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Reactions of Substituted Boryl Radicals with Nitroalkanes. EPR, Kinetic, and Product Studies

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The radical-initiated reaction of amine-boranes and phosphine-boranes, LBH_3 ($L = R_3N, R_3P$) with aliphatic nitro compounds has been investigated in order to explore the possibility of reducing tertiary nitroalkanes to the corresponding hydrocarbons. In all the examined cases boroxy nitroxides, $RN(O^\bullet)OBLH_2$, resulting from the addition of ligated boryl radicals, $LBH_2^\bullet$, to an oxygen atom of the nitro group were detected and characterized by EPR spectroscopy. This reaction occurs at room temperature with a rate constant of 1.5×10^7 M^{-1} s^{-1} for $LBH_2^\bullet = Me_3NBH_2^\bullet$ and $RNO_2 = Me_3CNO_2$. The boroxy nitroxides from tertiary nitroalkanes decay by a fragmentation reaction occurring with cleavage of the nitrogen−oxygen bond, rather than of the carbon−nitrogen bond as would be required for the reduction to the corresponding alkane to take place. The Arrhenius parameters for this fragmentation have been determined in few cases.

Introduction

The reduction of tertiary aliphatic nitro compounds to the corresponding alkanes using tributyltin hydride in the presence of radical initiators has been extensively used for synthetic purposes in recent years.[1−4] Mechanistic studies based on spectroscopic,[5] kinetic,[6] and eletrochemical[6] 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. A general scheme for this reaction is exemplified in the eqs 1−3.

$$R'_3MH + R\bullet \longrightarrow R'_3M\bullet + RH \tag{1}$$

$$R'_3M\bullet + RNO_2 \longrightarrow RN(O\bullet)OMR'_3 \tag{2}$$

$$RN(O\bullet)OMR'_3 \longrightarrow R\bullet + R'_3MON{=}O \tag{3}$$

$$RN(O\bullet)OMR'_3 \longrightarrow RN{=}O + R'_3MO\bullet \tag{3'}$$

Cleavage at the carbon−nitrogen bond is peculiar to tin adducts of nitro compounds, while fragmentation takes place preferentially at the nitrogen−oxygen bond (eq 3′) in the analogous adducts of carbon-centered radicals.[7] Also tris(trimethylsilyl)silane, which is a good substitute for tributyltin hydride in many reduction processes, is not able to reduce nitroalkanes because the nitroxide adducts fragment by cleavage of the nitrogen−oxygen bond,[8] similarly to the adducts of the alkyl radicals.

Searching for a possible substitute of the very toxic tin hydride we have examined the possibility of using, as reducing agent of aliphatic nitro derivatives, several boranes complexed by amines or phosphines. Examples of the homolytic reactivity of boranes are known in the literature. Actually the borane radical anion, $BH_3^{\bullet-}$, or ligated boryl radicals, $LBH_2^\bullet$ (with L = NR_3, PR_3 or SR_2)[9−15] have been reported to react with alkyl azides, alkyl cyanides, arenes, alkenes, and nitrones, affording paramagnetic adducts detected and characterized by EPR spectroscopy, and with alkyl halides and isocyanides giving rise to alkyl radicals. Boronitroxides have been obtained when reacting boryl radicals with nitroso compounds,[10,16−18] and recently we have reported the generation of boroxy nitroxides formed in the photochemical reaction of nitroalkanes and nitroarenes with BH_4NBu_4.[19]

Besides these spectroscopic and kinetic investigations, some synthetically useful procedures involving boryl radicals have also been described, such as the reduction of α-bromo esters[20] or that of tertiary alkyl bromides.[21]

In order to explore the possibility of reducing tertiary or resonance-stabilized nitroalkanes, we report here an investigation on the radical-initiated reaction of boranes LBH_3 complexed with amines and phosphines (**2a**−**g**) with the nitroalkanes RNO_2 (**1a**−**e**, **1g**) and with 2,4,6-tri-*tert*-butylnitrobenzene (**1f**); the latter compound can be considered more like a nitroalkane than a nitroarene,

