agent for $K^+$ ions. It produces a considerably higher fraction of $F^-,K^+$ separated ion pairs. The same observation was made by Izatt, *et al.*,[4] and by Frensdorff,[5] although in their experiments free $K^+$ ions in water and methanol, respectively, were involved in the complexation. It is interesting that even this powerful complexing crown ether (Pedersen[1] classified this ether in comparison to other crown ethers as the strongest complexing agent for $K^+$ ions) does not easily separate the $F^-,K^+$ ion pair. Its conformation may favor a complex where the $K^+$ ion slightly protrudes from the polyether, enhancing the stability of externally complexed contact ion pairs.

**Acknowledgment.** The authors gratefully acknowledge the support of this research by the National Institutes of Health through Grant No. GM15965 and by the Petroleum Research Fund, administered by the American Chemical Society. They are also indebted to S. Kopolow from this laboratory for assisting in the preparation of the macrocyclic polyethers.

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# Nitroxides in the Oxidation of Bicyclic Oximes. An Electron Paramagnetic Resonance Study

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*Received March 24, 1971*

**Abstract:** The nitroxide radicals RR′NO which appear in the oxidation of bicyclic oximes with lead tetraacetate have been investigated by means of epr spectroscopy. Three types of radicals were found to have the following characteristics: type i, $a_N \sim 13$ G, $g \sim 2.0061$; type ii, $a_N = 11.7$ G, $a_H = 9.6$ G, $g = 2.0061$; type iii, $a_N \sim 8$ G, $g \sim 2.0069$. Their structure and formation are discussed.

The oxidation of oximes with lead tetraacetate is known to yield iminoxy radicals $R_1R_2C{:}NO$, the characteristics of which have been extensively discussed[1,2] in earlier papers. Sometimes nitroxide radicals RR′NO are also pointed out.[2-4] As yet the question of their structure and origin has not been completely answered.[5]

In our epr study of the oxidation of bicyclic oximes, we have observed, besides the iminoxy radicals,[4,6,7] various nitroxides whose structure and relative concentrations seem to depend on the nature of the parent compound. It is the aim of this paper to report our observations on this subject.

## Results and Discussion

The investigated oximes were derivatives of bicyclo[3.3.1]nonane (I, II, III, IV, V, VI), bicyclo[3.2.1]octane (VII, VIII, IX, X), and bicyclo[4.2.1]nonane (XI, XII, XIII). Typical spectra are given in Figure 1. The parameters of the epr spectra of the observed nitroxides are summarized in Tables I and II.

As may be observed in most cases, proton hfs is lacking, so the $a_N$ and $g$ parameters had to be used in order to determine the structures of the nitroxide radicals. According to their epr parameters, the radicals are divided into three groups.

**Table I.** Parameters of the Epr Spectra of the Indicated Nitroxides

| Parent oximes | Radical type i $a_N$, G | $g$ | Radical type iii $a_N$, G | $g$ |
|---|---|---|---|---|
| I | 12.9 | 2.0062 | 7.8 | 2.0068 |
| II | 12.4 | 2.0061 | ... | ... |
| III | 12.4 | 2.0061 | 7.4 | 2.0068 |
| IV | 12.5 | 2.0061 | ... | ... |
| V | 13.6 | 2.0060 | 7.7 | 2.0068 |
| VI | 13.6 | 2.0061 | ... | ... |
| VII | 12.6 | 2.0063 | 7.3 | 2.0069 |
| VIII | 13.3 | 2.0061 | 8.0 | 2.0068 |
| IX | 12.8 | 2.0061 | ... | ... |
| X | 13.2 | 2.0062 | 7.8 | 2.0069 |
| XI | 13.2 | 2.0062 | 7.3 | 2.0070 |
| XII | 13.6 | 2.0061 | 8.0 | 2.0070 |
| XIII | 13.6 | 2.0061 | ... | ... |

**Table II.** Parameters of the Epr Spectra

| Parent oximes | Radical type ii $a_N$, G | $a_{NH}$, G | $g$ |
|---|---|---|---|
| II | 11.7 | 9.6 | 2.0061 |
| III | 11.7 | 9.6 | 2.0061 |

