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An EPR study of the radical addition to 3-nitropentan-2-one as an archetype of α -carbonylnitroalkanes

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Carbon, silicon, germanium, tin and lead-centered radicals were reacted with 3-nitropentan-2-one and 3-nitropentan-2-ol inside the cavity of an electron paramagnetic resonance spectrometer. In all cases, selective addition to the nitrogroup was observed with detection of the corresponding oxynitroxide radicals. In the case of the carbonyl substrate, alkyl acyl nitroxides were also detected because of α -photocleavage. The oxynitroxides decayed with a first order kinetics via fragmentation of the carbon–nitrogen bond (denitration). Unexpectedly, the activation parameters were fairly similar to those previously reported for the corresponding *tert*-butyl oxynitroxides and almost independent from the presence of a carbonyl or a hydroxyl group on the carbon adjacent to the one bearing the nitrogroup. Copyright © 2014 John Wiley & Sons, Ltd.

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Introduction

The nitrogroup is one of the most important organic functionalities, and indeed, nitrocompounds have been largely exploited since the early times of modern organic synthesis,^[1] the success of these derivatives being because of the relative easiness with which they can be transformed into amines, oximes, imines or into compounds characterized by a variety of different functionalities.^[2] Even more useful may be 1,2-difunctionalized and 1,4-difunctionalized nitroderivatives; in particular, *α*-nitroketones have been proven especially valuable synthetic intermediates^[3,4] to obtain natural products,^[5,6] as well as many other derivatives such as pyrazines^[7] and benzoxazines.^[8]

In many cases, these procedures involve as a key step a direct or indirect reductive denitration of nitroalkanes used as reagents for alkyl anion synthons;^[2] on the other hand, denitration can also be achieved through a radical process based on the use of tributyltin hydride.^[9] Actually, while the latter process takes place smoothly and efficiently with tertiary nitroalkanes, secondary nitroalkanes are generally very difficult to denitrate via radical reactions.^[10] However, activation of the nitrogroup by an α -electron withdrawing substituent such as cyano, carbonyl or ester functions makes the denitration of *sec*-nitroalkanes by tributyltin hydride a rapid and efficient process.^[11] Nitrogroups at benzylic or allylic positions are also readily denitrated with Bu₃SnH.^[9]

While detailed studies have been focused on the denitration of nitroxides originating from the addition of carbon, silicon, germanium or tin-centered radicals to 2-methyl-2-nitropropane,^[12,13] fewer mechanistic investigations have been addressed to the corresponding derivatives from secondary α -ketonitrocompounds.

We were therefore prompted to endeavor in a study of the addition of carbon, silicon, germanium or tin-centered radicals to 3-nitropentan-2-one **1**, chosen as the archetype of secondary α -carbonylnitroalkanes and of the decay of the resulting oxynitroxides. For the sake of comparison, we extended the study

to the reduced 3-nitropentan-2-ol **2**, i.e. the corresponding unactivated derivative (Fig. 1).

Results and Discussion

UV irradiation of oxygen-free benzene solutions of compound **1** or **2** and a number of radical precursors resulted in all cases in the observation of intense electron paramagnetic resonance (EPR) spectra, and the hyperfine parameters derived from their analysis are collected in Tables 1 and 2, respectively. While interpretable spectra were also observed when photolyzing a solution of compound **1** as such, under similar conditions a solution of **2** only led to the detection of extremely weak spectra that could not be rationalized.

Photolysis of 1 and 2

Photolysis of a benzene solution of nitroketone **1** afforded the spectrum shown in Fig. 2 consisting of the signals from two distinct aminoxyls that were identified as to two acyl-nitroxides because of their low nitrogen hyperfine splitting (hfs) constant $(0.7 < a_N < 0.8 \text{ mT})$ and their fairly high *g*-factor values (g = 2.0067).^[14]

One of these species (red dots) exhibited, in addition to that with the nitrogen atom, coupling of the unpaired electron with a hydrogen atom (I = one half), with an hfs constant value in line

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Figure 1. 3-Nitropentan-2-one 1 and 3-nitropentan-2-ol 2.

with the expectations for a *sec*-alkyl acyl-nitroxide; the second species (blue stars) that only showed three lines because of the nitrogen atom was instead identified as a *tert*-alkyl acyl-nitroxide.