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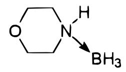
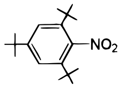
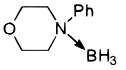
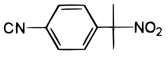
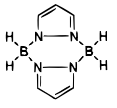
since steric hindrance prevents conjugation between the nitro group and the aryl ring from taking place. These reactions leading to the boroxy nitroxides **3ij** (see eqs 4–6) have been investigated by EPR spectroscopy and by means of kinetic and product studies.

$$(Me_3CO)_2 \xrightarrow{h\nu} 2Me_3CO\bullet \quad (4)$$

$$\underset{\mathbf{2j}}{Me_3CO\bullet + LBH_3} \longrightarrow Me_3COH + LBH_2\bullet \quad (5)$$

$$LBH_2\bullet + \underset{\mathbf{1i}}{RNO_2} \longrightarrow \underset{\mathbf{3ij}}{RN(O\bullet)OBLH_2} \quad (6)$$

	RNO_2		LBH_3
1a	$MeNO_2$	**2a**	Me_3NBH_3
1b	$EtNO_2$	**2b**	Et_3NBH_3
1c	$Me_2C(H)NO_2$	**2c**	Bu_3PBH_3
1d	Me_3CNO_2	**2d**	$Me_2(H)NBH_3$
1e	$CH_3(CH_2)_5NO_2$	**2e**	
1f		**2f**	
1g		**2g**	

Results and Discussion

Trialkylamine–boranes. Nitroalkanes (**1a–f**) were reacted at room temperature within the EPR cavity with trialkylamine ligated boryl radicals, $R'_3NBH_2^{\bullet}$, photolytically produced from **2a,b** and di-*tert*-butyl peroxide in deoxygenated benzene or *tert*-butylbenzene. When we started to irradiate the solutions, EPR spectra were immediately observed, showing nitrogen (ca. 27 G for **3aa–ea** and **3ab–eb** and ca. 22 G for **3fa** and **3fb**) and boron (ca. 3.5 G) coupling constants of the expected magnitude for boroxy nitroxides of general structure $RN(O^{\bullet})OBH_2NR'_3$. Under continuous photolysis of the solutions containing one of the nitroalkanes **1a–1e**, a second spectrum due to the dialkyl nitroxide, $R_2NO^{\bullet}$, grew up with time. If the light from the UV lamp was shut off, the EPR spectra of the boroxy nitroxides disappeared with decay times ranging from seconds to minutes depending on the nature of the various substituents and on the experimental conditions. In order to establish the preferred route of disappearance of these radicals and to determine the related kinetic constants, the decay of some of the nitroxides originated from the tertiary nitroalkane Me_3CNO_2 (**1d**), was carefully investigated.

Both $Me_3CN(O^{\bullet})OBH_2NMe_3$ (**3da**) and $Me_3CN(O^{\bullet})OBH_2NEt_3$ (**3db**) in the temperature ranges 283–328 K and 253–285 K, respectively, decayed following good first-order kinetics when stopping the irradiation. The Arrhenius plots (see Figure 1) provided the following activation parameters: $E_a = 21.82$ kcal mol^{-1}, $\log(A/s^{-1}) = 14.25$ for **3da** and $E_a = 17.82$ kcal mol^{-1}, $\log(A/s^{-1}) = 13.02$ for **3db**. Both the kinetics and the log *A* value are consistent[7] with the boroxy nitroxide decaying by a fragmentation reaction occurring either at the carbon–nitrogen bond (eq 7a) to afford *tert*-butyl radicals and O=NOBLH$_2$, or at the nitrogen–oxygen bond (eq 7b) to give 2-methyl-2-nitrosopropane and a ligated boroxyl radical.

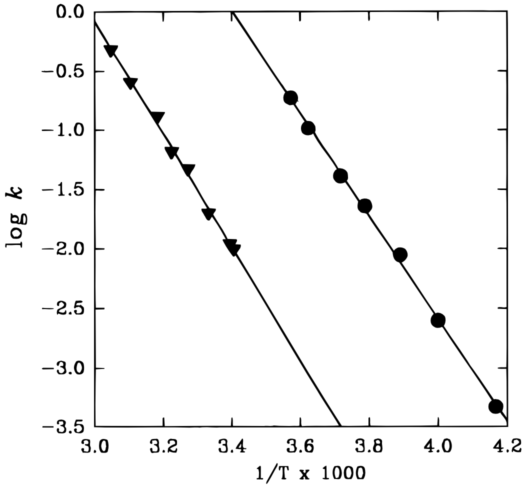


Figure 1. Arrhenius plot for the decay of the boroxy nitroxides **3da** (▼) and **3dc** (●) in *tert*-butylbenzene solutions.

