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ELECTRON SPIN RESONANCE SPECTRA OF SOME IMINOXY RADICALS[1]. III.

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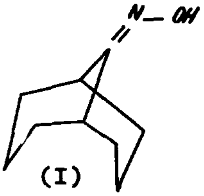
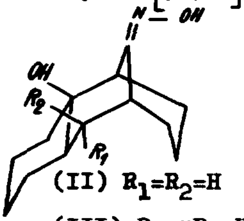
Preceding papers in this series[1,2] have been concerned with the study of the characteristics of σ-type iminoxy radicals $\left({}^{R_1}_{R_2}{>}C{=}N{-}O\right)$ as studied in bicyclic compounds with almost rigid molecular geometry.

It seemed worthwhile to check our previous observations on some derivatives (II, III, IV, V) of 3,4-cyclohexano-bicyclo [3.3.1]nonan-9-one oxime, which resemble the structure of bicyclo [3.3.1] nonan-9-one oxime (I)[1].



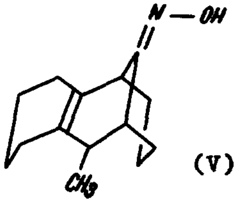
(I)



(II) $R_1=R_2=H$

(III) R_2 or R_1=H; R_1 or R_2=Me,Et,n-Pr,iso-Bu,Furyl

(IV) $(R_1,R_2)= -(CH_2)_5-$



(V)

The radicals were generated in the e.s.r. sample tube by adding 1-2 ml of solvent (benzene, cyclohexane) to the solid oxime-lead tetraacetate mixture. To prevent a rapid evolution of the reacting mixture towards final products, the use of a partly decomposed oxidant (lead tetraacetate) is required.The e.s.r. spectra were recorded on a JES-3B JEOL spectrometer, using X- as well as K-band frequencies. Hyperfine splitting (hfs) constants were measured by comparison with Frémy's salt. The oximes were prepared from the parent ketones by reaction with hydroxylamine[3-5].

The X-band spectra obtained from (II) and (III)[*] are rather complex(fig.1)

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[*] In this case the aspect of the spectrum is independent of the nature of the β-substituent.

due to the overlapping of the spectra of radicals with almost equal g-factors and nitrogen hfs constants. So K-band spectra were necessary in order to resolve these spectra (fig.2). The results are given in Table 1.

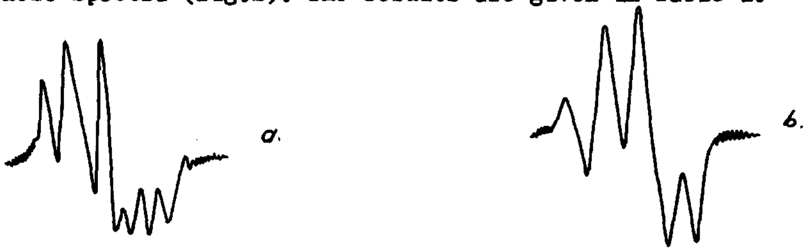


Fig.1 X-band spectra (low-field line of the nitrogen 1:1:1 triplet) of radicals obtained from (a) compound (II) and (b) compound (III)

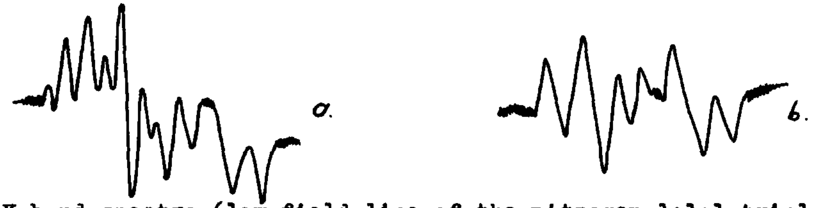


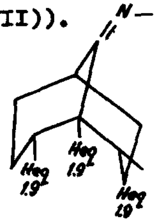
Fig.2 K-band spectra (low-field line of the nitrogen 1:1:1 triplet) of radicals obtained from (a) compound (II) and (b) compound (III)

Table 1

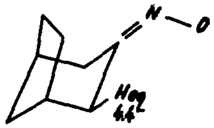
The radical from		a_N	a_H	No.of interacting protons
I		30.2	1.9	3
II	(i)	30.6	1.9	2
	(ii)	30.6	1.8	3
	(iii)	29.9	1.9	2
III	(i)	30.6	1.9	2
	(ii)	29.9	1.9	2
IV		30.6	1.9	2
V		30.6	1.9	2

For a symmetrical molecule, eg.(I), a single iminoxy radical is possible; it shows interaction with three equivalent protons (a_N 30.2; a_H 1.9 gauss) and as previously reported[1] is assigned structure (VI).The interacting protons are the equatorial ones in the α -(bridgehead) and β -positions, lying cis to the iminoxy group oxygen ; the 1.9 gauss hfs constant of the bridgehead proton is only about half of that reported by Gilbert and Norman[6] for a similar α-proton (a_H 4.4 gauss) on a secondary C-atom (see the nonflipping cyclohexanone oxime (VII)).