The formation of these two nitroxides is not obvious. Because of the simultaneous presence of a carbonyl group and a nitrogroup, the photobehavior of **1** may be fairly complex. Indeed, the unfiltered light of the Hg lamp can excite several intermediates leading to a large number of reactive species. Thus, in Scheme 1, we outline some possible pathways leading to the detected species, but we emphasize that they are markedly speculative and that while we believe them to represent a sensible route to the resulting species, we have no definite evidence of their actual relevance.

Table 1. EPR spectral parameters of radicals from the photoreactions of 1 with different radical precursors						
Radical precursor	X·	Rad.	a _N /mT	a _{other} /mT	g	
_	_	3 or 4	0.722	0.359 (1H)	2.0067 ₃	
		5 or 6	0.754	—	2.0067 ₅	
^t BuC(O) ^t Bu	^t Bu	1a	2.575	0.353 (1H)	2.0054 ₀	
		7 or 8	1.556	—	2.0059 ₄	
Et₃SiH/ ^t BuOO ^t Bu	Et₃Si	1b	2.762	0.428 (1H)	2.0052 ₈	
		5 or 6 ^a	0.754	—	2.0067 ₅	
Ph₃SiH/ ^t BuOO ^t Bu	Ph₃Si	1c	2.778	0.400 (1H)	2.0052 ₅	
		5 or 6 ^a	0.754	—	2.00675	
(Me ₃ Si) ₃ SiH/ ^t BuOO ^t Bu	(Me ₃ Si) ₃ Si	1d	2.757	0.482 (1H)	2.0051 ₂	
		1e	2.792	0.550 (1H)	2.0054 ₅	
Ph₃GeH/ ^t BuOO ^t Bu	Ph₃Ge	1f	2.732	0.472 (1H)	2.0052 ₃	
		5 or 6 ^a	0.754	—	2.0067 ₅	
Bu ₃ SnSnBu ₃	Bu₃Sn	1g	2.673	0.553 (1H)	2.0049 ₆	
		9	1.535	0.312 (1H)	2.0061 ₁	
Ph ₃ SnSnPh ₃	Ph₃Sn	10	1.372	0.364 (1H)	2.0060 ₆	
		5 or 6 ^a	0.754	—	2.0067 ₅	
^c Hex₃PbPb ^c Hex₃	^c Hex₃Pb	1i	2.791	0.387 (1H)	2.0053 ₀	
		11	1.389	0.439 (2H)	2.0058 ₀	
Ph ₃ PbPbPh ₃	Ph₃Pb	1k	2.661	0.515 (1H)	2.0062 ₀	
		12	1.436	0.244 (1H)	2.0057 ₉	
alweak signal after prolonged invadiation						

^a Weak signal after	prolonged irradiation.
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Radical precursor	X٠	Rad.	a _N /mT	a _{other} /mT	g	
_	_	Very weak signals				
^t BuC(O) ^t Bu	^t Bu	2a	2.592	0.204(1H)	2.0052 ₃	
		7	1.579		2.0057 ₄	
Et ₃ SiH/ ^t BuOO ^t Bu	Et₃Si	2b	2.751	0.270 (1H), 0.037 (m) ^a	2.0053 ₀	
		13 ^b	1.438	0.403 (2H)	2.0058 ₅	
Ph₃SiH/ ^t BuOO ^t Bu	Ph₃Si	2c	2.755	0.233 (1H)	2.0052 ₅	
(Me ₃ Si) ₃ SiH/ ^t BuOO ^t Bu	(Me ₃ Si) ₃ Si	2d	2.766	0.286 (1H), 0.037 (m) ^a	2.0052₅	
		13 ^b	1.438	0.403 (2H)	2.0058 ₅	
Ph₃GeH/ ^t BuOO ^t Bu	Ph₃Ge	2f	2.735	0.304 (1H), 0.034 (m) ^a	2.0052 ₈	
Bu ₃ SnSnBu ₃	Bu₃Sn	2g	2.700	0.378 (1H), 0.032 (m) ^a	2.0050 ₄	
		13 ^b	1.438	0.403 (2H)	2.0058₅	
$Ph_3SnSnPh_3$	Ph₃Sn	2h	2.722	0.354 (1H)	2.0047 ₁	
		13 ^b	1.438	0.403 (2H)	2.0058₅	
^c Hex ₃ PbPb ^c Hex ₃	^c Hex₃Pb	2i	2.776	0.225 (1H)	2.0048 ₈	
		14	1.460	0.300 (1H), 0.566 (1H)	2.0058 ₀	
Ph ₃ PbPbPh ₃	Ph₃Pb	Signal not interpreted				

^bAfter prolonged irradiation.