$$RN(O\bullet)OBLH_2 \rightleftharpoons R\bullet + O{=}NOBLH_2 \quad (7a)$$

$$RN(O\bullet)OBLH_2 \rightleftharpoons RN{=}O + \dot{O}BLH_2 \quad (7b)$$

$$RN{=}O + R\bullet \longrightarrow R_2N{-}O\bullet \quad (8)$$

To decide which of the two is the major process, the decay of $Me_3CN(O\bullet)OBH_2NMe_3$ (**3da**) was followed in the presence of a large amount of 2-methyl-2-nitrosopropane. Under these conditions the fragmentation *via* route 7b would give rise to boroxyl radicals rapidly adding to $Me_3CN{=}O$ (eq −7b) to regenerate the starting boroxy nitroxide with a consequent slowing down of its decay. On the other hand, if fragmentation *via* route 7a is taking place, the decay rate of the boroxy nitroxide is expected to remain the same observed in the absence of $Me_3CN{=}O$.

At room temperature the measured value of the first-order rate constant for the decay of **3da** was 1.83×10^{-2} s^{-1} in the absence and 3.54×10^{-3} s^{-1} in the presence of 0.16 M 2-methyl-2-nitrosopropane. This strong reduction clearly indicates that $Me_3CN(O\bullet)OBH_2NMe_3$ decays essentially by fragmentation at the nitrogen–oxygen bond (eq 7b). The detection of some dialkyl nitroxide (*vide supra*) can be explained in terms of photocleavage of the nitrosoalkane, RN=O, formed in reaction 7b, followed by addition of the resulting alkyl radicals, $R^{\bullet}$, to RN=O (eq 8).

The above experiment demonstrates that boroxy nitroxides fragment preferentially at the nitrogen–oxygen bond, although it does not allow us to decide if the rate constant measured for the first-order decay is the true rate constant or not. In fact, the boroxyl radical formed in reaction 7b might abstract an hydrogen atom from the borane to give a boryl radical which in turn can regenerate the boroxy nitroxide. In this case the apparent rate of decay of $Me_3CN(O\bullet)OBLH_2$ will decrease by increasing the borane concentration. In order to check this possibility the kinetics of the disappearance of **3da** was followed in the presence of variable concentrations of Me_3NBH_3 (from 0.05 to 0.70 M) and that of **3db** in the presence of Et_3NBH_3 in the range 0.13–1.3 M. Despite these large differences in the amount of borane present in solution, the rates of decay measured at room temperature remained essentially constant, i.e. $(8.3 \pm 0.6) \times 10^{-3}$ s^{-1} for **3da** and 1.1 ± 0.3 s^{-1} for **3db**. It seems therefore that the boroxyl radicals decay by some other route instead of abstracting an hydrogen atom from the borane. Although we have no experimental evidence about it, a possible path of decay might be an intramolecular 1,4- or 1,5-migration of hydrogen from carbon to oxygen. In this case, since the resulting carbon-centered radical is expected to react with a nearly diffusion-controlled rate constant with the boroxy nitroxide,[22] the measured rate constant of decay, k_{app}, will be twice the true rate of fragmentation of $RN(O^{\bullet})OBLH_2$.

Competition experiments were also carried out at 298 K by photolytically reacting Me_3NBH_3 (**2a**) with a mixture of the nitroalkane **1d** and of 2-methyl-2-bromopropane, in the presence of di-*tert*-butyl peroxide, in order to determine the kinetic constant value for the addition of boryl radicals to nitro compounds. In the assumption that the system under investigation can be described by reactions 6−11, the steady state concentration of the boroxy nitroxide is given by a rather cumbersome equation containing many terms including the unknown concentration of the nitroso compound, RN=O.

