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AN ELECTRON SPIN RESONANCE STUDY OF AZA-ALLYL RADICALS

DEREK C. NONHEBEL,*
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland

and

JOHN C. WALTON
Department of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, Scotland

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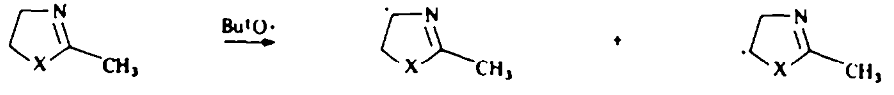
Abstract - The ESR spectrum of the 2-aza-allyl radical, $Me_2C\text{=}\dot{N}\text{=}CMe_2$, has been recorded. A series of 1-aza-allyl radicals have been generated by reaction of 2-alkyl-4,4-dimethyloxazolines with t-butoxyl radicals and their ESR spectra studied. In this reaction 2-alkyl-4,4-dimethyloxazolin-5-yl radicals are also formed.

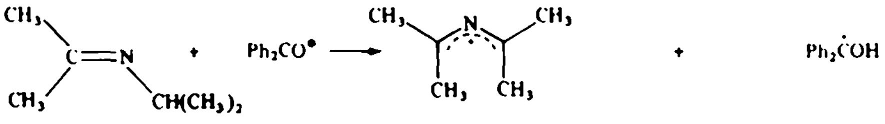
The radicals (**2a** and **2b**) derived from 2-methyloxazoline (**1a**) and 2-methylthiazoline (**1b**) are the only reported examples of simple 2-aza-allyl radicals which have been studied by ESR spectroscopy.[1] These radicals are produced together with the isomeric radicals (**3**) from the reactions of the parent heterocyclic compounds with t-butoxyl radicals.

There are no reports of the study of acyclic analogues of this class of radical by ESR spectroscopy though the radical (**5**) has been postulated in the photolytic reaction of isopropylideneisopropylamine (**4**) with benzophenone to yield 2,2,4,4-tetramethyl-5,5-diphenyloxazolidine.[2]



1 **2** **3**

a X = O
b X = S



4 **5**

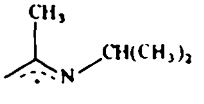
1-Aza-allyl radicals,

$$R_2C\text{=}CH\text{—}\dot{N}R' \leftrightarrow R_2\dot{C}\text{—}CH\text{=}NR$$

have not been reported either as reaction intermediates nor have they been the subject of ESR studies. In this paper we report an ESR study of both 1- and 2-aza-allyl radicals.

The ESR spectrum of the radical generated from reaction of isopropylideneisopropylamine (**4**) with t-butoxyl radicals appears to be a tridecet of 1 : 1 : 1 triplets [a(12H) = 1.22 and a(N) = 0.14 mT] though the outer two sets of lines on each side of the supposed tridecet were too weak for detection. The observed signals had the expected binomial intensities for a tridecet. This spectrum is compatible with it being due to the 2-aza-allyl radical (**5**) and it clearly cannot be assigned to the 1-aza-allyl radical (**6**) which could also be derived from **4**.

The equivalence of the protons in the four Me groups parallels the situation observed in ESR studies of 2-substituted 1,1,3,3-tetramethylallyl radicals (**7**).[3] The results in that instance were interpreted as indicating that the radicals were twisted because of the steric repulsion of the *endo*-Me groups. The proton coupling constants of **5** were very similar to those of a range of 2-substituted 1,1,3,3-tetramethylallyl radicals [a(12H) = 1.21–1.33 mT].[3] It thus seems that the aza-allyl radical (**5**) is also non-planar. The detection of this radical lends support to the proposal of it being an intermediate in the reaction of **4** and benzophenone. This is the first report of the detection of an acyclic 2-aza-allyl radical.