**Radical Type i.** This type of radical (Table I) has $a_N \sim 13$ G, a value characteristic of a few types of nitroxides only. Among them, bis(1-acetoxycyclohexyl) nitroxide ($a_N = 13.2$ G, $g = 2.0061$) (XIV), which was described by Wajer, Mackor, and de Boer,[8] suggests a similar structure (XV) for our type i bicy-

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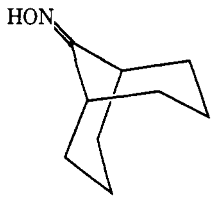
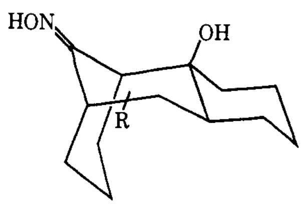
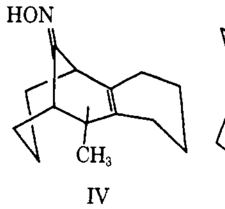

I


II, R = H
III, R = CH$_3$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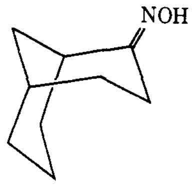
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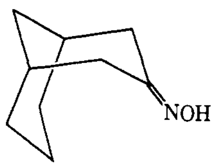
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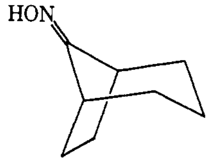
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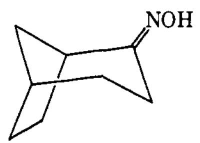
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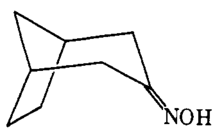
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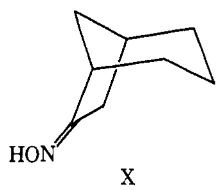
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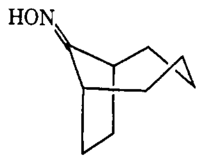
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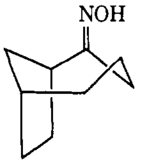
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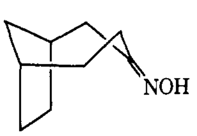
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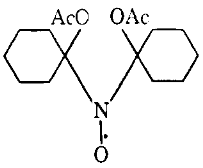
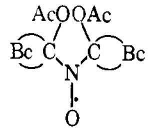
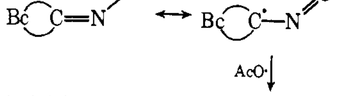
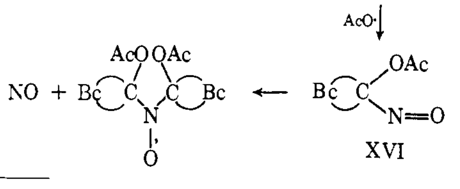

XIV


XV

clic nitroxides. Structure XV contains no $\alpha$ or $\beta$ protons, in agreement with the observed spectra; the two acetoxy groups are responsible for the lowering of the $a_N$ value[8,9] as compared with the corresponding dialkyl nitroxides ($a_N \sim$ 15–16 G).


(1)


(2)

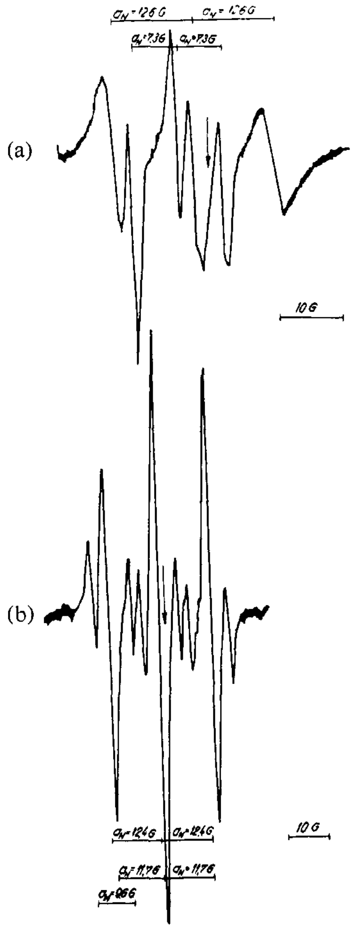
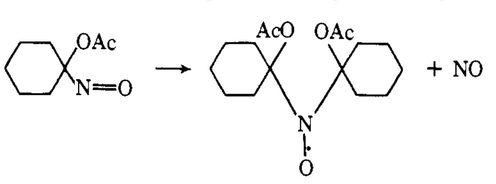


Figure 1. Solution spectra of nitroxides; the arrows indicate the field position corresponding to $g$ = 2.0055: (a) K-band spectrum of type i and iii nitroxides derived from VII; (b) X-band spectrum of type i and ii nitroxides derived from II.