Experimentally, when starting to irradiate the solutions, the height of the EPR signals due to the boroxy nitroxide, $RN(O^{\bullet})OBLH_2$, increases slowly reaching a plateau only after several minutes. This is due to the fact that initially the $R'^{\bullet}$ radicals are trapped by the nitroxide (eq 10) with reduction of its steady state concentration, while with time an increasingly large number or $R'^{\bullet}$ radicals is trapped by the nitroso compound RN=O (eq 11) which accumulates in solution under continuous photolysis conditions. Actually, if some $Me_3CN{=}O$ is added to the solution, the nitroxide concentration reaches a steady state almost immediately after starting to irradiate.

$$\xrightarrow{R_i} \dot{B}LH_2$$

$$\dot{B}LH_2 + RNO_2 \xrightarrow{k_6} RN(O\bullet)OBLH_2 \qquad (6)$$

$$\dot{B}LH_2 + R'Br \xrightarrow{k_9} LBH_2Br + R'\bullet \qquad (9)$$

$$RN(O\bullet)OBLH_2 \xrightarrow{k_7} RN{=}O + \dot{O}BLH_2 \qquad (7b)$$

$$RN(O\bullet)OBLH_2 + R'\bullet \xrightarrow{k_{10}} \text{Products} \qquad (10)$$

$$RN{=}O + R'\bullet \xrightarrow{k_{11}} RR'NO\bullet \qquad (11)$$

$$[RN(O\bullet)OBLH_2] = \frac{R_i}{k_7\{1 + k_9[R'Br]/k_6[RNO_2]\}} \qquad (12)$$

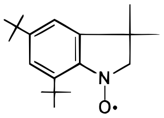
In the experimental conditions where reaction 10 can be neglected with respect to 11, the equation giving the steady state concentration of the boroxy nitroxide simplifies to 12. The latter equation was then used to determine the ratio k_9/k_6 as follows.

At first we determined the ratio R_i/k_7 by measuring the steady state concentration of the boroxy nitroxide radical in the absence of alkyl bromide; then, the intensity of the EPR spectra of $RN(O^{\bullet})OBLH_2$ at different concentrations of alkyl bromide was measured under the same conditions. By plotting the inverse of the nitroxide concentration as function of $[R'Br]/[RNO_2]$ a nice straight line was obtained providing a value for the ratio k_9/k_6 of 3.3 for the trimethylamine−boryl radical, $Me_3NBH_2^{\bullet}$. The value of k_9 was then estimated by combining data reported by Roberts and co-workers.[10,14] Since the β-fragmentation reaction (13) of $(i\text{-}Pr)_2EtNBH_2^{\bullet}$, characterized by the Arrhenius parameters $\log(A/s^{-1}) = 12.5$ and $E_a = 7.81$ kcal mol^{-1}, is at 255 K faster by a factor of 33 than the bromine abstraction from ethyl bromide by the same boryl radical, $k_9^{255\ K}$ can be calculated as 2.1×10^7 M^{-1} s^{-1}. Moreover, at 246 K the rate of bromine abstraction by boryl radicals from Me_3CBr is 1.2 times larger than from EtBr and, assuming for log *A* the normal value of 9.5, the rate constant for bromine abstraction from *tert*-butyl bromide at room temperature can be estimated as $k_9^{298\ K} = 5 \times 10^7$ M^{-1} s^{-1}.

$$(i\text{-}Pr)_2EtNBH_2\bullet \xrightarrow{k} i\text{-}Pr\bullet + (i\text{-}Pr)EtN{=}BH_2 \qquad (13)$$

The rate constant k_6 for the addition of $Me_3NBH_2^{\bullet}$ to 2-methyl-2-nitropropane was calculated from these data as 1.5×10^7 M^{-1} s^{-1}. For comparison, the addition to nitroalkanes of *tert*-butyl radicals[7] takes place with a rate constant of 1.2×10^3 M^{-1} s^{-1} and the addition of triethylsilyl radicals[23] to the same substrates with $k = 4.3 \times 10^7$ M^{-1} s^{-1}.

When using the 2,4,6-tri-*tert*-butylnitrobenzene (**1f**) the experimental behavior was more complicated. Irradiation inside the EPR cavity of solutions containing the boranes **2a,b** and **1f**, in the presence of peroxide, led at room temperature to the formation of two paramagnetic species. One was the corresponding boroxy nitroxide, and the other was the cyclic nitroxide radical with structure **4**, whose formation takes place *via* an initial intramolecular hydrogen abstraction from an *ortho tert*-butyl substituent by the photoexcited nitro group.[19,24]



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To avoid the photochemical formation of this species we generated the boryl radicals by thermal decomposition of di-*tert*-butyl hyponitrite at 330 K; initially, only the boroxy nitroxide was observed, but after several minutes two new species could be detected. One was the boroxy aminyl radical **5**, formed by the attack of boryl radicals to 2,4,6-tri-*tert*-butylnitrosobenzene, while the EPR spectrum of the other radical could not be fully interpreted due to its complexity.

