

## Radical Addition to Aromatic Aldoximes

Loris Grossi, Lodovico Lunazzi, and Giuseppe Placucci \*

*Istituto di Chimica Organica, Università, Viale Risorgimento 4, 40136 Bologna, Italy*

The e.s.r. spectra of the hydronitroxide radicals  $\text{ArCHX-NH}\dot{\text{O}}$ , obtained by reaction of a number of aromatic aldoximes  $\text{ArCH=NOH}$  ( $\text{Ar}$  = phenyl, 3- and 4-pyridyl, 2- and 3-thienyl, 2-furyl) with radicals  $\text{X}^\cdot$  ( $\text{X}$  = MeS,  $\text{Bu}^n\text{S}$ ,  $\text{Et}_3\text{Si}$ ,  $\text{Ph}_3\text{Ge}$ ), have been detected. Assignment of the  $\alpha$ - and  $\beta$ -proton splittings has been achieved by means of deuterium labelling. The analysis of the hyperfine splittings supports the hypothesis that the radicals  $\text{ArCH(SR)-NH}\dot{\text{O}}$  adopt a single preferred conformation whereas the radicals  $\text{ArCH(SiEt}_3\text{)-NH}\dot{\text{O}}$  and  $\text{ArCH(GePh}_3\text{)-NH}\dot{\text{O}}$  undergo a rotational pathway through a variety of torsional conformers.

Oximes can give iminoxyl radicals detectable by e.s.r. spectroscopy when oxidized with cerium salts<sup>1-3</sup> or lead tetracetate.<sup>4,5</sup> They also undergo hydrogen abstraction when treated with  $\text{Bu}^t\text{OOBu}^t$ <sup>3,6</sup> or when irradiated with  $\gamma$ -rays.<sup>7</sup> Addition of radicals  $\text{Y}^\cdot$  ( $\text{Y}$  = OH,  $\text{NH}_2$ ,  $\text{CH}_2\text{OH}$ ,  $\text{O}_2\text{H}$ ,  $\text{CO}_2^-$ ) to aliphatic oximes has been reported to yield, in aqueous solutions, short-lived hydronitroxide radicals of structure  $\text{Y}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{NH}-\dot{\text{O}}$ .<sup>8-10</sup> Analogous additions to aromatic oximes were not observed.<sup>10</sup> Additions of photolytically generated radicals in organic solvents have not been reported in the case of oximes. The only exception seems to be the observation of Ingold *et al.* who, in producing iminoxyl radicals by hydrogen abstraction from oximes, identified a 'secondary' radical.<sup>3</sup> To this radical the structure  $\text{Bu}^t\text{O}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{NH}\dot{\text{O}}$  was attributed. The radical was believed to be the result of the addition of  $\text{Bu}^t\text{O}^\cdot$  to aliphatic oximes.

### Results and Discussion

We report here that, contrary to what is generally believed, a number of radicals generated by photolysis in organic solvents add to aromatic oximes and that the initial adducts subsequently rearrange similarly to their aliphatic counterparts.

The reaction scheme has been represented<sup>3,8-10</sup> as (1). However, the second step in (1) is rather unlikely since no authentic 1,2 hydrogen-atom transfer has been shown to occur in aprotic organic solvents, although a few formal 1,2 hydrogen migrations have been observed in aqueous systems.<sup>11</sup> It is thus possible that the process is intermolecular rather than intramolecular, *via* a radical-molecule reaction of type (2).

Attempts to generate these nitroxides thermally in our solvent (using  $\text{Bu}^t\text{ONNOBu}^t$  as a source of  $\text{Bu}^t\text{O}^\cdot$  to produce  $\text{X}^\cdot = \text{Et}_3\text{Si}^\cdot$  from  $\text{Et}_3\text{SiH}$ ) failed in that no radical was detected.

The e.s.r. spectrum of the resulting hydronitroxide radicals shows three hyperfine splitting (h.f.s.) constants, one due to a nitrogen atom and two others due to the hydrogens in positions  $\alpha$  and  $\beta$  to the nitrogen atom. We were able to add to many aromatic oximes radicals centred on sulphur, silicon, and

germanium, whereas radicals centred on carbon or tin failed to produce the corresponding hydronitroxides under the same conditions.