Figure 2. EPR spectrum observed at room temperature upon photolysis of a benzene solution of compound **1**. Red dots and blue stars identify the lines of two acyl-nitroxides.

On one side, it is well established that UV-vis irradiation of aliphatic carbonyl compounds may result in the fragmentation of a C(O)-C bond leading to alkyl and acyl radicals. While the cleavage may take place on either side of the carbonyl group, it seems reasonable that the cleavage leading to the more stable radical be slightly favored. Thus, in the case of 1, the formation of acetyl radical **A**, with the concomitant formation of a secondary alkyl radical **B**, might be favored over that of acyl radical **C** and of the less stable methyl radical.

It is also well known that aliphatic nitrocompounds are photolabile species, their photolysis resulting in the loss of an \cdot NO₂ and the formation of an alkyl radical, in the present case **D**. Recombination of these two species does not necessarily lead back to the starting compound: indeed, \cdot NO₂ may exist in different mesomeric forms in one of which, namely \cdot O– \ddot{N} =O, one of the oxygen atoms bears the unpaired electron. Its recombination with **D** would afford the unstable nitrite **E** that would further decompose to give the alkoxy radical **F** and nitric oxide \cdot NO. The latter might also result from some photoexcited intermediates. Hydrogen abstraction by the latter may eventually lead to pentan-3-ol-2-one, while recombination of nitric oxide with **D**

would result in **G**, an α -carbonyl-nitrosoderivative that by trapping of acyl radicals **A** or **C** may account for the detected *sec*-alkyl acylnitroxide **3** or **4**. A third possibility is that photoexcitation of **1** results in the formation, via intermolecular hydrogen abstraction, of the α -hydroxy-alkyl and α -nitro-alkyl radicals **H** and **J**, respectively, which may recombine with nitric oxide to give the *tert*-alkyl nitrosoderivatives **K** and **L**. The former can, in turn, trap acyl radicals **A** or **C** to afford the detected *tert*-alkyl acyl-nitroxide **5** or **6**, while a similar process involving species **L** should be discarded as the resulting acyl-nitroxides would be expected to exhibit, contrary to what is found, a spectrum indicating the interaction of the unpaired electron also with the nitrogen atom of the α -nitrogroup.

As already stated, and at variance with 1, photolysis of solutions of nitroalcohol 2 only resulted in the detection of extremely weak EPR signals that could not be interpreted. Because of the lack of the carbonyl function, photolysis of 2 cannot obviously result in the formation of acyl-nitroxides, while denitration is still possible. In analogy to what is proposed for compound 1, photofragmentation of 2 (Scheme 2) will lead to the alkyl radical **M** and \cdot NO₂ that may recombine to nitrite **N**, the decomposition of which will afford nitric oxide and the alkoxy radical **P**. Combination of \cdot NO and radical **M** would result in the formation of the nitrosoderivative **Q** that might act as a trap for another radical **M** to eventually give the di-*sec*-alkyl nitroxide **R**.

The fact that neither this nor other nitroxides could be detected seems an indication that photodenitration of 2 is not as efficient as that of 1 and that the presence of the electron-withdrawing carbonyl group favors the loss of the nitrofunction when the latter compound is photolyzed.

Besides, as outlined in Scheme 3, the radical resulting from the cleavage of 1 may receive additional resonance stabilization from delocalization of the unpaired electron onto the oxygen atom, stabilization instead impossible for the analogous radical from 2.

Radical addition to 1 and 2

When **1** or **2** were photolyzed in the presence of 2,2,4,4tetramethyl-3-pentanone (a photolytic source of *tert*-butyl radicals) or of Group 14 organometallic hydrides in the presence of di-*tert*-butyl peroxide, very intense and similar EPR spectra



Scheme 1. Suggested pathways leading to sec-alkyl acyl-nitroxides 3/4 and to tert-alkyl acyl-nitroxides 5/6.



Scheme 2. Hypothetical photoevolution of 3-nitropentan-2-ol, 2.