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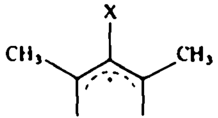

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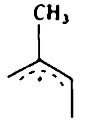
It is interesting to note that none of the isomeric 1-aza-allyl radical (**6**) could be detected even though any deviation from planarity in this species would be expected to be minimal and hence this radical might have been expected to be generated in preference to **5**. Reaction of 2,4-dimethylpent-2-ene with t-butoxyl radicals was reported to give a mixture of *endo*- and *exo*-1-isopropyl-2-methylallyl radicals (**8** and **9**): none of the 1,1,3,3-tetramethylallyl radical was detected. It is also relevant to note that none of the 1-aza-allyl radicals (**10a** and **10b**) could be detected from the reaction of **1** with t-butoxyl radicals.[1] These results would seem to suggest that 2-aza-allyl radicals are formed more readily than 1-aza-allyl radicals.



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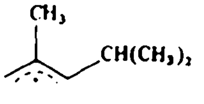

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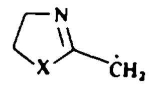

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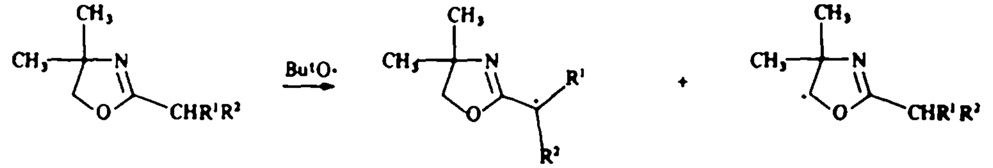
a X = O
b X = S

The magnitude of the nitrogen coupling constant (0.14 mT) in **5** was lower than that in the heterocyclic aza-allyl radicals (**2a** and **2b**) [a(N) = 0.32 and 0.39 mT]. This difference is probably caused by the slight differences in geometry of the two types of radical. There seems to be no reason for not considering **5** as a π-radical. The nitrogen coupling constant of the central nitrogen in the 1,3-dimethyldiazenyl radical, $\mathrm{CH_3N{=}\dot{N}{=}NCH_3}$, a σ-radical, is very much larger [a(N) = 1.15 mT].

We have examined the reactions of a number of imines with t-butoxyl radicals but have been unable to obtain satisfactory ESR spectra in any instance.

We have also examined the reaction of a series of 2-alkyl-4,4-dimethyloxazolines (**11**) with t-butoxyl radicals to see whether it was possible to detect the formation of any 1-aza-allyl radicals (**12**) and, if so, to determine their ESR spectral characteristics. The *gem*-dimethyl group at the 4-position precludes the formation of any 2-aza-allyl radical.



11 **12** **13**

The reaction gave both the 1-aza-allyl radical (**12**) and the 2-alkyl-4,4-dimethyloxazolin-5-yl radical (**13**). The proportion of the 1-aza-allyl radical increased with increasing substitution at the radical centre from 10% ($R^1 = R^2 = H$) to 30% ($R^1 = H$, $R^2 = Me$), and to 60% ($R^1 = R^2 = Me$). Figure 1 records the ESR spectral parameters of the 1-aza-allyl radicals. The assignments are made by analogy with the reported ESR spectrum of the 1,1-dimethylallyl radical for which the couplings of the *endo*-proton and *endo*-Me group are greater than those of the corresponding *exo*-groups.[6] Furthermore in the allylic radical derived from methylene-cyclopentane the coupling constant of the '*endo*' proton (relative to the allylic system) is less than that of the '*exo*' proton.[7] On this basis in the radical derived from 2-ethyl-4,4-dimethyloxazoline, the Me group attached to the radical centre is '*exo*' to the allylic system and the proton is '*endo*'. The magnitude of the nitrogen coupling constant decreases with increasing substitution at the carbon terminus of the allylic system: this could conceivably be as a consequence of decreased spin density at the nitrogen.