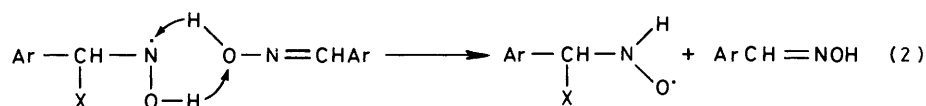
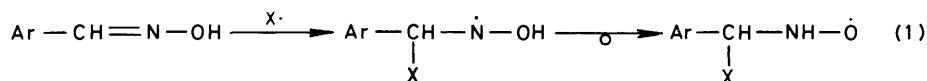
The radicals  $\text{X}^\cdot$  were produced according to reactions (3)–(7). Oximes (1)–(8) were selected for study. The hydronitroxide radicals  $\text{Ar-CHX-NH}\dot{\text{O}}$  produced are indicated in Table 1.

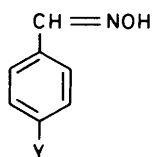
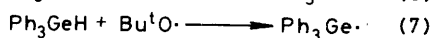
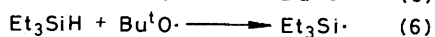
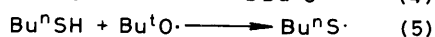
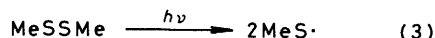
It is interesting to observe that when the methylthiyl radical ( $\text{MeS}^\cdot$ ) is produced by the conventional reaction (3), addition occurs only with acetoxime ( $\text{MeCH=NOH}$ ) or with benzaldoxime (1) to give (9;  $\text{X} = \text{MeS}$ ). On the other hand, reaction (5) is much more efficient and allows the detection of all the sulphur-containing hydronitroxides in the series investigated [(9)–(16) ( $\text{X} = \text{Bu}^n\text{S}$ )]. Attempts to add  $\text{Bu}^t\text{S}^\cdot$  and  $\text{PhS}^\cdot$  radicals starting from the corresponding thiols were unsuccessful.

When the sulphur-containing hydronitroxides  $\text{Ar-CH(SR)-NH}\dot{\text{O}}$  ( $\text{R} = \text{Me}$ ,  $\text{Bu}^n$ ) are produced either with reaction (3) or (5), a secondary radical is also observed in the e.s.r. spectrum. This radical, depending on the conditions, can even become more intense than the primary one. The corresponding spectrum consists of six lines of equal intensity with  $a_N$  ca. 16 and  $a_H$  ca. 3 G which are almost independent of the aromatic oxime employed. It might be that  $\text{RS}^\cdot$  behaves in a way similar to that reported<sup>3</sup> for  $\text{Bu}^t\text{O}^\cdot$  toward aliphatic oximes. In other words, once the first radical is formed, the secondary reaction would proceed according to pathway (8).

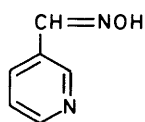
This structure would explain the presence of only one small  $a_H$  splitting in the e.s.r. spectrum; furthermore, the  $a_N$  value (16 G) is larger than for the hydronitroxides reported in this work but lower than in alkyl alkoxy nitroxides.<sup>3,12a</sup> Electronegative substituents bonded to nitrogen (like OR and F) greatly enhance the  $a_N$  values of nitroxides:<sup>12a</sup> since sulphur is less electronegative than oxygen this enhancement will be reduced. The  $a_N$  value of 16 G should be compared, for instance, with the value (17 G)<sup>12b</sup> of  $\text{RSN}(\text{Bu}^t)\text{O}^\cdot$  and the value of 14 G (see Table 2) observed in nitroxides  $\text{PhCH(SR)-N}(\text{Bu}^t)\dot{\text{O}}$  (17) and (18) obtained by addition of  $\text{RS}^\cdot$  *via* reaction (3) or (5) to the nitrone  $\text{Ph-CH=N}(\text{Bu}^t)\text{O}^-$ .

