The standard procedure below results in high yields of the α-phenylseleno ketones from five-, six-, seven-, and eight-membered cyclic ketones, but the elimination reaction gives lower yields and less pure products than for the cases outlined above. Table I presents the results for the preparation of three cyclohexenones. The ratio of exo- and endocyclic olefins from 2,6-dimethylcyclohexanone depends on the elimination conditions, suggesting that stereochemical control may be possible in more complicated cases.

The experimental procedure is convenient. Of the selenium containing compounds involved, only benzeneselenenyl bromide is sufficiently volatile to have a detectable odor and, since it is prepared in solution and used directly, this does not present a problem. A solution of 3.0 mmol of lithium diisopropylamide (prepared from 0.42 ml of diisopropylamine and 1.47 ml of 2.05 *M* butyllithium in hexane) in 15 ml of THF was prepared under nitrogen at −78° and 0.56 g (2.5 mmol) of 1,4-diphenyl-1-butanone (**2**) in 3 ml of THF was added dropwise. The solution was stirred for 10 min and 3.0 mmol of benzeneselenenyl bromide (prepared by addition 0.081 ml of bromine to 0.47 g of diphenyl diselenide[10] in 3 ml of THF) was added rapidly dropwise. The solution was warmed to 0°, 1.5 ml of water, 0.3 ml of acetic acid, and 1.4 g of 30% hydrogen peroxide were added,[11] and the reaction temperature was maintained below 25° until the vigorous gas evolution had ended (30 min). The solution was poured into 50 ml of saturated sodium bicarbonate solution and 50 ml of 1:1 ether–pentane, and the organic layer was washed successively with water, 0.1 *N* hydrochloric acid, water, and saturated sodium chloride. The product was separated from 8% of starting ketone **2** by thin layer chromatography, and the enone was sublimed, giving 0.47 g of **3** (85% yield, 92% based on recovered starting material): mp 40–41°; ir $\nu_{\mathrm{CCl_4}}$ 1672 cm^{-1}; nmr $\delta_{\mathrm{CCl_4}}$ 3.58 (d, J = 5.9 Hz, 2 H), 6.8 (d, J = 15.7 Hz, 1 H), 7.0–7.5 (m, including a partially obscured dt, J = 15.7, 5.9 Hz, 9 H), 7.8–8.0 (m, 2 H).

Literature methods for the conversion of ketones to enones have involved bromination–dehydrobromination[12a] or direct oxidation of ketones using Collins reagent[12b] or other oxidizing agents.[12c] The method described here clearly has advantages in terms of yield, convenience, and mildness of reaction conditions.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. H. J. R. wishes to express his appreciation to the Du Pont Company for a Du Pont Young Faculty Grant.

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[10] Sharpless and Lauer[2] have discussed the use of diphenyl diselenide as a stoichiometric reagent.

[11] The oxidation is strongly exothermic, and for larger scale reactions slow addition of hydrogen peroxide at 10–15° is necessary.

[12] (a) T. A. Spencer, R. A. J. Smith, D. L. Storm, and R. M. Villarica, *J. Amer. Chem. Soc.*, **93** 4856 (1971); (b) W. G. Dauben, M. Lorber, and D. S. Fullerton, *J. Org. Chem.*, **34**, 3587 (1969); (c) R. J. Theissen, *ibid.*, **36**, 752 (1971).

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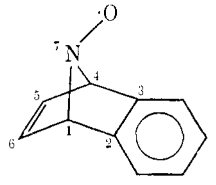
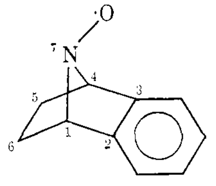
Electron Spin Resonance Spectra of Bicyclic Nitroxide Radicals. 7-Azabenzonorbornadiene-7-oxyl and 7-Azabenzonorbornene-7-oxyl

Sir:

It has been reported[1] that the mode of electron spin distribution depends quite sensitively on the conformation and geometry of a σ-bonded molecule. In order to gain further insight into stereospecificity of the electron spin transmission in the σ skeleton, we have studied here the esr spectra of new stable bicyclic nitroxide radicals, 7-azabenzonorbornadiene-7-oxyl (I)[2] and 7-azabenzonorbornene-7-oxyl (II)[2]. These spectra showed noteworthy features: (1) anomalously large nitrogen hyperfine splitting constants (hfsc's) as compared with other dialkyl nitroxides and (2) marked differences between the proton hfsc's of I and II. From these results stereospecific orientation of a nitroxide group is concluded.



