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ELECTRON SPIN RESONANCE SPECTRA OF SOME IMINOXY - RADICALS

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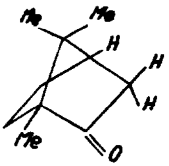
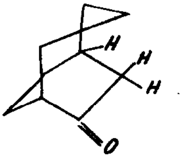
In the conformational study of some substituted bicyclic compounds, the radicals obtained under the oxidising action of lead tetra-acetate on the oximes of some bicyclic ketones (1) have been investigated. The parent ketones are:

K_I	Camphor
K_{II}	Bicyclo [3,2,2] nonan-6-one
K_{III}	Bicyclo [2,2,2] octan-2-one
K_{IV}	Bicyclo [3,3,1] nonan-2-one
K_V	Bicyclo [3,2,1] octan-2-one
K_{VI}	Bicyclo [4,2,1] nonan-2-one
K_{VII}	Bicyclo [3,2,1] octan-3-one
K_{VIII}	Bicyclo [4,2,1] nonan-9-one,

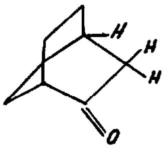
the corresponding oximes being denoted by O_I - O_{VIII}.



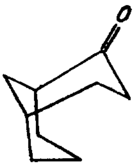
K_I



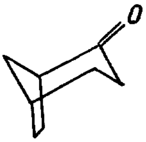
K_{II}



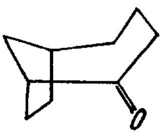
K_{III}



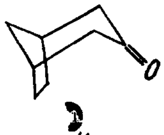
K_{IV}



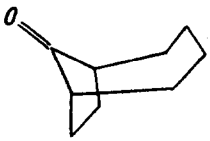
K_V



K_{VI}



K_{VII}



K_{VIII}

The radicals were obtained directly in the sample tube, by adding a few drops of solvent to the oxime-lead tetra-acetate solid mixture. Radicals were in this way continuously generated during some minutes in the required concentration for recording the complete spectrum. All measurements were performed with a JEOL X-band spectrometer, using 100 kc/sec field modulation. The choice of the solvent, rather than other conditions (cooling of the sample, deoxygenation) is critical. Trial measurements with pyridine, 1:1-dimethoxy-ethane, tetrahydrofuran, methylene dichloride, dimethyl sulphoxide and acetic acid as solvents have been performed. Satisfactory recording conditions were achieved in benzene.

Complex E.S.R. spectra resulting from the superposed signals of a number of radicals with different life times were found. The remarkable feature of all these spectra is the presence of some short-life radical lines, showing a large nitrogen hyperfine splitting (h.f.s) ($a_N \sim 30$ gauss). The three (1:1:1) lines usually have a specific h.f. pattern determined by the interaction between the unpaired electron and some of the protons in the molecule. Interesting structural information can be infered from these data.

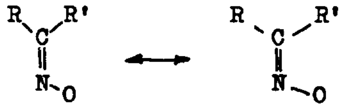
TABLE 1

Hyperfine splitting constants (gauss) measured at room temperature in benzene. The number of equivalent protons is indicated in parentheses.

The parent oxime	Sigma radicals		Other radicals	
	a_N	a_H	a_N	a_N
§ O_I	29.9	2.4 (3)	-	-
O_{II}	29.0	2.5 (3)	-	11.0
O_{III}	29.9	2.7 (3)	7.6	12.3
O_{IV}	30.9	2.6 (3)	8.2	12.5
O_V	28.6	2.6 (3)	7.6	12.6
O_{VI}	29.7	2.6 (3)	7.7	13.4
§ O_{VII}	29.9	4.7 (1)	-	-
		2.2 (2)		
		0.7 (1)		
O_{VIII}	28.4	-	6.9	12.5

§ See also (3)

We assigned these spectra to iminoxy-radicals of general formula:



The orbital of the unpaired p-electron is orthogonal to the C-N pi-system and has a considerable s-type contribution. This type of radical, known as a sigma-radical, was described for other oximes in recent literature (2,3,4,5) with the following properties:

(a) There is a long-range interaction which is transmitted through the sigma-bond system of the molecule.

(b) The interaction with the components of the molecule lying cis, relative to the oxygen atom, is essentially stronger than with those lying trans.

(c) The interaction is most effective when the H-$(C)_n$-N-O fragment is planar.

The radicals of O_{II} and O_{III} are representative for compounds having the iminoxy-group attached to a boat-form cyclohexane-ring. The 1:3:3:1 h.f. pattern of each nitrogen line arises from three approximately equivalent protons and is easily interpreted using the analogy with camphor oxime (2,3). The protons which interact with the unpaired electron are those indicated in the structural formulae.

The spectra of O_{IV} and O_V radicals also indicate interaction with three equivalent protons, but conformational considerations, based on the above mentioned (a,b,c) properties, as well as comparison with results obtained for 2-, 4-and 2,4-substituted cyclohexanone oxime radicals(3), with the same rigid chair conformation, cannot be correlated with the observed spectra.

The same is true for O_{VI}, the seven-membered ring introducing little modification in the molecular geometry around the oxime group. For comparison purposes the spectrum of the O_{VII} radical, belonging to the substituted rigid chair-form cyclohexanone oximes was also recorded. Our data are in good agreement with those previously reported for this compound (3).

In case of O_{VIII} radical the h.f.s. was not resolved, a slight tendency of resolution being nevertheless observed in 1:1 dimethoxyethane.

Results for other radicals, with lower nitrogen h.f.s. which always appear in the reacting mixture, are also recorded in the table. Recent attempts to give structural assignments for similar radicals of some alicyclic and aliphatic oximes have been reported (6).

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