3a** which is characterized by spectral parameters only slightly different from those of **2a**. The main reaction sequence can therefore be exemplified as follows.

$$\mathrm{Me_3CO{-}OCMe_3} \xrightarrow{h\nu} \mathrm{2Me_3CO^{\bullet}} \qquad (4)$$

$$\mathrm{Me_3CO^{\bullet} + (Me_3Si)_3SiH \rightarrow Me_3COH + (Me_3Si)_3Si^{\bullet}} \qquad (5)$$

$$\underset{}{\mathrm{(Me_3Si)_3Si^{\bullet}}} + \underset{\mathbf{1}}{\mathrm{RNO_2}} \rightarrow \underset{\mathbf{2}}{\mathrm{RN(O^{\bullet})OSi(SiMe_3)_3}} \qquad (6)$$

$$\mathrm{RN(O^{\bullet})OSi(SiMe_3)_3 \rightarrow RN{=}O + (Me_3Si)_3SiO^{\bullet}} \qquad (7)$$

$$\mathrm{(Me_3Si)_3SiO^{\bullet} + (Me_3Si)_3SiH \rightarrow (Me_3Si)_3SiOH + (Me_3Si)_3Si^{\bullet}} \qquad (8)$$

$$\mathrm{(Me_3Si)_3SiO^{\bullet} \rightarrow Me_3SiO{-}\dot{S}i(SiMe_3)_2} \qquad (9)$$

$$\mathrm{Me_3SiO{-}\dot{S}i(SiMe_3)_2 + RNO_2} \rightarrow \underset{\mathbf{3}}{\mathrm{RN(O^{\bullet})OSi(SiMe_3)_2OSiMe_3}} \qquad (10)$$

$$\mathrm{2RN(O^{\bullet})OSi(SiMe_3)_2OSiMe_3 \rightarrow products} \qquad (11)$$

$$\mathrm{Me_3CO^{\bullet} + RN{=}O} \rightarrow \underset{\mathbf{4}}{\mathrm{RN(O^{\bullet})OCMe_3}} \qquad (12)$$

Reaction 12 ($k^{298} = 2.1 \times 10^7$ M^{-1} s^{-1} for R = Me$_3$C)[20] is expected to be important only with a low silane concentration since it must compete with the hydrogen abstraction from TTMSS ($k_5^{298} = 1.1 \times 10^8$ M^{-1} s^{-1}).[23]

The kinetic treatment of the above equations in the conditions of continuous photolysis and when reaction 12 can be neglected leads to eq 13 if the usual steady-state approximation is assumed.

$$[\mathbf{2a}]/[\mathbf{3a}] = (R_i 2k_{11})^{1/2}(1 + k_8[(\mathrm{Me_3Si})_3\mathrm{SiH}]/k_9)/k_7 \qquad (13)$$

Here R_i is the rate of radical initiation, $I[(\mathrm{Me_3CO})_2]$. Since [**2a**]/[**3a**] was independent of the silane concentration when the latter was 0.1 M or less, eq 13 can be simplified to 14.

$$[\mathbf{2a}]/[\mathbf{3a}] = (R_i 2k_{11})^{1/2}/k_7 \qquad (14)$$

Equation 14 provides a rationalization of the observed dependence of the ratio between the two nitroxides on the square root of the rate of radical initiation. The validity of eq 14 rather than eq 13 also means that the rearrangement of the [tris(trimethylsilyl)silyl]oxy radical is a very fast process which successfully competes with hydrogen abstraction from TTMSS; the lower limit of k_9 at room temperature can be estimated as 10^7 s^{-1} by assuming that k_8 is approximately the same as k_5.[23]