Similar species were obtained by Roberts et al.[10] when reacting the nitrosobenzene with boranes in the presence of $Me_3CON{=}NOCMe_3$ at 320 K.

Phosphine−Borane. The photochemical reaction of nitroalkanes **1a−e** with Bu_3PBH_3 (**2c**) was carried out at room temperature in benzene free of oxygen in the presence of di-*tert*-butyl peroxide, as previously reported for trialkylamine boranes. In all cases, immediately after starting to irradiate the solution, well resolved EPR spectra were obtained (see Figure 2), showing nitrogen and boron coupling constants (a_N = ca.28 G, a_B = ca. 1.1

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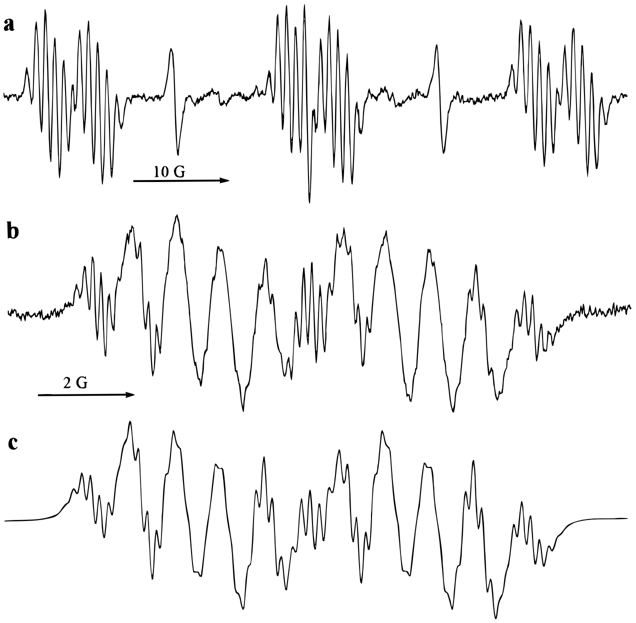
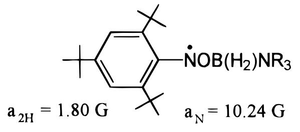


Figure 2. EPR spectrum (a) of the boroxy nitroxide obtained by photolysis of a benzene solution of di-*tert*-butyl peroxide in the presence of Bu_3PBH_3 and 2-methyl-2-nitropropane. Expansion (b) of the central multiplet and (c) corresponding simulation.

G) and *g*-factors characteristic of boroxy nitroxides, $RN(O^\bullet)OBH_2PR'_3$. As expected, the radical from **1f** showed a nitrogen splitting slightly smaller (21.67 G) and the absence of the boron coupling presumably because of the conformation adopted by the radical in solution. With time a second spectrum due to more persistent dialkyl nitroxides began to superimpose on that of the primary radical.

Also the phosphorated boroxy nitroxide **3dc** decayed following good first-order kinetics over a wide range of temperature (241−279 K) when stopping the irradiation. The Arrhenius parameters, i.e. $\log(A/s^{-1}) = 14.69$ and $E_a = 19.74$ kcal mol^{-1}, were similar to those measured for the fragmentation of the trialkylamine−boryl adducts to nitroalkanes. Product studies confirmed that, also in this case, the nitroxide decays by cleavage of the nitrogen−oxygen bond (*vide infra*).

In order to determine the value of the kinetic constant for the addition of phosphine−boryl radicals to nitro compounds, competition experiments were carried out at 298 K in benzene containing a mixture of 2-methyl-2-nitropropane (**1d**) and 2-methyl-2-bromopropane. Using the method previously described for trimethylamine-borane, we could determine the ratio k_9/k_6 as 3.7 by measuring the concentration of boroxy nitroxide at different concentrations of alkyl bromide and by assuming the same kinetic scheme.