The sequence of reactions shown in eq 1 and 2, which also supports structure XV, is proposed to account for the formation of type i nitroxides. The nitroso compound XVI has been separated and identified among the reaction products (similar compounds have been reported generally in the oxidation of unhindered or partly hindered oximes with lead tetraacetate[3,5,10,11]). Nitroso compounds (in monomer form) add unstable free radicals to yield nitroxides,[12,13] and, as they undergo decomposition under mild conditions, symmetric nitroxides often are formed. For instance, bis(1-acetoxycyclohexyl) nitroxide is obtained by uv or red-light irradiation of the *gem*-acetoxynitrosocyclohexane[8] (eq 3). These properties of the nitroso compounds together with the identification of XVI and NO justify eq 2.


(3)

An interesting experimental fact supports the idea contained in eq 1 and eq 2 that type i nitroxides represent a step in the decomposition of iminoxy radicals:

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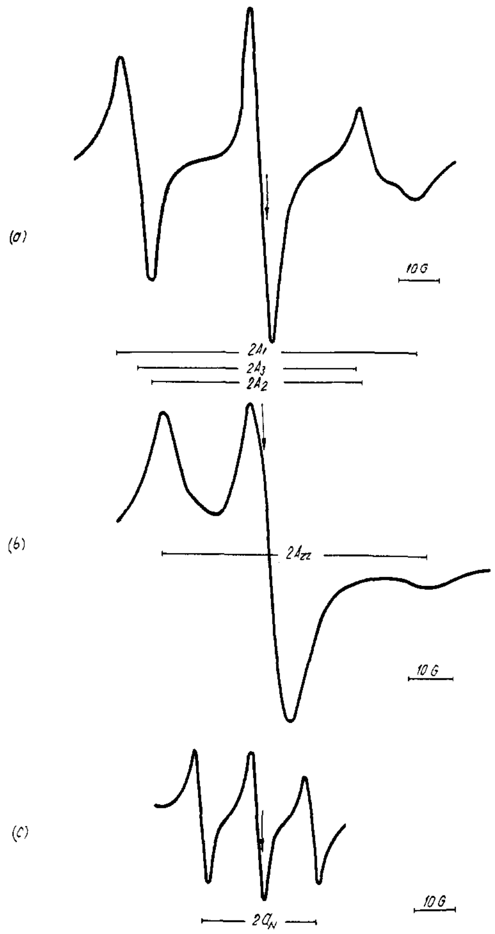
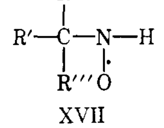


Figure 2. X-Band spectra of a $\gamma$-irradiated sample of I; the arrows indicate the field position corresponding to $g = 2.0055$: (a) the iminoxy radical observed shortly after irradiation of the polycrystalline sample, (b) the same sample after about 2 months (a typical nitroxide spectrum is observed), (c) the solution spectrum obtained by dissolving the sample mentioned in (b) in benzene.

polycrystalline samples of oximes, when $\gamma$ irradiated, yield selectively iminoxy radicals[14] (Figure 2a). We observed that in a few days these decay and nitroxide radicals gradually appear (Figure 2b). The latter radicals have also been observed in solution (Figure 2c) when the irradiated samples are dissolved. For instance, a nitroxide with $a_N = 13.6$ G and $g = 2.0060$ is obtained when I is dissolved in benzene; similar values have been found for the other compounds.

Special attention should be given at this point to the fact that the mechanism discussed above represents only one reaction path and others also interfere, as indicated by the large number of final products and by other observations which will be discussed in the following sections.