The rate constant for the fragmentation of radical **2a**, measured by following its first-order decay, was $k_7^{297} = 0.20$ s^{-1}. The activation parameters determined in the temperature range 293–331 K, i.e., log (A/s^{-1}) = 13.46 ± 0.54 and E_a = 19.25 ± 0.78 kcal/mol, are very similar to those found for the cleavage of the nitrogen–oxygen bond in Me$_3$CN(O$^{\bullet}$)OCMe$_3$, i.e., log (A/s^{-1}) = 13.52 and E_a = 20.44 kcal/mol.[8]

By decreasing the temperature below 290 K the decay of **2a** begins to obey mixed first and second order and eventually good second-order kinetics, which suggests that at low temperatures this radical decays by self-reaction (eq 15). Consistent with this observation, only nitroxide **2a** was seen at 240 K under continuous photolysis.

$$\mathrm{2RN(O^{\bullet})OSi(SiMe_3)_3 \rightarrow products} \qquad (15)$$

Self-reaction is instead the dominant reaction path of nitroxide **3a** (eq 11) below ca. 310 K, as inferred from its second-order decay. Presumably, this reaction leads to a hydroxylamine and a nitrone, similar to that reported by Ingold and co-workers for dimethyl and for primary and secondary dialkyl nitroxides.[24] The rate constant for reaction 11, $k_{11}^{298} = 1 \times 10^4$ M^{-1} s^{-1}, obtained by analyzing the last part of the decay curve of **3a**, that is from the time when the sequence of reactions 7, 9, and 10 do not contribute anymore to signal intensity changes, is very close to the rate constant for disproportionation reported for dimethyl nitroxide in benzene, $k^{298} = 2.1 \times 10^4$ M^{-1} s^{-1}.[24c]

When the temperature was increased the decay curves of **3a** began to deviate from second order, and at temperatures of ca. 320 K or higher followed approximately first-order kinetics. At the same time, the ratio [**2a**]/[**3a**] became independent on the light intensity and/or peroxide concentration. This means that, at higher temperatures, the nitroxide **3a** is decaying by cleavage of the nitrogen–oxygen bond (eq 16) rather than by self-reaction. By

$$\mathrm{RN(O^{\bullet})OSi(SiMe_3)_2OSiMe_3 \rightarrow RN{=}O + Me_3SiOSi(Me_3Si)_2O^{\bullet}} \qquad (16)$$

judging from the relative intensities of the spectra of **2a** and **3a**, the rate of fragmentation of the latter seems about 1 order of magnitude lower than that of **2a**.

With regard to the fate of the Me$_3$SiOSi(SiMe$_3$)$_2$O$^{\bullet}$ radical, it is known that it undergoes a 1,2-shift of a Me$_3$Si group from silicon to oxygen to give (Me$_3$SiO)$_2\dot{\mathrm{S}}$iSiMe$_3$ which may easily abstract hydrogen from TTMSS.[18]

Nitroethane (1b). The behavior of EtNO$_2$ when reacted photolytically with TTMSS in the presence of (Me$_3$CO)$_2$ was similar to that of nitromethane; two spectra showing very similar hyperfine splittings and g-factors (see Table I) were again observed, and their relative intensities could be varied by changing the rate of radical initiation and the temperature. We identified the species characterized by the higher and lower nitrogen coupling as **2b** and **3b**, respectively. The overlap of the two spectra was larger than with the nitroxides from nitromethane due to the additional splitting from the three methyl protons (0.3 G), and therefore kinetic studies were more difficult to carry out. We only determined the first-order rate constant for fragmentation of **2b**, $k_7^{300} = 0.21$ s^{-1}.

When using concentrations of TTMSS ≤0.01 M a third spectrum, attributed to EtN(O$^{\bullet}$)OCMe$_3$ (**4b**), was also detected.