5 $g = 2.0043$

Dialkylamine−Boranes. Room-temperature irradiation of deoxygenated benzene solutions of **2d**, **2e** and **1a**, **1b**, **1c**, and **1f** in the presence of di-*tert*-butyl peroxide gave rise to paramagnetic species showing EPR spectra where unresolved couplings due to the entering ligated boryl groups contribute to the very large line width. However, the values of both the nitrogen hyperfine splitting constants and *g*-factors are indicative of boroxy nitroxides (see Table 1).

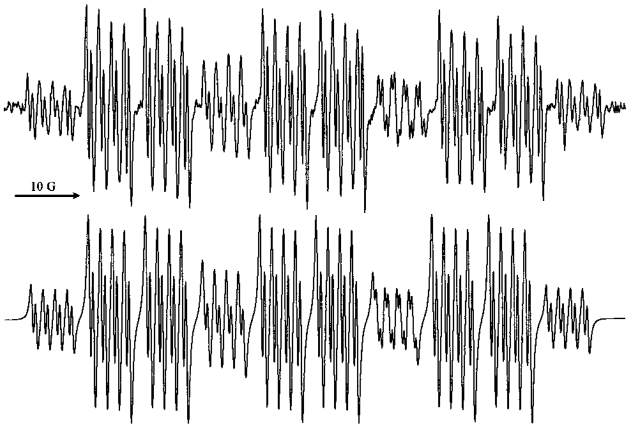
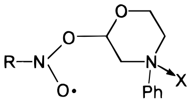


Figure 3. Experimental (upper) and simulated EPR spectrum of the boroxy nitroxide obtained by photolyzing a benzene solution of pyrazabole and $MeNO_2$ in the presence of di-*tert*-butyl peroxide. Second-order effects have been taken into account for the simulation.



6 X=none, BH_3

Phenylmorpholine−Borane. With phenylmorpholine−borane (**2f**) the reaction with the nitroalkanes **1a,b** and **1d,e** under the same conditions reported for trialkylamine−boranes and phosphine−boranes led to simple and well resolved EPR spectra showing nitrogen coupling constants (ca. 28.5 G) and *g*-factors (2.0053−2.0054) characteristic of alkoxy nitroxides. In no case, however, could we observe resolved coupling to the boron atom or to any other nucleus from the borane. Similar spectra were obtained by photoreacting *N*-phenylmorpholine with the above nitro derivatives in the presence of di-*tert*-butyl peroxide. The resulting nitroxide radicals show spectral parameters consistent with structure **6** where X = BH_3 in the case of **2f**.[25] No EPR signals could be obtained with **1c** and **1f** at room temperature.

Pyrazabole. Photolytic reaction of **2g** with the nitroalkanes **1a−f** at room temperature in benzene in the presence of di-*tert*-butyl peroxide afforded intense and well resolved EPR spectra easily interpretable (see Figure 3). The magnitude of the nitrogen and boron coupling constants (a_N = ca. 28 G, a_B = 1.2−1.9 G for **3ag−eg**; a_N = 21.94 G, a_B = 0.84 G for **3fg**) and of the *g*-factors suggests that these spectra are due to the expected boroxy nitroxide radicals.

Product Studies. Reduction of compound **1g** was attempted by using Bu_3PBH_3 as the reducing agent. This reaction, when carried out at 110 °C in toluene and in the presence of the radical initiator dibenzoyl peroxide, gave in 2 h less than 5% conversion. In previous papers[7] it has been shown that the reaction of **1g** with *n*-Bu_3SnH at 85 °C in toluene, in the presence of the radical initiator

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[25] One of the referees suggested that the results obtained with *N*-phenylmorpholine−borane can be explained by admitting that the *tert*-butoxyl radical does abstract hydrogen from boron initially, but that the *N*-phenylamine−boryl radical produced then rapidly rearranges to an aminyl−phenylborane radical which undergoes subsequent reactions.