I



II

I and II were prepared by hydrogen peroxide oxidation in an aqueous solution (in the presence of a small amount of ethanol) of parent amines[3] containing sodium tungstate and EDTA (ethylenediaminetetraacetic acid). Figure 1 presents the esr spectra of I (g value = 2.0061) and II (g = 2.0062) in dichloromethane solution at room temperature. The prominent feature of these spectra common to I and II is 1:1:1 triplet splitting (22.6 G for I and 23.1 G for II) which is, no doubt, due to hyperfine interaction with the nitrogen nucleus. These hfsc's are much larger than those for most of the dialkyl nitroxide radicals that have been reported so far.[4] These unusually large values of the nitrogen hfsc's could be attributed to the pyramidal structure around the nitrogen atom

In order to substantiate theoretically this feature, we carried out INDO–UHF MO calculations[5,6] for several conformations of dimethyl nitroxide (DMNO) as a model (Figure 2). ψ is the angle between the $C_\alpha NC'_\alpha$ plane and the N–O bond, and θ designates the angle between the two N–C_α bonds. Figure 2 shows that for the unstrained DMNO (θ = 120°) the

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[1] See, for instance, the following and the references cited therein: (a) T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, **92**, 1267 (1970); (b) I. Morishima, K. Okada, T. Yonezawa, and K. Goto, *ibid.*, **93**, 3922 (1971); (c) I. Morishima, K. Okada, and T. Yonezawa, *ibid.*, **94**, 1425 (1972); (d) Z. Luz, *J. Chem. Phys.*, **48**, 4186 (1968); (e) M. Barfield, *J. Phys. Chem.*, **74**, 621 (1970).

[2] The derivatives of 7-azanorbornen-7-oxyl are expected to be stable, because nitron formation is prohibited in these nitroxide radicals by Bredt's rule; see A. R. Forrester, J. H. May, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, London and New York, Chapter 5.

[3] The parent amines were prepared by the method of L. A. Carpivo and D. E. Barr, *J. Org. Chem.*, **31**, 764 (1966).

[4] For example, 16.2G for di-*tert*-butyl nitroxide (see ref 2) and 19.5 G for 1,5-dimethyl-8-azabicyclo[3.2.1]octan-3-one-8-oxyl; A. Rassat and J. Ronzaud, *J. Amer. Chem. Soc.*, **93**, 5041 (1971). In this paper, they reported pyramidal structure around the nitrogen atom in this bicyclic nitroxide.

[5] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

[6] In this calculation, the bond lengths (Å) are chosen as follows: N–O = 1.2, N–C = 1.47, C–C = 1.54, C–H = 1.09, and C=C = 1.33.