**Radical Type ii.** Nitroxides of this type have been found in two cases only (Table II). The experimental data are suited best by structure XVII. Radicals with

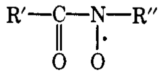


$$R'-\overset{\overset{\large R''}{|}}{\underset{\underset{\large R'''}{|}}{C}}-\underset{\underset{\large O}{|\cdot}}{N}-H$$

XVII

slightly different parameters (for instance, $a_N = 12.8$ G, $a_{NH} = 11.5$ G, $g = 2.0062$ for the cyclohexyl nitroxide as compared to $a_N = 11.7$ G, $a_{NH} = 9.6$ G, $g = 2.0061$ for the bicyclic nitroxides) have recently been reported[15] to form in static systems from reduction of the corresponding nitroso compounds. In our case, a nitroso compound which could be responsible for the type ii nitroxide is the already mentioned compound XVI, but it is not clear how the reduction occurs.

**Radical Type iii.** This type of nitroxide (Table I) has a much lower $a_N$ value ($\sim$8 G) and a higher $g$ factor ($\sim$2.0069). These parameters suggest a higher degree of delocalization for the unpaired spin, including an atom with a high spin–orbit coupling constant. Similar values have been observed[11,16,17] for a series of nitroxides all of which have a carbonyl group attached directly to the nitrogen atom. Only this type of radicals has the indicated parameters. Therefore, our type iii nitroxides have the general formula XVIII.

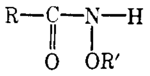


$$R'-\underset{\underset{\large O}{\|}}{C}-\underset{\underset{\large O}{|\cdot}}{N}-R''$$

XVIII

We assume that the formation of the $\alpha$-carbonyl group proceeds *via* a ring opening (breaking or enlargement). One way would be through a Beckmann rearrangement followed by the oxidation of the resulting lactam. Nevertheless, we must remark that attempts of other authors[18] to oxidize the NH group in compounds with an $\alpha$-carbonyl group failed to yield the corresponding nitroxides.

Another way is suggested by the work of Just and Dahl.[11] These authors have studied the oxidation by lead tetraacetate of sterically hindered alicyclic oximes and have found derivatives of hydroxamic acids (XIX)



$$R-\underset{\underset{\large O}{\|}}{C}-\underset{\underset{\large OR'}{|}}{N}-H$$

XIX

as final products. Their formation implies the opening of the ring. The type iii nitroxides could be oxidation products of XIX.

Mechanisms implying a ring opening are supported by our observation that compounds such as VII, X, and XI, which have the oxime group on a strained five-membered ring, preferentially yield type iii nitroxides, the situation being reversed to the advantage of the type i nitroxides for the other compounds.

It was established in a previous paper[11] that the final products in the oxidation of alicyclic oximes with lead tetraacetate depend on the degree of steric hindrance around the oxime group. Our results indicate that a parallel exists between the final products obtained in different specific cases and the nitroxides which appear in corresponding situations. (a) Unhindered oximes lead to *gem*-acetoxynitroso compounds, ketones, and $NO_2$; correspondingly, in the case of compounds VI, IX, and XIII, we have found nitroxides of type i only.

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[15] Th. A. J. W. Wajer, A. Mackor, and Th. J. de Boer, *Tetrahedron*, 25, 175 (1969).

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(b) Sterically hindered oximes give rise to derivatives of hydroxamic acids, which can account for type iii radicals. (c) Partly hindered oximes give mixtures of both types of compounds and, as expected for our bicyclic oximes I, III, V, VII, VIII, X, XI, and XII, nitroxides of both types i and iii appear.

## Experimental Section

**Oxidized Samples.** The nitroxides were prepared in the sample tube by mixing the reagents (oxime and lead tetraacetate) in benzene at room temperature.

**Irradiated Samples.** A 500-Ci $^{60}$Co $\gamma$-ray source was employed for the irradiation of powder samples of oximes. Dosages of the order of $5 \times 10^5$ to $2 \times 10^6$ rads were given. The irradiation, storage, and epr measurements were carried out at room temperature. To eliminate the virtual influence of oxygen, a series of samples was evacuated to $10^{-6}$ Torr and sealed off before irradiating. No differences have been noticed as compared with samples irradiated at air pressure. The epr spectra of the powder samples were recorded at different time intervals and the evolution of the spectra (Figure 2) was followed. The solution spectra are obtained by dissolving the samples in benzene.

**Epr Spectra.** All epr spectra were recorded on a JES-3B (Jeolco) spectrometer with 100-kHz field modulation using X- as well as K-band frequencies. The hfs constants and $g$ factors were measured by comparison with potassium peroxylamine disulfonate ($a_N$ = 13.0 G, $g$ = 2.0055).