Scheme 3. Resonance stabilization of the radical resulting from photodenitration of 1 with respect to that originating from 2.

were detected. In all cases, these consisted in triplet of doublets (Fig. 3a) characterized by *g*-values = 2.0050 and by fairly large nitrogen splittings in the range $2.6 < a_N < 2.8$ mT. The only notable difference in the spectra from the two compounds was that the doublet splittings in the radicals from **2** were smaller than those shown by the radicals from **1**, the decrease of the splitting being in the range from 30 to 45%.

Carbon-centered radicals can readily add to the nitrogroup of nitroalkanes. In the case of 1, addition would lead to oxynitroxides of general structure T in Scheme 4. On the other hand, they normally react with ketones through addition to the carbonyl carbon thus leading to alkoxy radicals, usually undetectable under 'normal' EPR conditions, that is, in fluid solution at ambient temperature. In the case of compound 2,



Figure 3. EPR spectra observed at room temperature upon photolysis of (a) a benzene solution of compound **1**, Et₃SiH and ^tBuOO^tBu, (b) a benzene solution of compound **1**, (Me₃Si)₃SiH and ^tBuOO^tBu and (c) a benzene solution of compound **1** and Ph₃PbPbPh₃.

only addition to the nitrogroup is instead possible. This is expected to result in oxynitroxides of general structure U having spectral parameters very similar to those exhibited by radicals akin to T. On this basis, the observed spectra were assigned to *tert*-butoxynitroxides **1a** and **2a**. When reacting **1** or **2** with ^{*t*} butyl, along with the signals from 1a and 2a, an additional three-line signal was also detected with spectral parameters typical of di-tert-alkyl nitroxides. We attribute these three-line spectra to di-tert-butyl nitroxide 7: indeed, as shown in Schemes 1 and 2, nitric oxide is formed in the photodegradation of 1 and 2. This adventitious NO might then combine with the ^tbutyl radicals present in the system to give 2-methyl-2-nitrosopropane [Me₃C–N=O] that, in turn, would trap again a ^tbutyl radical to give di-tert-butyl nitroxide 7 [Me₃CN(O·)CMe₃]. While in the case of 2, this assignment seems unambiguous, this might not be the case for 1, as its photodegradation may also lead to the tert-alkyl nitrosoderivative **K** (Scheme 1) that by acting as a trap for ^t butyl radicals would eventually afford a tert-alkyl tert-butyl nitroxide 8 [EtCH(NO₂)C(OH)(Me)–N(O·)CMe₃] with spectral parameters hardly distinguishable from those of di-tert-butyl nitroxide 7.

Organometallic radicals centered at a Group 14 element can readily add to a carbonyl group or to a nitrogroup, leading to ketyl radicals in the former case^[15] and to oxynitroxides in the latter.^[16] Thus, when reacting compound **1** with Group 14 radical precursors, the formation of these two kinds of radical adducts **S** and **T** can be envisaged (Scheme 4), both of them being in principle EPR detectable while characterized by very different spectral parameters. Thus, adducts of general structure **S** are expected to exhibit a quartet splitting because of a methyl group, conformationally dependent additional splittings from a hydrogen and a nitrogen atom and *g*-factor values in the range 2.0035 to 2.0045,^[17] whereas the spectra of adducts having structure **T** should predictably show a nitrogen splitting slightly smaller



Scheme 4. Possible radical adducts resulting from addition of ·MR₃ radicals to compounds 1 or 2.

than 3.0 mT, a hydrogen splitting in the range 0.2 to 0.6 mT and g-factors in between 2.005 and 2.006. $^{[14]}$

On the basis of their spectral parameters and because of the similarity of the spectra of the adducts from 1 and 2, the detected radicals (1b-k and 2b-i in Tables 1 and 2) were therefore identified as oxynitroxides $R_3MON(O\cdot)R'$ with general structure T or U, where M is a silicon, germanium, tin or lead atom, R is an alkyl or aryl group and R' is the pentanone or pentanol residue. Because of the similarity of the nitrogen splitting in radicals 1b-i and 2b-i, the lower value of the α -hydrogen splittings exhibited by the latter nitroxides should originate from different conformational situations. This might, in principle, be the result of a hydrogen bonding of the hydroxylic hydrogen by the nitroxidic oxygen in species 2b-i, but it should be noted that such interaction should also result in a stabilization of the polar mesomeric form of the nitroxides that would lead to larger nitrogen splitting actually not observed.