Inspection of Table 1 shows that, in the radicals formed by addition of  $\text{Et}_3\text{Si}^\cdot$  and  $\text{Ph}_3\text{Ge}^\cdot$ , the smaller  $a_H$  splitting has

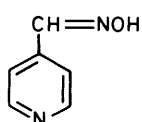




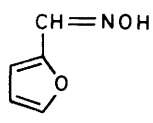
- (1) Y = H  
(2) Y = Me  
(3) Y = MeO



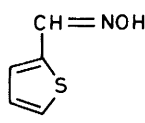
(4)



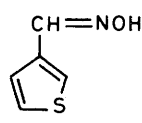
(5)



(6)



(7)



(8)

been assigned to  $H_\alpha$  and the larger to  $H_\beta$  with the exception of (12) and (13) that contain the pyridyl ring. This follows from a number of deuterium-labelling experiments carried out on oximes (1), (5), (6), and (8). The OH hydrogen of these oximes was replaced by deuterium and the spectra of the labelled hydronitroxides derived from  $\text{ArCH}=\text{NOD}$  were observed. The disappearance of the smaller  $a_H$  splitting (a doublet) and the appearance of a 1:1:1 triplet with splitting reduced by a factor of 6.5 indicates that in (9), (14), and (16) ( $X = \text{Et}_3\text{Si}$ ) as well as in the  $\text{Ph}_3\text{Ge}$  analogues the hydrogen in the  $\alpha$ -position has the smaller splitting whereas in (13;  $X = \text{Et}_3\text{Si}$  and  $\text{Ph}_3\text{Ge}$ ) it has the larger splitting. The same assignment was used for the other radicals that have very similar splittings. The Figure shows a typical spectrum, due to a mixture of  $\text{PhCH}(\text{GePh}_3)\text{-NH}\dot{\text{O}}$  and  $\text{PhCH}(\text{GePh}_3)\text{-ND}\dot{\text{O}}$ . This type of assignment parallels that reported for some aliphatic hydronitroxides.<sup>13</sup>

The h.f.s. constants of Table 1 also show that the sulphur-containing hydronitroxides (9)–(16) ( $X = \text{Bu}^n\text{S}$ ) have much smaller  $H_\beta$  splittings than those containing silicon ( $X = \text{Et}_3\text{Si}$ ) or germanium ( $X = \text{Ph}_3\text{Ge}$ ). This was verified by deuterium labelling of radical (9;  $X = \text{Bu}^n\text{S}$ ). Such a large reduction in the  $H_\beta$  splitting is a clear indication that the sulphur-containing radicals have different conformational behaviour from that of the corresponding silicon- and germanium-containing hydronitroxides. The  $a_{H\beta}$  coupling is known to depend, through the relationship  $a_H = A + B\rho_N\pi\cos^2\theta$ , on the dihedral angle  $\theta$  between the CH bond and the direction of the  $p$ -orbital bearing the unpaired electron.<sup>12,14,15</sup> Therefore, the angle  $\theta$  defined as above should be larger in these sulphur-containing radicals than in the silicon and germanium analogues. This trend actually parallels that observed in carbon-centred radicals.<sup>16,20</sup>

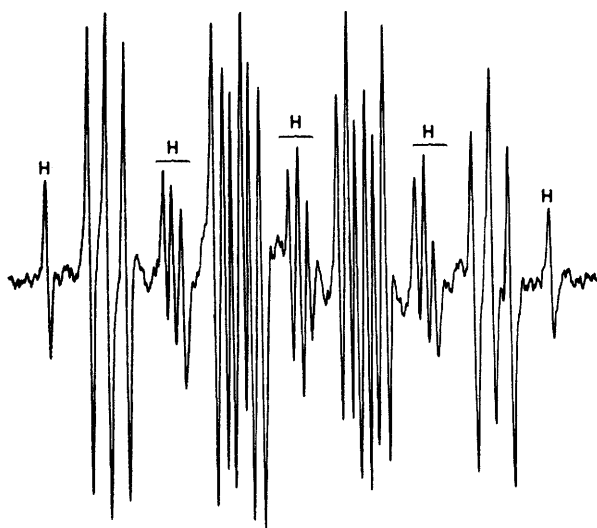
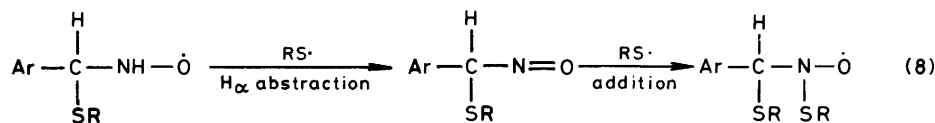
In the case of aliphatic hydronitroxides containing a secondary alkyl substituent on nitrogen (*e.g.*  $\text{Me}_2\text{CH-NH}\dot{\text{O}}$ ) it was suggested that there is free rotation about the C-N bond since the  $a_{\text{CH}}$  splitting<sup>12</sup> is very close to the  $a_{\text{Me}}$  value of  $\text{CH}_3\text{NH}\dot{\text{O}}$ .<sup>12</sup>