**Identification of Some Final Products. (a) 9-Acetoxy-9-nitrosobicyclo[3.3.1]nonane (XX).** The oxidation of I (which was available in adequate quantity) was carried out on a preparative scale by adding small portions of lead tetraacetate to a benzene solution of oxime, under continuous stirring at room temperature. A blue-green solution (A) was formed from which XX was separated after liquid–liquid, column chromatography and tlc fractionation. From the 12 compounds so isolated, XX was identified by its specific ir ($\nu_{C=O}$ 1750, $\nu_{C-C=O}$ 1250, and $\nu_{C-O}$ 1060 cm$^{-1}$ for the acetoxy group and $\nu_{N=O}$ 1550 cm$^{-1}$ for the nitroso group) and visible ($\lambda_{N=O}$ 680 nm) absorption bands. With the reaction mixtures of the other oximes, a similar visible absorption band is always found.

The following procedure leads to the isolation of XX. The solvent was removed from A and the fraction (B) soluble in petroleum ether (30–60°) at room temperature was extracted; B was then passed over a silica gel (BDH) column and the benzene eluate (C) was retained. C was chromatographed again on an alumina (Merck, according to Brockmann) column, the fraction (D) eluted by petroleum ether being then concentrated to a blue-green oil. This was separated by preparative tlc on chromatoplates coated with a 500-$\mu$ thick layer of silica gel H (Merck, according to Stahl) which were activated at 110° and developed with a 5:3.5:1:0.5 (v/v/v/v) mixture of petroleum ether–toluene–acetone–methanol.

**(b) Bicyclo[3.3.1]nonan-9-one.** This ketone was separated by tlc directly from the reaction mixture using the pure ketone as internal and external standard. The identity of the ketone was then checked by its ir and uv spectra.

**(c) Nitrous Gases.** Brown vapors were observed to evolve from the reaction mixture. A filter paper moistened with a sulfuric acid solution of diphenylbenzidine turned blue when held in these vapors. This reaction was attributed to the nitrous gases, as other oxidizing gaseous products are not expected.

**Acknowledgments.** The derivatives of bicyclo[3.3.1]-nonane, bicyclo[4.2.1]nonane, and bicyclo[3.2.1]octane were kindly supplied by Professor M. Hartmann, and the tricyclo[7.3.1.0$^{2,7}$]tridecane derivatives by Professor N. Bărbulescu, to whom we are very grateful. In addition, we wish to thank Mrs. Simona Badilescu for the ir spectra.

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# Molecular-Beam Microwave Spectra of HNCO and DNCO

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*Received May 3, 1971*

**Abstract:** Deuteron quadrupole coupling in DNCO was obtained from splittings of the $1_{01}$ rotational state. The measured quadrupole coupling strength for the $1_{01}$ rotational state is $eqQ(1_{01})$ = 53.6 ± 0.2 kHz, which leads to a value along the D–N bond $eqQ_{DN}$ = 345 ± 2 kHz. Hyperfine splittings were observed using a molecular-beam maser spectrometer with 6-kHz resolution. The nitrogen quadrupole coupling strengths were $eqQ(1_{01})$ = 2123.0 ± 1.0 kHz for DNCO and $eqQ(1_{01})$ = 2052.7 ± 1.0 kHz for HNCO. High-precision values for the line-center frequencies and spin–rotation constants are also reported.

Quadrupole coupling strengths, dipole moments, and molecular quadrupole moments provide detailed information about the electronic structure of molecules. For simple molecules, we can obtain precise values for these parameters using molecular-beam maser spectroscopy.

HNCO (isocyanic acid) is a slightly asymmetric top with a nearly linear configuration. Other similar molecules are HNCS (isothiocyanic acid), $HN_3$ (hydrogen azide), and, of recently determined structure,[1] HCNO (fulminic acid). The heavy atoms of all of these molecules are rigidly held in a straight line, and the hydrogen atom is displaced off this axis. The structure for HNCO was first determined by Jones, Shoolery, Shulman, and Yost.[2] The structure was obtained from infrared data by Reid and Herzberg.[3,4] Jones, *et al.*, determined the structure of the molecule from a combination of microwave transitions for HNCO and DNCO and the assumption that the atoms N, C, and O were in a straight line. A series of higher frequency transitions of HNCO and DNCO in the range 80–150 GHz were reported by Kewley, Sastry, and Winne-

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