These results provide evidence that Group 14 organometallic radicals react with nitroketones via selective addition to the nitrogroup. Although, in principle, an initial addition of the \cdot MR₃ radicals to the carbonyl group followed by trapping of the resulting **S** ketyl radicals by another molecule of **1** to give oxynitroxides **T** should not be discarded 'a priori', it seems that such a possibility can be safely discarded as all the resulting oxynitroxides would basically have almost identical structures and should therefore be characterized by the same spectral parameters, which was not the case as indicated by the data collected in Table 1.

It is worth noting that in the case of the reaction of **1** with tris (trimethylsilyl)silyl radical, the spectra showed the presence of two species, 1d and 1e, with very similar spectral parameters (Fig. 2b). Because of the large bulk of the tris(trimethylsilyl)silyl group, it is envisageable that rotation of the OMR₃ residue around the N-O bond may become hindered, and the two species might be tentatively identified as different conformers of the corresponding oxynitroxide, characterized by almost equal nitrogen and slightly different hydrogen splittings. It is also possible that the presence of two conformers be favored by some sort of coordination of a silicon atom by the carbonyl oxygen, an interaction that in the case of 2, for which only the adduct 2d was detected, might be hampered by the presence of the hydroxylic hydrogen atom. On the other hand, the detection of two species with very similar EPR spectroscopic parameters has been reported for the addition of tris(trimethylsilyl)silyl radicals to 2-nitropropane.^[18] In that case, the second species was identified as the adduct of a [trimethylsilyloxy-bis(trimethylsilyl)silyl radical \cdot Si(SiMe₃)₂OSiMe₃ resulting from a 1,2 silicon to oxygen migration of a trimethylsilyl group in the tris(trimethylsilyl)silyloxy radical \cdot OSi(SiMe₃)₃ deriving from the fragmentation of the nitrogen–oxygen bond of the primary adduct Me₃CN(O·)OSi(SiMe₃)₃. In this line, it seems therefore sensible to identify radical **1e** as R' N(O·)OSi(SiMe₃)₂OSiMe₃, despite the fact that a similar radical **2e** was not observed.

It should be further mentioned that when photoreacting **1** with the organometals, a weak signal from acyl nitroxide **5** or **6** was observed along with the dominating signal of the organometallic oxynitroxide **1b**, **1c** or **1f**. Thus, although the addition of Group 14 organometallic radicals to the nitrogroup is a fast process, a small fraction of **1** underwent photofragmentation.

Finally, prolonged photolysis of solutions of 1 and a tin-centered or lead-centered radical precursor, namely hexabutyl ditin, hexaphenylditin, hexa-^chexyldilead or hexaphenyldilead, resulted in the appearance of other spectra (Fig. 2c) that exhibited spectral parameters consistent with *tert*-alkyl-sec-alkyl nitroxides $(1.4 \le a_N \le a_$ 1.5 mT, $0.21 < a_H < 0.35$ mT, $q = 2.006)^{[14]}$ for radicals **9**, **10** and **12** and with a di-sec-alkyl-nitroxide for radical 11. Photolysis of ditin or dilead compounds [R₃M–MR₃] normally results in the cleavage of the metal-metal bond (formation of ·MR3 radicals), but in some instances, R radicals may be formed as well. In this light, radical 11 might be identified with di-^chexyl nitroxide for which spectral parameters in line with those presently measured have been reported,^[18] while the possibility that **11** be in fact a nitroxide **V** resulting from the trapping of radical **D** by the nitrosoderivative G (Scheme 5) seems unlikely as if this were the case, this species should have been observed in all cases, independently of the organometallic reagent being used.

As for species **9**, **10** and **12**, in principle, it is possible to envisage the formation of radicals akin to species **Y** according to two different pathways shown in Scheme 5. One of these only involves fragmentation of nitroketone **1**, eventually leading to the *tert*-alkyl *sec*-alkyl nitroxide **W**. On the other hand, this assignment would collide with the fact that **9**, **10** and **12** exhibit different spectral parameters and, secondly, that these nitroxides were not detected when photolyzing solutions of **1** alone. A second possibility is that for tin and lead-centered radicals, addition to the carbonyl group leading to adduct **S** may compete with addition to the nitrogroup. Then, a coupling of these ketyl radicals with ·NO from the concomitant photofragmentation of



Scheme 5. Possible route to radicals 9, 10 and 12.