Table 1 records the ESR parameters of the 2-substituted 4,4-dimethyloxazolin-5-yl radicals (**13**). They are characterised by a relatively low coupling constant due to the α-proton indicating considerable bending at the radical centre. The magnitude of this coupling constant for the parent 4,4-dimethyloxazolin-5-yl radical shows a negative temperature dependence. The coupling constants to both the α-proton and the nitrogen are very similar to those reported for the radical (**2a**).[1]

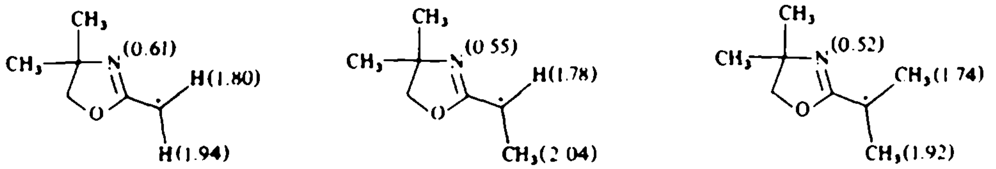
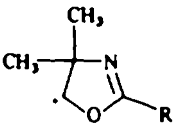


Fig. 1. ESR parameters for 1-aza-alkyl radicals (mT).

Table 1. ESR parameters of 2-substituted 4,4-dimethyloxazolin-5-yl radicals



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	Temperature (K)	Coupling constants (mT)			
		$a(\alpha\text{-H})$	$a(\text{H-1})$	$a(\text{CH}_3)$	$a(\text{N})$
H	220	1.415	0.071	0.058	0.058
H	255	1.406	0.071	0.059	0.059
H	330	1.343	0.071	0.059	0.059
CH_3	250	1.33		0.062	0.062
CH_3CH_2	250	1.33		0.060	0.060
$(CH_3)_2CH$	250	1.32		0.060	0.060

EXPERIMENTAL

ESR spectra were recorded with a Bruker ER200D or a Varian E-104 spectrometer on degassed samples, sealed in spectrosil tubes, photolysed with light from a 500 W high pressure Hg arc. Samples were examined as 10% soln in di-t-butylperoxide.

Isopropylidene isopropylamine

This was prepared by the method of Norton *et al.*[8] purified by distillation through a spinning-band column, b.p. 93° (lit.,[8] 93.5°).

Oxazolines

4,4-Dimethyloxazoline and 2,4,4-trimethyloxazoline were commercial materials and used as supplied. 2-Ethyl- and 2-isopropyl-4,4-dimethyloxazolines were prepared by lit. procedures[9,10] and purified by distillation through a spinning-band column. 2-Ethyl-4,4-dimethyloxazoline had b.p. 129° (lit.,[9] 129–130°) and 2-isopropyl-4,4-dimethyloxazoline, b.p. 137° (lit.,[10] 135–136°).

REFERENCES

[1] L. Grossi, L. Lunazzi and G. Placucci, *Tetrahedron Letters* 251 (1981).

[2] A. A. Baum and L. A. Karnischky, *J. Am. Chem. Soc.* **95**, 3072 (1973).

[3] W. H. Davis and J. K. Kochi, *Tetrahedron Letters* 1761 (1976).

[4] J. K. Kochi, P. J. Krusic and D. R. Eaton, *J. Am. Chem. Soc.* **91**, 1879 (1969).

[5] J. C. Brand and B. P. Roberts, *J. Chem. Soc. Perkin Trans. 2* 1549 (1982).

[6] P. J. Krusic, P. Meakin and B. E. Smart, *J. Am. Chem. Soc.* **96**, 6211 (1974).

[7] L. Lunazzi, G. Placucci and L. Grossi, *J. Chem. Soc. Perkin Trans. 1* 1063 (1980).

[8] D. G. Norton, V. E. Haury, F. C. Davis, L. J. Mitchell and S. A. Ballard, *J. Org. Chem.* **19**, 1054 (1954).

[9] P. Allen and J. Ginos, *J. Org. Chem.* **28**, 2759 (1963).

[10] A. I. Meyers, E. M. Smith and M. S. Ao, *J. Org. Chem.* **38**, 2129 (1973).