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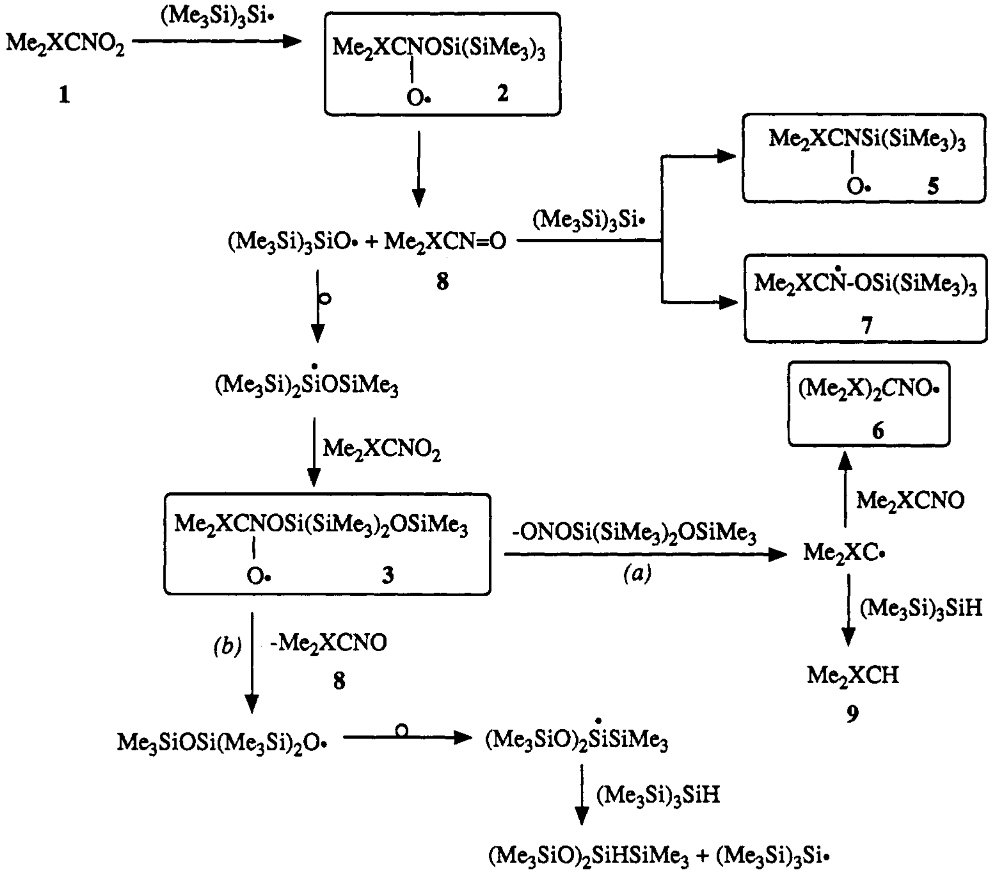
Scheme I



2-Nitropropane (1c). With Me_2CHNO_2 strongly overlapping spectra due to nitroxides **2c** and **3c** were also observed (see Table I); the former decayed following first-order kinetics with $k_7^{291} = 0.077\ s^{-1}$. Prolonged irradiation led in this case to the appearance of three additional radical species, one of them being $Me_2CHN(O^\bullet)OCMe_3$ (**4c**). Of the other two, one had an unusually small nitrogen coupling and a very large g-factor (a_N 10.63 G, g 2.0070) and was identified as $Me_2CHN(O^\bullet)Si(SiMe_3)_3$ (**5c**) formed by addition of tris(trimethylsilyl)silyl radicals to nitrosopropane (vide infra). The third species had spectral parameters typical of $(Me_2CH)_2NO^\bullet$ (**6c**), and its formation can be accounted for by photolytic cleavage of the carbon-nitrogen bond of 2-nitrosopropane formed in reaction 7 and subsequent addition of the isopropyl radical to $Me_2CHN{=}O$.