Table 1. Hyperfine Splitting Constants (in Gauss = 10^{-4} Tesla) and *g*-Factors for the Boroxy Nitroxides 3aa–3fg

		2a	2b	2c	2d	2e	2f	2g
1a	a_N	27.29	27.04	27.47	27.43	27.43	28.55	27.86
	a_B[a]	3.28	3.36	1.26				1.91
	a_{3H}	9.00	8.89	9.27	10.13	10.13	9.05	9.20
	a_{others}			5.03 (P)				0.71 (1H)
				0.96 (2H)				
	g	2.0054	2.0054	2.0054	2.0054	2.0054	2.0054	2.0054
1b	a_N	27.29	27.13	27.65	27.45	27.45	28.51	27.85
	a_B	3.52	3.43	1.18				1.87
	a_{2H}	7.61	7.91	8.20	9.31	9.31	8.46 (1H)	8.13
	a_{others}			5.10 (P)			8.10 (1H)	0.68 (1H)
				0.91 (2H)				
	g	2.0054	2.0054	2.0054	2.0054	2.0054	2.0053	2.0054
1c	a_N	27.49	27.54	27.91	27.71	27.71	undetected	28.30
	a_B	3.25	3.20	1.05				1.58
	a_H	3.75	3.70	4.66	5.43	5.43		4.55
	a_{others}			4.92 (P)				0.84 (1H)
				1.01 (2H)				
	g	2.0055	2.0055	2.0054	2.0054	2.0054		2.0055
1d	a_N	27.60	27.65	28.03	27.8	27.8	28.58	28.45
	a_B	3.30	3.20	0.99	1.18	1.18		1.24
	a_{others}			4.92 (P)	0.19			0.86 (1H)
				1.11 (2H)	0.57			
				0.20 (9H)	0.41			
	g	2.0054	2.0054	2.0055	2.0054	2.0054	2.0053	2.0055
1e	a_N	26.84	26.80	27.22	26.93	26.93	28.40	27.65
	a_B	3.55	3.54	1.24				1.85
	a_{2H}	8.01	8.02	8.49	9.11	9.11		8.14
	a_{others}			4.60 (P)			8.70 (1H)	0.64 (1H)
				1.15 (2H)			7.63 (1H)	
	g	2.0054	2.0054	2.0055	2.0054	2.0054	2.0054	2.0054
1f	a_N	21.81	21.74	21.67	21.52	21.52	undetected	21.94
	a_B	0.71						0.84
	a_{2H}	1.22	0.87	0.85				1.64
	a_{others}		1.82 (2H)	5.32 (P)				0.64 (1H)
				2.03 (2H)				0.62 (2N)
	g	2.0054	2.0054	2.0053	2.0053	2.0053		2.0053

[a] a_B denotes the coupling at the ^{11}B isotope.

azobis(isobutyronitrile) (AIBN), gave in 1 h 100% conversion. Therefore, the replacement of a tertiary nitro group by hydrogen using tributyltin hydride is an efficient process that cannot be obtained when using Bu_3PBH_3. The low consumption of nitroalkanes observed in the latter case indicates that the reaction follows a path different from that for the reduction with tin hydride and also that the average kinetic chain length is very short. Since the radical chain length is sufficiently long when phosphorated boranes are used to reduce tertiary alkyl bromides,[16] some inhibiting material is presumably produced during the initial part of the reaction. On the basis of what was observed by EPR, this inhibitor can be identified as the nitrosoalkane formed in the fragmentation reaction 7b.

Conclusions

Ligated amine– and phosphine–boryl radicals give a very fast addition reaction with nitroalkanes affording boroxy nitroxides. The adduct radicals obtained from tertiary nitroalkanes decay by cleavage of the nitrogen–oxygen bond to give nitrosoalkanes. Since these nitroso derivatives are inhibitors of free radical chain reactions, the ligated boranes are very poor reducing agents for nitro compounds under free radical conditions.

Experimental section

Materials. *p*-Cyano-α-nitrocumene[26] and di-*tert*-butyl hyponitrite[27] were prepared according to literature procedures. All other chemicals were commercially available and used as received.

EPR Measurements. The EPR spectra were recorded on a Bruker ESP 300 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 perylene radical cation in concentrated H_2SO_4 ($g = 2.00258$). Photolysis was carried out by focusing the unfiltered light from a 500 W high pressure mercury lamp on the EPR cavity. 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 boroxy nitroxide with that given by a 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) solution of known concentration and by using an artificial ruby crystal as internal standard.

General Procedure for Product Studies. A solution containing the nitro compound (ca. 0.1 M), the borane (ca. 0.5 M), and dibenzoyl peroxide as radical initiator in toluene was heated at 110 °C and then analyzed by GC. Yield and consumption were quantified using an internal standard and authentic samples to calibrate the response of the detector.

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