1 would result in the tertiary nitrosoderivative **X** that, upon trapping of a secondary radical **D**, would eventually afford the *tert*-alkyl *sec*-alkyl nitroxide **Y**. We then attribute to radicals **9**, **10** and **12** the general structure **Y** that would account for the slight but definite differences of their spectral parameters with the nature of the MR₃ residue and with the fact that these species are only observed in the presence of ditin or dilead compounds.

Prolonged photoreaction of **2** with the organometals eventually resulted in the disappearance of the spectra from oxynitroxides **2b-h** that were in all cases replaced by that of a symmetric di-*sec*-alkyl nitroxide **13** to which we assign the structure **R**. Because this species is not observed when photolyzing compound **2** alone, it cannot be formed as shown in Scheme 2, and in Scheme 6 we outline a different possible route to radical **13**.

Thus, decay of 2b-h would lead to radical M that may subsequently combine with nitric oxide to give the nitrosoderivative Q, which, in turn, would eventually afford 13 through the trapping of another radical M. It cannot be, however, excluded that in the decay of 2h, the fragmentation of the N–O bond may compete to some extent with that of the N–C bond, resulting again in the formation of the nitrosoderivative Q.

Coming eventually to radical **14**, its spectral parameters are indicative of an asymmetric di-*sec*-alkyl nitroxide that we identify as 2-hydroxypent-3-yl ^ckexyl nitroxide resulting from the trapping of a ^chexyl radical by the nitrosoderivative **Q**.

Decay of oxynitroxides from 1 and 2

All oxynitroxides **1a–k** and **2a–i** were fairly persistent species, with half-life times ranging from several seconds to a few minutes. The decay of these radicals, which reflects their fragmentation to a diamagnetic molecule and a radical fragment, may involve two different processes: the cleavage of the carbon–nitrogen bond results in the formation of a *sec*-alkyl radical and a nitrite ($O=N-OMR_3$), whereas the cleavage of the nitrogen–oxygen bond leads to a nitrosoderivative and an OMR_3 radical. The

decay of *tert*-alkyl oxynitroxides has been previously investigated, particular attention having been addressed to Me₃CN(O·)OMR₃ species, where M is a carbon, a silicon, a germanium or a tin atom, and it has been shown that these oxynitroxides decay via cleavage of the nitrogen–oxygen bond when MR₃ is a *tert*-butyl^[12] or a tris (trimethylsilyl)silyl group,^[19] whereas when MR₃ is a tributyltin group, the decay involves cleavage of the nitrogen–carbon bond, and accordingly, tributyltin hydride has been widely exploited for the reductive denitration of tertiary aliphatic nitrocompounds.^[20] It has been subsequently shown that SiPh₃, GePh₃ *tert*-alkyl oxynitroxides also decay via cleavage of the N–O bond.^[13]

Not being aware of detailed studies of the decay of *sec*-alkyl oxynitroxides, we have studied the decay of oxynitroxides **1c**, **f** and **g** and **2c**, **f** and **g** in the wider possible temperature range, i.e. 253 to 323 K. The radicals were generated by photolysis of solutions of **1** or **2** containing di*-tert*-butylperoxide and triphenylsilyl hydride (**1c** and **2c**) or triphenylgermyl hydride (**1f** and **2f**) or simply hexabutylditin (**1g** and **2g**) at the desired temperature. Once the signal had reached a stationary level, irradiation was switched off and the signal decrease of a clean spectral line was monitored in time.

Because in all cases very clean spectra were observed with virtually no signal from the adventitious dialkyl nitroxides that might result from a combination of the two aforementioned decay processes, it was concluded that the oxynitroxides fragmented preferentially at the nitrogen–carbon bond, as indicated in Scheme 7. The decay process can therefore be described by reactions 1 and 2 in the case of the tin derivatives **1g** and **2g**, whereas reaction 3 should also be considered for the silyloxy nitroxides and germyloxy nitroxides **1c**, **1f**, **2c** and **2f** (where Xis either radical **D** or **M** shown in Scheme 5):

$$XN(O \cdot)OMR_3 \rightarrow X \cdot + O = NOMR_3$$
(1)

$$X \cdot + XN(O \cdot)OMR_3 \rightarrow XN(OX)OMR_3$$
 (2)



Scheme 6. Possible routes to radical **13**.