To check whether the radicals under investigation also behave in the same way, nitroxides of general formula

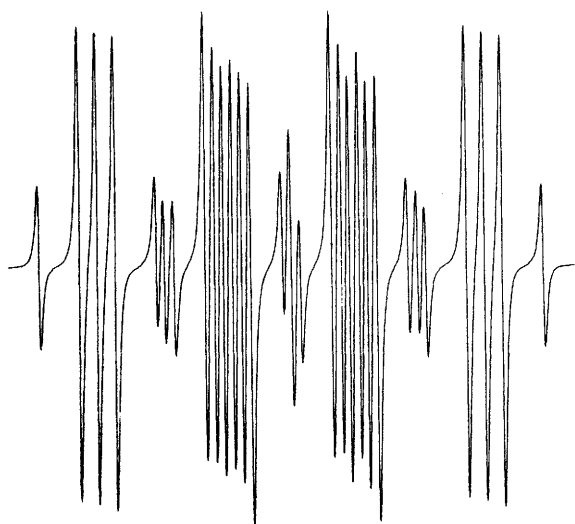
Table 1. Room-temperature hyperfine splitting constants (G) of  $\text{ArCH(X)NH}\dot{\text{O}}$  in benzene

Radical	X	$a_{H\alpha}$	$a_{H\beta}$	$a_N$	$a_{H(\text{SR})}$
 (9)	MeS	11.6	6.7	12.9	0.5 (3 H)
	Bu <sup>n</sup> S	11.5	6.55	12.9	0.5 (2 H)
	Et <sub>3</sub> Si	12.15	14.8	13.45	
	Ph <sub>3</sub> Ge	12.25	14.1	13.1	
 (10)	Bu <sup>n</sup> S	11.25	6.25	12.6	0.5 (2 H)
	Et <sub>3</sub> Si	12.1	14.75	13.4	
	Ph <sub>3</sub> Ge	11.75	13.75	13.0	
 (11)	Bu <sup>n</sup> S	11.05	6.25	12.6	0.5 (2 H)
	Et <sub>3</sub> Si	12.15	15.1	13.5	
	Ph <sub>3</sub> Ge	11.9	13.75	13.0	
 (12)	Bu <sup>n</sup> S	10.75	6.6	12.25	0.5 (2 H)
	Et <sub>3</sub> Si	11.25	10.25	13.0	
	Ph <sub>3</sub> Ge	11.5	10.5	12.75	
 (13)	Bu <sup>n</sup> S	10.9	6.6	12.25	0.5 (2 H)
	Et <sub>3</sub> Si	11.6	9.75	13.0	
	Ph <sub>3</sub> Ge	11.6	9.6	12.5	
 (14)	Bu <sup>n</sup> S	10.0	5.5	12.1	0.5 (2 H)
	Et <sub>3</sub> Si	11.6	14.5	13.25	
	Ph <sub>3</sub> Ge	11.5	13.0	13.0	
 (15)	Bu <sup>n</sup> S	10.5	5.25	12.5	0.5 (2 H)
	Et <sub>3</sub> Si	11.25	13.5	13.5	
	Ph <sub>3</sub> Ge	11.5	12.25	13.0	
 (16)	Bu <sup>n</sup> S	10.9	5.5	12.5	0.6 (2 H)
	Et <sub>3</sub> Si	11.75	13.4	13.4	
	Ph <sub>3</sub> Ge	11.75	12.5	13.1	