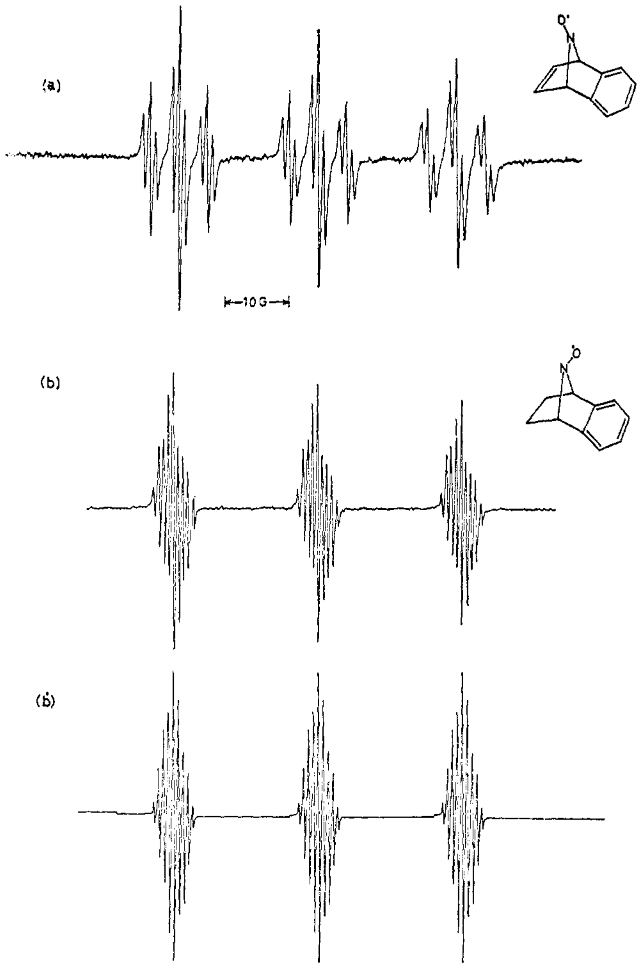

Figure 1. Esr spectra of (1a) 7-azabenzonorbornadien-7-oxyl (I) and of (1b) 7-azabenzonorbornen-7-oxyl (II). 1b′ represents a computer-simulated spectrum of 1b.

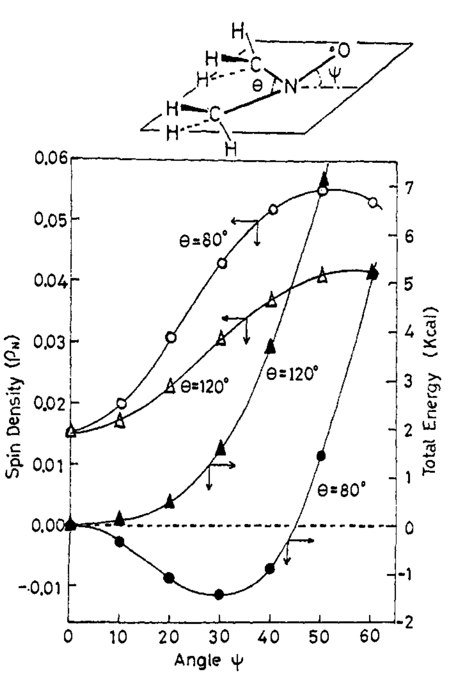

Figure 2. INDO spin densities on the nitrogen s atomic orbital in DMNO for the structures of $\theta = 120°$ (△) and $\theta = 80°$ (○), and the total energies for the structures of $\theta = 120°$ (▲) and $\theta = 80°$ (●) relative to the energy of the planar structure ($\theta = 0°$) as a function of angle ψ (see text).

geometry with a planar (or nearly planar) radical center ($\psi = 0°$) has the lowest energy. However, when the C_α–C–N–C'_α bond is strained to $\theta = 80°$,[7] the pyramidal structure ($\psi = 30°$) becomes most stable. This corresponds to the generalization that nonplanarity of the radical center of an alkyl radical increases as the bond angle θ is decreased.[8] The calculated spin density on the nitrogen s atomic orbital increases with the angle ψ to a greater extent for the strained conformation ($\theta = 80°$) than for the unstrained one ($\theta = 120°$). From these results and discussion the pyramidal structure around the nitroxide group is concluded.