Scheme 7. Formation and decay reactions of radicals 1c, f and g and 2c, f and g.

$$X \cdot + HMR_3 \rightarrow XH + \cdot MR_3$$
 (3)

The decay process of 1g and 2g can therefore be expressed as

$$-d[XN(O\cdot)OMR_3]/dt = 2k_1[XN(O\cdot)OMR_3]$$
(4)

while in the case of 1c, 1f, 2c and 2f, it becomes

$$-d[XN(O\cdot)OMR_3]/dt = 2k_2k_1[XN(O\cdot)OMR_3]^2/\{k_3[HMR_3]$$
(5)
+ $k_2[XN(O\cdot)OMR_3]\}$

It should, however, be taken into account that the recombination reaction 2 must be very fast, and the value of k_2 can be safely estimated as ~10⁹ m⁻¹ s⁻¹; besides, although the rates of hydrogen abstraction from triphenylsilane and triphenylgermane by secondary alkyl radicals are not available, by combining kinetic data available in the literature for reactions involving these species, ^[21,22] it can be estimated that the k_3 value should not exceed 10³ m⁻¹ s⁻¹ for Ph₃SiH and 2×10⁴ m⁻¹s⁻¹ for Ph₃GeH. Thus, for oxynitroxide concentrations not lower ~10⁻⁵ m, as it was the case in our experiments, and for low organometallic hydride concentrations as those we have been using ([HMR₃] \leq 10⁻¹ m), in Eqn (5), the term k_3 [HMR₃] can be disregarded as negligible with respect to k_2 [XN (O·)OMR₃], and Eqn 5 reverts to Eqn (4) also for oxynitroxides **1c** and **f** and **2c** and **f**. Based on Eqn 4, first-order decay kinetics were expected for the six investigated oxynitroxides, and this was what we actually found (Fig. 4) provided that the critical maximum concentration of the organometallic hydride was respected. Indeed, a mixing of different order kinetics were instead observed if $[HMR_3] > 10^{-1}$ M were used.

An Arrhenius treatment of the kinetic data obtained at the different temperatures led to the activation parameters collected in Table 3, where those taken from the literature for the corresponding *tert*-butyl organometaloxynitroxides are also reported. The first feature to emerge from an analysis of Table 3 is that the activation parameters determined in this study are fairly similar to those previously determined for the corresponding *tert*-butyl oxynitroxides, being about half a kcal mol⁻¹ larger when M is silicon, about half a kcal mol⁻¹ smaller when M is germanium and *ca* 1 kcal mol⁻¹ smaller when M is tin. The easiness of the cleavage of the C–N bond should reflect the stability of the resulting radical and diamagnetic species. In the present case, the latter fragment is the same, i.e. an organometallic nitrite R₃MO–N=O, and therefore, the easiness of the cleavage should reflect the stability of the resulting carbon-centered radicals.

On this basis, we would have expected for the fragmentation of the *sec*-alky oxynitroxides from **1** and **2** activation energy values larger than those found for the corresponding *tert*-butyl derivatives. In particular, we would have expected **1c**, **f** and **g** and **2c**, **f** and **g** to exhibit E_a values up to ca 3 kcal mol⁻¹ larger than those of the corresponding *tert*-alkyl derivatives, a bond



Figure 4. Time profile of the EPR signal observed upon a short UV irradiation of benzene solutions of compound **1**, Ph_3GeH and $^tBuOO^tBu$ at 275 K (upper trace), and of compound **2**, Ph_3SiH and $^tBuOO^tBu$ at 365 K (lower trace). In the inserts, the Arrhenius plots for the corresponding adducts **1f** and **2c**.

Table 3. Activation parameters for the cleavage of the nitrogen-carbon bond for some selected alkyl organometalloxy nitroxides					
Radical/#	MR ₃	E_a /kcal mol ⁻¹	Log (A/s ⁻¹)	Reference	
D–N(O·)OMR ₃ /1c	SiPh₃	19.36 ± 0.55	13.37 ± 0.39	This work	
D–N(O·)OMR ₃ /1f	GePh ₃	17.06 ± 0.32	12.71 ± 0.24	This work	
D–N(O·)OMR ₃ /1g	SnBu₃	6.66 ± 0.37	5.00 ± 0.29	This work	
M–N(O·)OMR ₃ /2c	SiPh₃	19.40 ± 0.95	11.52 ± 0.58	This work	
M–N(O·)OMR ₃ /2f	GePh ₃	17.37 ± 1.25	9.69 ± 0.76	This work	
M–N(O·)OMR ₃ /2g	SnBu₃	6.96 ± 0.15	4.42 ± 0.10	This work	
Me ₃ C–N(O·)OMR ₃	SiPh₃	18.80 ± 0.92	11.13 ± 0.64	Ref. [13]	
$Me_3C-N(O \cdot)OMR_3$	GePh ₃	17.86 ± 0.72	9.86 ± 0.48	Ref. [13]	
$Me_3C-N(O \cdot)OMR_3$	SnBu₃	8.11 ± 0.56	5.58 ± 0.36	Ref. [13]	
Residues D and M as defined in Scheme 7.					