$\text{PhCHX-N}(\text{Bu}^t)\dot{\text{O}}$  (19) and (20) were prepared by means of reactions (6) and (7) using the nitron  $\text{Ph-CH=N}(\text{Bu}^t)\text{O}^-$ . As reported in Table 2 the nitroxides (19) and (20) do have a



Ph-CH(GePh<sub>3</sub>)-ND $\dot{\text{O}}$  20 G



Experimental and computer-simulated spectrum of PhCH(GePh<sub>3</sub>)-ND $\dot{\text{O}}$ . Since deuteration was not complete, the lines marked with H are those of the spectrum of the unlabelled radical (ca. 18%)

much smaller  $H_\beta$  splitting than the corresponding hydronitroxides (9; X = Et<sub>3</sub>Si and Ph<sub>3</sub>Ge). Since the presence of the bulky *t*-butyl group is likely to force the radicals (19) and (20) into a single conformation,<sup>21</sup> the large value of the  $H_\beta$  splitting in (9; X = Et<sub>3</sub>Si and Ph<sub>3</sub>Ge) similar to that in the freely rotating Me<sub>2</sub>CH-NH $\dot{\text{O}}$  seems to indicate that the unhindered hydronitroxides containing the silicon and germanium groups also approach free rotation. However, owing to the presence of quite large substituents like Ar-CH-SiEt<sub>3</sub> and Ar-CH-GePh<sub>3</sub>, it seems unlikely that the motion about the CH-N bond can be called, as in the case of Me<sub>2</sub>CH-NH $\dot{\text{O}}$ ,

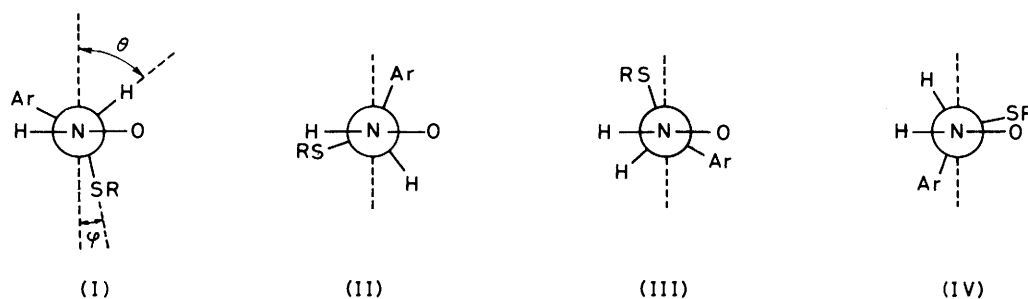
Table 2. Hyperfine splitting constants (G) in benzene for the room-temperature e.s.r. spectra of nitroxides (17)–(20) of general formula Ph-CH(X)-N(Bu') $\dot{\text{O}}$

Radical	X	$a_N$	$a_{H\beta}$	$a_{H(SR)}$
(17)	MeS	14.1	2.2	0.6 (3 H)
(18)	Bu <sup>n</sup> S	13.9	2.1	
(19)	Et <sub>3</sub> Si	14.6	5.5	
(20)	Ph <sub>3</sub> Ge	14.5	5.5	

free rotation. The  $H_\beta$  constants of (9; X = Et<sub>3</sub>Si and Ph<sub>3</sub>Ge) decrease, in fact, on raising the temperature and approach the value<sup>12</sup> of CH<sub>3</sub>-NH $\dot{\text{O}}$  which is freely rotating. Thus we feel it would be more appropriate to consider it a motion between a definite number of relatively stable rotamers: the large  $a_{H\beta}$  values should thus be the weighted average of the  $H_\beta$  splittings of all these conformers. In fact, not only are the  $\beta$ -splittings of the radicals containing the bulkier Ph<sub>3</sub>Ge group lower than those containing the Et<sub>3</sub>Si group but a reduction in the  $\beta$ -splitting of (9; X = Et<sub>3</sub>Si) is also obtained if the bulkier Ph<sub>3</sub>Si is substituted for Et<sub>3</sub>Si. In fact, the hydronitroxide PhCH(SiPh<sub>3</sub>)-NH $\dot{\text{O}}$  has  $a_N$  13.2,  $a_{H_\alpha}$  12.1, and  $a_{H\beta}$  13.2 G. In other words, the bulkier substituents are expected to modify the relative populations of the various rotamers contributing to the  $H_\beta$  splitting. Accordingly,  $a_N$  and  $a_{H_\alpha}$  are only slightly affected in PhCH(SiPh<sub>3</sub>)-NH $\dot{\text{O}}$  relative to the corresponding PhCH(SiEt<sub>3</sub>)-NH $\dot{\text{O}}$  whereas  $a_{H\beta}$  varies more considerably.