2-Methyl-2-nitropropane (1d). When reacting $(Me_3Si)_3Si^\bullet$ radicals with Me_3CNO_2 a three-line spectrum (a_N ca. 29 G) was initially obtained. Careful examination of the low- and high-field lines showed that they are slightly asymmetric, this being the only indication that also in this case the spectrum consists of the superimposition of two spectra due to nitroxides **2d** and **3d**. The large line width arising from unresolved coupling at the *tert*-butyl protons prevents the individual lines of the two species to be separately detected. To measure the spectral parameters of radicals **2d** and **3d** (Table I) we recorded the spectra at 240 and 320 K where the former and the latter nitroxides, respectively, are expected to be the dominant species. A peculiarity of 2-methyl-2-nitropropane with respect to the other nitroalkanes is that a third spectrum, growing up with time and due to a very persistent radical, was almost immediately observed when starting to irradiate the reaction mixture at room temperature. At lower temperatures (≤240 K) a fourth species, much shorter lived and which disappeared when increasing the temperature, was also detected. We assign these spectra to the persistent (silyloxy)aminyl radical **7d** and to the more labile

$Me_3C\dot{N}OSi(SiMe_3)_3$

7d


$Me_3CN(O^\bullet)Si(SiMe_3)_3$

5d

silyl nitroxide **5d**, respectively, whose spectral parameters are reported in Table I. Actually, the same radicals could be easily observed when photoreacting $(Me_3Si)_3SiH$ with 2-methyl-2-nitrosopropane, $Me_3CN{=}O$, in the presence of peroxides. Both the nitrogen coupling and the g-factor of the aminyl radical **7d** are very close to those reported by Roberts and co-workers for $Me_3C\dot{N}OSiMe_3$ (a_N 14.6 G, g 2.0051).[25] The assignment to nitroxide **5d** of the spectrum due to the less persistent species is based on the low nitrogen coupling and the unusually large g-factor which are characteristic of silyl nitroxides[26,27] and on the observed ^{29}Si hyperfine splittings. From the time dependence of the signals of the two radicals when stopping the irradiation, it is inferred that **5d** rearranges to **7d** even at low temperatures. This behavior is opposite to the reverse 1,2-silicon shift from oxygen to nitrogen reported for the rearrangement of $Me_3Si\dot{N}OSiMe_3$ to give $(Me_3Si)_2NO^\bullet$.[25,26] The relative stability of the nitroxide and oxyaminyl radicals is determined both by the strength of the Si–O and Si–N bonds,[17] which should favor the oxyaminyl radical, and by the intrinsic stability of the nitroxyl

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function, which depends on the nature of the substituents at nitrogen. The different behavior observed in the two systems is likely due to a different balance of these stabilizing effects.

Prolonged irradiation of the reaction mixture led also to the appearance of the spectra of $Me_3CN(O^{\bullet})OCMe$ (**4d**) and $(Me_3C)_2NO^{\bullet}$ (**6d**). The detection of nitroxides **4d**, **5d**, **6d**, and of the aminyl **7d** provides further support to the occurrence of reaction 7.

Nitroalkanes 1e and 1f. Similar to the observations with 2-methyl-2-nitropropane, photolysis of nitroalkane **1e** (or **1f**) gave the spectra of **2e** and **3e** (or of **2f** and **3f**) which were superimposed and could not be resolved. With both compounds, shortly after starting the photolysis, signals from secondary radicals were detected (see Table I), those of the aminyls $R\dot{N}OSi(SiMe_3)_3$ being particularly strong. This was due to the persistence of these species which decayed very slowly compared to the initially formed radicals. In the case of **7e** the decay followed first-order kinetics with $k^{298} = 1.12 \times 10^{-3}\ s^{-1}$ ($\tau_{1/2}$ ca. 600 s).

With the nitroalkane **1f** an intense triplet spectrum (a_N 16.2 G, *g* 2.0048) was also detected. Although the *g*-factor seems characteristic of an aminyl radical there were no other elements which could allow us to identify this species.