(VI)



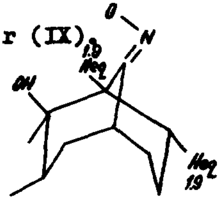
(VII)



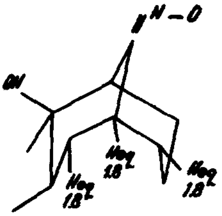
In our compounds the two isomers of iminoxy group are different because of moleculer asymmetry and the assignments we produce take account of this possibility.

By analogy with (VI), of the three radicals obtained from (II), that which showed the greater nitrogen hfs constant (a_N 30.6 gauss) and interaction with two protons (a_H 1.9 gauss)(which was found for all compounds) is assigned configuration (VIII), and the other with the same nitrogen hfs constant (a_N 30.6 gauss) but interaction with three protons (a_H 1.8 gauss) is its geometrical isomer (IX).

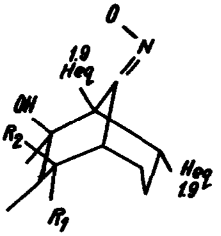
(VIII)

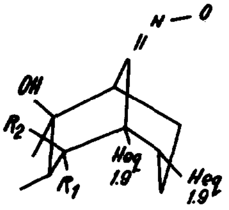


(IX)



Of the two radicals derived from (III), that with the greater nitrogen hfs constant (a_N 30.6 gauss) and interaction with two protons (a_H 1.9 gauss) is assigned either (X) or (XI) isomeric conformation, the equality of corresponding values of a_N and a_H of these isomers being expected as was observed for (VI)(a_N 30.6; a_H 1.9 gauss) and (VII)(a_N 30.6; a_H 1.8 gauss). It is reasonable to suppose that in this case too, both isomers ((X) and (XI))are present in the reacting mixture. To be consistent with this assignment, the β-substituent should always be equatorial ; this is expected but not established yet either by synthesis or other methods. In compound (IV) the ambiguity concerning the position of the β-substituent is excluded; the same spectrum (a_N 30.6; a_H 1.9 gauss) was obtained and for the same reasons it was assigned to the (XII) or (XIII) isomers.





(X) R_2orR$_1$=H; R_1orR$_2$=Me, Et, n-Pr, iso-Bu, Furyl

(XI) R_2orR$_1$=H; R_1orR$_2$=Me, Et, n-Pr, iso-Bu, Furyl

(XII) $(R_1,R_2)=-(CH_2)_5-$

(XIII) $(R_1,R_2)=-(CH_2)_5-$

For the iminoxy radicals from (II) and (III) with smaller nitrogen hfs constant (a_N 29.9 gauss) and interaction with two protons (a_H 1.9 gauss) there corresponds a structure with lower spin density on the nitrogen atom. This could be due to the intramolecular hydrogen bonds between the OH hydrogen and the iminoxy group nitrogen or oxygen. IR spectra of (II) and (III) which showed the existence of such bonds confirm this as a possibility.

All iminoxy radicals investigated have an α-bridgehead proton (which is thus on a tertiary C-atom) in an equatorial position. The splitting of 1.9 gauss is always found for this proton, according to the spectrum of (I) and a series of other bicyclic compounds[1,2] and differs from observations in the case of compounds with α-protons on secondary carbon atoms[6]. Thus, mechanisms other than direct overlapping probably have an important contribution to the unpaired spin density transmission.

REFERENCES

1. A.Caragheorgheopol, M.Hartmann, R.Kühmstedt and V.E.Sahini, Tetrahedron Letters, 42, 4161 (1967).
2. A. Caragheorgheopol, V. Gräfe, M.Hartmann, V.E.Sahini and K.Wermann, preceding paper.
3. N. Bărbulescu, Rev.Chim.(Bucuresti), 1, 45 (1956).
4. N. Bărbulescu, G.Bădiţă and M.N.Tilicenco, Zhur.obshchei Khim., 33, 4027(1963).
5. L.Ivan and N.Bărbulescu, Anal.Univ.(Bucuresti), 41, 155 (1963)
6. B.C.Gilbert and R.O.C.Norman, J.Chem.Soc.(B), 86 (1966).