As mentioned before, the hydronitroxides (9)–(16) (X = Bu<sup>n</sup>S) containing sulphur have  $H_\beta$  splittings much smaller than the corresponding radicals containing silicon and germanium (see Table 1). Actually, their  $H_\beta$  values are similar to those of the hindered nitroxides (19) and (20). This supports the hypothesis that hydronitroxides with an SR group in the  $\beta$ -position stay in a single, preferred conformation probably because of possible interactions between the electron lone pair on sulphur and the unpaired electron of the NH $\dot{\text{O}}$  moiety. However, a reliable determination of the value of the angle  $\theta$  in the hydronitroxides with X = Bu<sup>n</sup>S cannot be achieved for many reasons. In particular, the spin density on the nitrogen ( $\rho_N^{\cdot}$ ) cannot be accurately determined: its value depends, among other things, on the geometry at the nitrogen atom, *i.e.* how large is its deviation from planarity.<sup>14,15,22</sup> Furthermore, the value of the term B also depends on the type of the heteroatom X in the  $\beta$ -position which is expected to be smaller<sup>16</sup> for sulphur than for silicon. Accordingly, only a qualitative estimate of the conformational preference can be made in the present case. Owing to the asymmetry of these radicals there are, in principle, four possible stable conformers (I)–(IV) for a given  $\theta$  value.

Since the experimental  $H_\beta$  splitting is quite low and since it is known<sup>17,18,23</sup> that second-row elements prefer an eclipsed conformation (the dihedral angle  $\varphi$  between the C-S bond and the  $p_z$  orbital of the unpaired electron is approximately zero) the most likely conformation should be either (I) or (III). In view of the larger size of oxygen than hydrogen, rotamer (I), with Ar close to hydrogen, seems the most likely conformer. This agrees with the observation that when the hydrogen of the NHO moiety is replaced by a bulky *t*-butyl group, as in



Scheme.

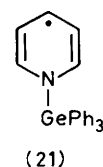
PhCH(SR)-N(Bu')O (17) and (18), the  $H_\beta$  splitting is further reduced (Table 2). In conformer (I) of the Scheme, in fact, substitution of the hydrogen atom bonded to N with Bu' is expected to push away the Ar group favouring now conformer (III) rather than (I). Also the angle  $\phi$  will be reduced and the angle  $\theta$  increased: as a consequence, the value of the  $H_\beta$  splitting will be lowered.

The silicon- and germanium-containing radicals have a quite large variation of  $a_{H\beta}$  when the aromatic substituent is a pyridine ring (see Table 1). Such a reduction of the  $H_\beta$  splitting does not seem to depend on electronic effects since substituents in the *para*-position of the phenyl ring do not affect the  $H_\beta$  values.\* Moreover, the low value of the  $H_\beta$  splitting is the same in the 3- and 4-pyridyl-containing radicals despite the different electronic properties expected for the two situations. This fact seems indicative of a conformational change induced by interactions with the medium.

The pyridine ring is far more basic than all the other aromatic substituents examined in this series and the excess of unchanged oxime containing the pyridine ring could interact with the hydrogen of the NHO moiety of the radical. If this interaction occurs, the rotational behaviour of NHO in the silicon- and germanium-containing radicals could be affected in that the relative populations of the rotamers would be modified. As a consequence the average  $H_\beta$  splitting could be substantially changed as observed in radicals (12) and (13) (X = Et<sub>3</sub>Si and Ph<sub>3</sub>Ge). To check that the source of this modification is the presence of the basic pyridine ring, we added a certain amount of pyridine to the solution containing radical (9; X = Et<sub>3</sub>Si). Indeed, the  $H_\beta$  value was dramatically reduced (from 14.8 to 12 G) whereas the other splittings were almost unaffected. The same happened when pyridine was added to radical (16; X = Et<sub>3</sub>Si) ( $H_\beta$  changed from 13.4 to 11.7 G). On the other hand, when pyridine was added to radical (12; X = Et<sub>3</sub>Si) which already possesses a pyridyl moiety, no effect on  $H_\beta$  was detected.