Product Studies on the Tertiary Nitroalkanes. Reduction of compounds **1d–f** was attempted by using either tributyltin hydride or tris(trimethylsilyl)silane. Reaction of each derivative with n-Bu_3SnH or $(Me_3Si)_3SiH$ at 85 °C in toluene and in the presence of the radical initiator azobisisobutyronitrile (AIBN), gave in 1 h conversions of 100% and 10%, respectively. Therefore, with tertiary nitroalkanes, the replacement of a nitro group by hydrogen using tributyltin hydride is an efficient process, in agreement with the literature data,[1-3] while the nitro function cannot be replaced when using tris(trimethylsilyl)silane. The low consumption of nitroalkanes observed in the latter case indicates that the reaction follows a different path from that with tin hydride and also that the average kinetic chain length is very short presumably because some inhibiting material is formed during the initial part of the reaction. The identification of two peaks in GC as products **8** and **9** together with the spectroscopic results suggests the mechanistic scheme shown below (Scheme I), where all species enclosed within a box have been detected by EPR.

With regard to the decomposition of radicals **3d–f**, we conceive the two different paths a and b, implying fragmentation at the nitrogen–carbon and at the nitrogen–oxygen bond, respectively. The detection of products **9** in GC/MS experiments and of radicals **6** by EPR indicates that path a is followed to some extent; however, we have no way to assess the relative importance of path b which is the only route of fragmentation of radical **3a** at high temperature. Actually, the formation of $(Me_3SiO)_2SiHSiMe_3$ does not give any indication about that, since this product is always present as a substantial impurity in the starting TTMSS.

Experimental Section

EPR Measurements. EPR spectra were recorded on a Bruker ESP300 spectrometer equipped with a Hewlett-Packard 5350B frequency counter for the determination of the *g*-factors, which were corrected with respect to that of the perylene radical cation (2.002 58). Photolysis was carried out with the light from a 500-W high-pressure mercury lamp filtered with an AEO interference filter (maximum transmittance 366.3 nm). Measurements at variable light intensity were done by using metal screens of known transmittance. The temperature was controlled with a standard variable-temperature accessory and was monitored before and after each run with a copper–constantan thermocouple. Radical concentrations were measured by comparing the double integral of the EPR spectrum of the nitroxide with that given by a DPPH solution of known concentration and by using an artificial ruby crystal as internal standard.

Materials. Tris(trimethylsilyl)silane,[28] 4-nitro-2,2,4-trimethylpentane,[29] and *p*-cyano-α-nitrocumene[30] were prepared following literature procedures. All other chemicals were commercially available and were used either as received or after further purification.

General Procedure for the Product Studies. A solution containing the nitro compound, TTMSS (1.2 equiv) or Bu_3SnH (1.2 equiv), and AIBN (3–10%) as initiator in toluene was heated at 85 °C for 1 h and then analyzed by GC. Yield and consumption were quantified by GC using an internal standard and authentic samples.

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Registry No. **1a**, 75-52-5; **1b**, 79-24-3; **1c**, 79-46-9; **1d**, 594-70-7; **1e**, 5342-78-9; **1f**, 58324-82-6; **2a**, 124716-11-6; **2b**, 137743-58-9; **2c**, 137743-61-4; **2d**, 124687-55-4; **2e**, 137743-68-1; **2f**, 137743-72-7; **3a**, 137743-56-7; **3b**, 137743-59-0; **3c**, 137743-62-5; **3d**, 137743-65-8; **3e**, 137743-69-2; **3f**, 137743-73-8; **4a**, 137743-57-8; **4b**, 137743-60-3; **4c**, 137743-63-6; **4d**, 52323-95-2; **5c**, 137743-64-7; **5d**, 137743-66-9; **5e**, 137743-70-5; **6c**, 3229-59-2; **6d**, 2406-25-9; **6f**, 137743-74-9; **7d**, 137743-67-0; **7e**, 137743-71-6; **7f**, 137743-75-0; TTMSS, 1873-77-4; $(MeSi)_3Si^{\bullet}$, 26121-01-7.

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