In the spectrum of I (Figure 1a) each splitting of the 1:1:1 triplet due to the nitrogen nucleus splits further into a 1:2:1 triplet (4.6 G) of triplet (0.94 G). In the spectrum of II (Figure 1b), however, each of the 1:1:1 triplet signals is resolved further into nine splittings. Spectral simulation (Figure 1b′) allows us to interpret the spectrum as resulting from the interaction of the unpaired electron with one nitrogen nucleus ($a_N = 23.1$ G), two equivalent protons ($a_H = 1.67$ G), and four equivalent protons ($a_H = 0.82$ G).[8a] In order to facilitate further interpretation of these splitting constants, we performed INDO–UHF MO calculations[9,10] for 7-azanorbornadien-7-oxyl (III) and two conformers (IV and V) of 7-azanorbornadien-7-oxyl in which the N–O bond bends 30°[11] from the C_α–N–C_α plane. The calculated proton hfsc's[10] (in gauss) are shown below. Comparison of the observed hfsc's of I with the calculated proton hfsc's for III may allow us to assign 4.6 G splitting to 5- and 6- protons and 0.94 G to 1- and 4- protons, although the calculated splitting constants for III are uniformly smaller than the observed ones. The very small value of the α proton (1- and 4- protons) hfsc is attributable to the geometry in which the dihedral angle between the odd electron orbital on the nitrogen atom and the C_α–H bond is nearly 90°. It is also to be noted that there is a great difference between calculated hfsc's of β hydrogens[12,13] in III. The spin den-

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[7] 80° is adopted tentatively for the model of strained C_α–N–C_α' skeleton.

[8] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *Chem. Commun.*, 1353 (1969); *J. Chem. Soc. A*, 124 (1971); T. Kawamura, T. Koyama, and T. Yonezawa, *J. Amer. Chem. Soc.*, **95**, 3220 (1973).

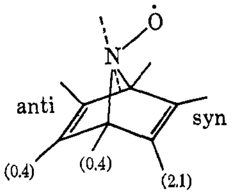
[8a] Note Added in Proof. The values of 1.58, 0.88, and 0.90 G improve appreciably the match between the experimental and calculated spectra with regard to the relative intensities of the third line of each triplet signal of II (details will be given in a full paper).

[9] In these calculations, the H–C–H angles are assumed to be 109° 28′ and the other bond angles are selected so as to be consistent with the bond lengths (see ref 6), referring the structure of norbornane reported by J. F. Chiang, *et al.*: J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *ibid.*, **90**, 3149 (1968).

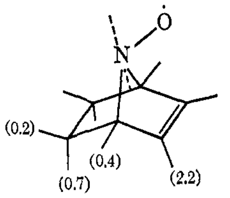
[10] Proton hfsc's (a_H) are calculated by using the following relation. $a_H = 539.86\rho_H$ where ρ_H is the spin density on the hydrogen 1s orbital. See ref 5.

[11] In I and II, the angle θ between two N–C_α bonds is nearly 90° (ref 9). Referring the MO theoretical results for the optimum geometry of DMNO with $\theta = 80°$, we assume that the angle between C–N–C plane and the N–O bond is nearly 30° in these radicals.

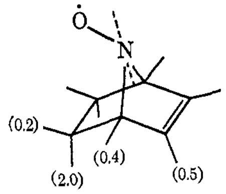
[12] It is well-established that a large spin density is induced on the β-proton that lies on the "zigzag" arrangement of the carbon skeleton in a σ-radical, while the proton that lies on the "folded" arrangement senses a small amount of spin density.[1b,13] Hence, this large difference in the hfsc's of syn and anti β-hydrogens is attributable to the different arrangement of the N–C–C–H_β skeleton.



III



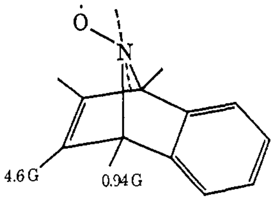
IV

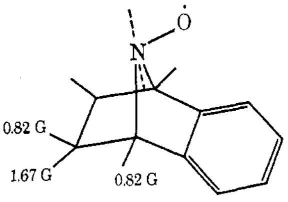


V

sity induced on the syn proton (with respect to the bent N–O bond) is much larger than that on the anti proton.[12] The observed large hfsc (4.6 G) in I could be attributed to the syn β proton, and it could be, therefore, concluded that in I the N–O bond tilts in the opposite side of the benzene ring (toward the double bond).