It should also be mentioned that in radicals (12; X = Et<sub>3</sub>Si and Ph<sub>3</sub>Ge) the  $H_\beta$  splitting increased on raising the temperature whereas  $a_N$  and  $a_{H\alpha}$  were constant. This is consistent with the proposed interaction between NHO and the basic nitrogen of pyridine since the latter will certainly be reduced at higher temperatures.

Further support for this interpretation comes from the observation that the  $H_\beta$  splittings of sulphur-containing



radicals are not affected by the pyridyl moiety. In fact, radicals (12) and (13) (X = Bu<sup>n</sup>S) have  $H_\beta$  splittings very close to that of the corresponding benzene derivative (9; X = Bu<sup>n</sup>S). Since these sulphur-containing radicals are already in a single preferred conformation, it is obviously impossible to modify their rotational behaviour. As a consequence, even when pyridine is added to radical (9; X = Bu<sup>n</sup>S), no appreciable change of  $H_\beta$  is observed in contrast to what happens when pyridine is added to (9; X = Et<sub>3</sub>Si).

The effect of the introduction of a basic compound like pyridine upon the  $H_\beta$  values further supports the conclusion that in sulphur-containing hydronitroxides NHO prefers to stay in a single conformation contrary to the silicon- and germanium-containing hydronitroxides.

### Experimental

Most of the oximes were commercially available and were crystallized or distilled before use. The others were prepared from the corresponding aldehydes by standard methods.<sup>25</sup> The deuteriated oximes, when solids, were obtained by dissolving the compound in MeOD. After 1 h the deuteriated solvent was pumped away. In the case of (1) (a liquid), the reaction was carried out with D<sub>2</sub>O that was then absorbed on sodium sulphate. The filtered liquid was used without further purification. The samples for the e.s.r. studies were prepared by using a saturated solution of the proper oxime in benzene (in some cases *t*-butylbenzene was used) to which were added the required reactants.

The mixtures were inserted into Suprasil quartz tubes and were thoroughly degassed with nitrogen. They were then irradiated in the e.s.r. cavity with a 500 W mercury lamp. The  $g$  values for all the radicals containing the SR moiety were  $2.0067 \pm 0.0001$  and for all the radicals containing silicon and germanium  $2.0063 \pm 0.0003$ .

It is also worth mentioning that we failed to obtain radical (12; X = Ph<sub>3</sub>Ge) in the presence of pyridine. In fact, Ph<sub>3</sub>Ge<sup>•</sup> prefers to react under these conditions with the nitrogen of pyridine itself to give (21),  $a_N$  5.1,  $a_{H-2,6}$  6.25,  $a_{H-3,5}$  1.1;  $a_{H-4}$  11.1 G.

### Acknowledgements

We thank Drs. K. U. Ingold, N.R.C., Ottawa, and P. J. Krusic, Dupont, Wilmington, for helpful comments. A grant from the Ministry of Public Education, Rome, is gratefully acknowledged.

\* Attempts to measure the  $H_\beta$  value in a *para*-nitro derivative (in particular 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-CH=NH-O) failed, in that the hydro-

nitroxide radical could not be obtained. In fact, when the NO<sub>2</sub> group is present, addition of Et<sub>3</sub>Si<sup>•</sup> occurs at the nitro-group<sup>24</sup> rather than to the double bond of the oxime thus generating the radical 4-Et<sub>3</sub>SiO-N-C<sub>6</sub>H<sub>4</sub>CH=NOH.