dissociation energy difference of $2.7 \text{ kcal mol}^{-1}$ having been estimated for Me₃C-H (93.9 kcal mol⁻¹) and Me₂HC-H $(96.3 \text{ kcal mol}^{-1})$.^[23] In principle, one might infer that the C-N bond cleavage of oxynitroxides 1c, f and g would lead to a radical fragment featuring a carbonyl group adjacent to the radical center. As shown in the left-hand side of Scheme 3, this may result in resonance stabilization and hence in lowerthan-expected fragmentation activation energy values, similar to those measured for the processes leading to a tert-alkyl radical. While this may appear a sensible proposition, it has to be stressed that for the decay of radicals **2c**, **f** and **q**, activation energy values almost equal to those determined for 1c, f and g were obtained, which collides with the lack of resonance stabilization in the radicals from the former derivatives. At this moment, we are therefore unable to offer a clear-cut explanation to account for the similarity of the activation energy values of fragmentations of oxynitroxides leading to sec-alkyl and tert-alkyl radicals.

A further point that cannot go unnoticed is provided by the frequency factor values found for the decay of oxynitroxides **1g** and **2g**, values unusually small for unimolecular reactions. Similar values have been found when the apparent rate constant for decay contains the monomer–dimer equilibrium constant, and it might not be by chance that a similar effect was also observed previously also for the decay of the Me₃CN(O·)OSnBu₃ oxynitroxide.^[13] To check this possibility, temperature jump experiments were carried out during the decay of **1g** and **2g**, but no effects were observed in the available temperature range.

Experimental

Reagents

3-Nitro-2-pentanone (1) was prepared as described in the literature^[24] from 3-nitro-2-pentanol (2) that was commercially available (Columbia Chemicals, USA), as were triethylsilane, triphenylsilane, tris(trimethylsilyl)silane, triphenylgermanium hydride, bis(tributyltin), bis(triphenyltin), di-*tert*-butylperoxide (the Sigma-Aldrich Group, USA) and bis(triphenyllead) (Strem Chemicals, Inc., USA), while bis(cyclohexyllead) was a gift from the Inorganic Chemistry group at Sussex University, UK.

Apparatus and procedures

Electron paramagnetic resonance spectra were recorded by means of an upgraded ER200D/ESP 300 Bruker spectrometer operating in the X-band (~9.3 GHz) and equipped with a

dedicated data station for the acquisition and manipulation of the spectra, an NMR-Gaussmeter for the calibration of the magnetic field and a Systron-Donner frequency counter for the determination of *g*-factors that were corrected with respect to that of perylene radical cation in concentrated sulfuric acid $(g = 2.0025_8)$.^[25] The temperature of the sample was controlled through a standard variable temperature accessory and monitored with a chromel–alumel thermocouple inserted inside the sample tube. During photolysis, the unfiltered light from a 200-W Hg–Xe lamp (Hamamatsu LC8-06) was focused on the spectrometer cavity by means of a fused silica light guide.

In a typical experiment, $200 \,\mu$ I of a benzene solution of the substrate (~ 10^{-3} M), the radical precursor (~ 10^{-2} M) and di-*tert*-butylperoxide (~ 10^{-3} M, if needed) was thoroughly degassed in a quartz sample tube (i.d. 4 mm) that was subsequently inserted inside the EPR cavity. In the decay kinetics experiments, after choosing the field value corresponding to the top of a 'clean' spectral line, the irradiation was switched off, and the decrease of the signal was followed operating the spectrometers in the time-sweep mode.

When not straightforward, the interpretation of the EPR spectra was based on computer simulations obtained through the use of a custom-made simulation program based on a Monte Carlo self-minimization procedure.^[26]

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