By comparison with radical I and with the predicted splitting constants obtained for models IV and V, 0.82 G splitting in radical II is attributable to the bridgehead (1 and 4) and β-exo protons and 1.67 G splitting to the β-endo protons. The predicted splitting constants for III are a factor of 2 smaller than the experimental values of I. Arguing by analogy, one might expect that the conformation of IV is responsible for the esr splitting of II. On the basis of above discussion, we propose that the N–O bond of II tilts toward the benzene ring, contrary to the case of I.





The different orientation of the N–O bond in I and II appears to be quite interesting in terms of the study of neighboring group participation in these radicals.[14] Specific orientation of the nitroxide group in II, for example, may stimulate us to study preferential participation of the N–O group with ethylene or benzene π electrons (the bishomoallylic or bishomobenzylic participation). Further detailed investigations are now under progress.

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(13) G. A. Russel, "Radical Ions," Interscience, New York, N. Y., 1968, Chapter 4.

(14) Note Added in Proof. It is of interest to take a look at the preferential orientation of radical lobe on the nitrogen atom in I and II in relation to that in the corresponding hydrocarbon radicals. The bent structure of radical II is comparable to 7-norbornenyl radical in which the radical lobe occupies the anti position with respect to the double bond (J. K. Kochi, P. Bakuzis, and P. J. Krusic, *J. Amer. Chem. Soc.*, **95**, 1516 (1973)). In radicals I and II, the odd-electron orbital is also away from the ethylene double bond. Based on these discussions, stereoselectivity of reactions proceeding through the intermediacy of the 7-benzonorbornenyl radical could be expected.

Crystal and Molecular Structure of a Cobalt(III) Complex Containing Adenine as a Unidentate Ligand

Sir:

Recent advances in electron microscopy offer hope that the direct visualization of single heavy atoms will become a useful, rapid means of sequential analysis of nucleic acid biopolymers.[1] The small number of purine and pyrimidine bases (four) which constitute the nucleic acids make these biopolymers, in theory, most amenable to sequencing studies. However, the sequencing method requires that the heavy-metal-containing moiety exhibit some selectivity toward a particular base.[1] One way of solving this latter problem is to utilize the different interactions between the purine and pyrimidine bases and other ligands attached to the metal. This type of approach has received little attention and it is our purpose here to determine whether specific interligand interactions are of possible importance.

A reaction which exhibits interesting steric dependence is

$$\textit{trans}\text{-}[\mathrm{Co(en)_2Cl_2}]^+ + \text{base} \longrightarrow \textit{cis}\text{-}[\mathrm{Co(en)_2Cl(base)}]^{2+} + \mathrm{Cl}^-$$

where en is the bidentate ligand ethylenediamine. This reaction proceeds readily when base = glycine esters,[2] but does not proceed with alanine or other amino acid esters.[3] Of the four nucleic acid bases tested, only adenine gives a reaction. Thus the above reaction of adenine with *trans*-[Co(en)$_2$Cl$_2$]$^+$ exhibits base selectivity.

In order to understand what interactions, both bonding and nonbonding, may be present, we have determined the structure of the complex *cis*-[adeninatochlorobis(ethylenediamine)cobalt(III)]$^+$, [Co(en)$_2$Cl(C$_5$N$_5$H$_4$)]$^+$. The complex was prepared according to the above reaction scheme with adenine acting as the base. While Sletten[4] has determined the structure of a dimeric copper(II) complex with deprotonated adenine as a bidentate ligand, this is to our knowledge the first report of a complex containing deprotonated adenine acting as a unidentate ligand. Although relatively few crystal structures of transition metal complexes con-

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(1) D. W. Gibson, M. Beer, and R. J. Barrnett, *Biochemistry*, **10**, 3669 (1971); T. Koller, M. Beer, M. Muller, and K. Muhlethaler, *Cytobios*, **4**, 369 (1971); J. W. Wiggins and M. Beer, *Anal. Chem.*, **44**, 77A (1972).

(2) M. D. Alexander and D. H. Busch, *Inorg. Chem.*, **5**, 602 (1966).

(3) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, unpublished results.

(4) E. Sletten, *Acta Crystallogr., Sect. B*, **25**, 1480 (1969).