## References

- 1 J. R. Thomas, *J. Am. Chem. Soc.*, 1964, **86**, 1446.
- 2 W. M. Fox and W. A. Waters, *J. Chem. Soc.*, 1965, 4628.
- 3 J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *J. Am. Chem. Soc.*, 1972, **94**, 7040.
- 4 H. Lemaire and A. Rassat, *Tetrahedron Lett.*, 1964, 2245; M. Bethoux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 1964, 1985; B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. B*, 1966, 86, 722; 1967, 981; 1968, 123.
- 5 J. J. Zeilstra and J. B. F. N. Engberts, *Tetrahedron*, 1973, **29**, 4299.
- 6 A. Alberti, G. Barbaro, A. Battaglia, M. Guerra, F. Bernardi, A. Dondoni, and G. F. Pedulli, *J. Org. Chem.*, 1981, **46**, 742.
- 7 W. M. Fox and M. C. R. Symons, *J. Chem. Soc. A*, 1966, 1503.
- 8 J. Q. Adams, *J. Am. Chem. Soc.*, 1967, **89**, 6022.
- 9 D. J. Edge and R. O. C. Norman, *J. Chem. Soc. B*, 1969, 182; 1970, 1083.
- 10 P. Smith and W. M. Fox, *Can. J. Chem.*, 1969, **47**, 2227.
- 11 A. L. J. Beckwith and K. U. Ingold in 'Rearrangements in Ground and Excited States' in 'Free Radical Rearrangement,' ed. P. de Mayo, Academic Press, New York, 1980, p. 162.
- 12 (a) E. G. Jenzen in 'Topics in Stereochemistry,' eds. E. Eliel and N. Allinger, Wiley, New York, 1971, vol. 6, p. 177; (b) I. H. Leaver and G. C. Ramsay, *Tetrahedron*, 1969, **25**, 5669; R. G. Gasanov, R. G. Petrova, and R. Kh. Freidlina, *Dokl. Chem. (Engl. Transl.)*, 1976, **227**, 264; J. R. Bolton, K. S. Chen, A. H. Lawrence, and P. de Mayo, *J. Am. Chem. Soc.*, 1975, **97**, 1832.
- 13 Th. A. J. W. Wajer, A. Mackor, and Th. J. De Boer, *Tetrahedron*, 1969, **25**, 175.
- 14 J. Donady, Y. Ellinger, A. Rassat, R. Subra, and G. Berthier, *Mol. Phys.*, 1969, **17**, 217.
- 15 Y. Ellinger, R. Subra, A. Rassat, J. Donady, and G. Berthier, *J. Am. Chem. Soc.*, 1975, **97**, 476.
- 16 L. Lunazzi, G. Placucci, L. Grossi, and M. Guerra, *J. Chem. Soc., Perkin Trans. 2*, 1982, 43.
- 17 J. K. Kochi and P. J. Krusic 'Essay in Free Radical Chemistry,' Chem. Soc. Special Publication, 1971, vol. 24, p. 147.
- 18 P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1971, **93**, 846.
- 19 T. Kawamura, P. Meakin, and J. K. Kochi, *J. Am. Chem. Soc.*, 1972, **94**, 8065.
- 20 L. Lunazzi, G. Placucci, and L. Grossi, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1761; 1981, 703.
- 21 H. Chandra, I. M. T. Davidson, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1353.
- 22 C. Chatgililoglu and K. U. Ingold, *Can. J. Chem.*, 1981, **59**, 1745.
- 23 K. S. Chen and J. K. Kochi, *J. Am. Chem. Soc.*, 1974, **96**, 1383; D. Griller and K. U. Ingold, *ibid.*, p. 6715; J. K. Kochi, in 'Advances in Free-radical Chemistry,' ed. G. H. Williams, Elek Science, London, 1975, vol. 5, ch. 4, p. 189; I. C. Scaiano and K. U. Ingold, *J. Phys. Chem.*, 1976, **80**, 275.
- 24 L. Lunazzi, G. Placucci, and N. Ronchi, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1132; C. M. Camaggi, L. Lunazzi, and G. Placucci, *J. Org. Chem.*, 1974, **39**, 2425; C. M. Camaggi, L. Lunazzi, G. Pedulli, G. Placucci, and M. Tiecco, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1126.
- 25 A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' Longman Green and Co., London, 3rd. edn., pp. 341 and 346.

Received 1st February 1983; Paper 3/148