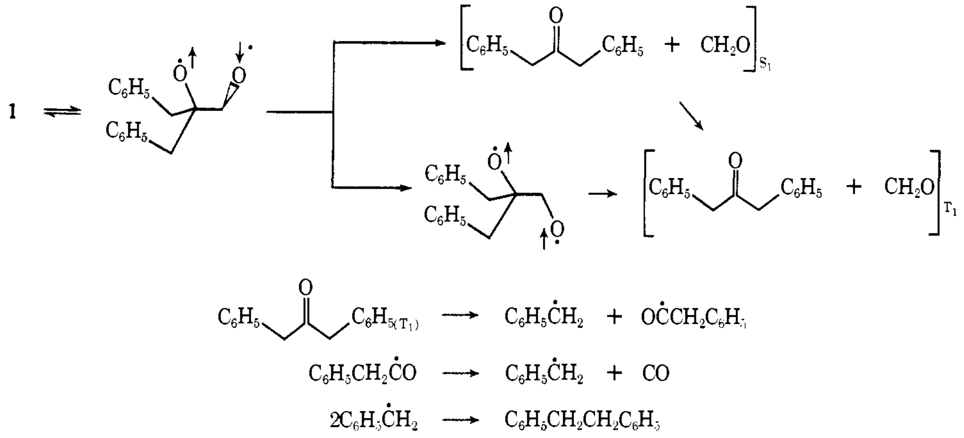
Scheme I



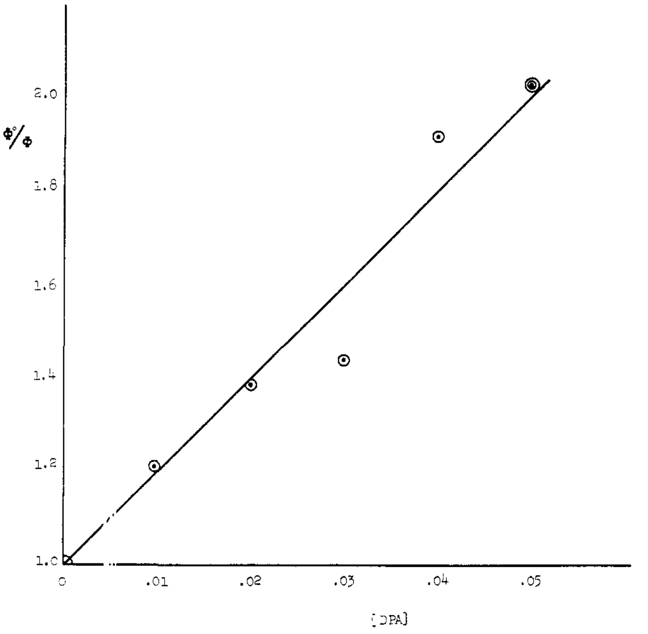


Figure 1. Quenching of bibenzyl production from 1.04×10^{-3} *M* **1** in benzene at 60° with 9,10-diphenylanthracene. In the absence of quencher, $\Phi^0 = 2.2\%$ yield bibenzyl and Φ is the yield of dibenzyl ketone in the presence of 9,10-diphenylanthracene.

An extension of this mechanism which will adequately explain the decomposition of **1** is given in Scheme I. For the two-step mechanism, where the initial step is reversible, a singlet biradical is required. The singlet biradical may undergo spin conversion to the triplet biradical, which can fragment to triplet carbonyl products. Alternately, the singlet biradical may give excited singlet state carbonyl species, which undergo intersystem crossing to the triplet state. This latter route was shown to be relatively unimportant in the thermal decomposition of tetramethyl-1,2-dioxetane.[1e]

Thermochemical calculations indicate that a 1,2-dioxetane can produce only one excited state carbonyl species.[9a] Indeed, recent reports indicate that one excited state carbonyl molecule is produced per 1,2-dioxetane decomposed.[1e,1d] The energy available for the excited state carbonyl species should be partitioned between dibenzyl ketone and formaldehyde as indicated by the brackets. Providing that the excited singlet state pathway is relatively unimportant,[1e,10] the distribution of excited state carbonyl species can be calculated from the triplet state energies of dibenzyl ketone and formaldehyde by the Boltzmann equation. Alternatively, from the yields of bibenzyl and dibenzyl ketone produced from **1** and the photochemical quantum yield for bibenzyl production from triplet dibenzyl ketone ($\Phi = 0.7$),[3] the *difference* between triplet energies of dibenzyl ketone and formaldehyde ($E_{T_{DK}} - E_{T_{CH_2O}}$) is calculated to be 2.2 kcal/mol with the assumption that one excited state carbonyl molecule is produced from **1**.[1e,1d] The triplet state energy of formaldehyde in the gas phase is reported to be 72.5 kcal/mol,[11] while the value for triplet dibenzyl ketone in solution is estimated to be 79 kcal/mol.[3a] The discrepancy between the difference in these reported values (6.5 kcal/mol) and our value of 2.2 kcal/mol may be due to the uncertainty of the reported value for dibenzyl ketone and the fact that the energy for formaldehyde is obtained in the gas phase.

Acknowledgments. We thank the Army Research Office (Durham) and the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. Informative discussions with Professors N. J. Turro and P. J. Wagner are gratefully acknowledged.

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(10) If the singlet–triplet splittings of the two carbonyl species are similar, the calculated distribution will be valid, even though the S_1 process is important.

(11) J. C. D. Brand and D. G. Williamson, *Advan. Phys. Org. Chem.*, 1, 365 (1963).

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Electron Paramagnetic Resonance of Free Radicals in an Adamantane Matrix. V. Neutral Alkylhydrazyl Radicals

Sir:

We would like to report the first epr detection of neutral alkylhydrazyl free radicals, $R_2N\dot{N}H$, which we have prepared by room temperature X irradiation of the corresponding alkylhydrazines trapped in an adamantane matrix.[1] Although DPPH (α,α-diphenyl-

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(1) D. E. Wood, R. V. Lloyd, and W. A. Lathan, *J. Amer. Chem. Soc.*, **93**, 4145 (1971), and references contained therein.

Table I. Hyperfine Splitting Constants (hfs) of Alkylhydrazyl Radicals (gauss)

Radical	Temp, °C[b]	H_1	H_β	N_1[a]	N_2
$(CH_2)_6N\dot{N}H$	RT	13.7	4.8	10.6	9.9
$(CH_2)_4N\dot{N}H$	60	13.4	10.6	10.6	10.6
	−34	13.3	11.7	9.9	9.5
$(CH_3)_2N\dot{N}H$	RT	13.6	6.7	11.4	9.6

[a] As it is not known which hfs belongs to N_1, the larger value is assigned for convenience. [b] RT = room temperature.

Table II. INDO, 4-31G, and STO-3G Energy Optimization Results

Radical	hfs, G					π-orbital spin density		Bond angles, deg			Bond lengths, Å			
	H_1	H_2	H_3	N_1	N_2	N_1	N_2	α	β	γ	A	B	C	D
$(CH_3)_2N\dot{N}H$[a] INDO	−16.3	5.9[b]	4.7[b]	9.8	3.9	0.74	0.23	109	126	116	1.08	1.30	1.41	1.41
$H_2N\dot{N}H$ INDO	−14.6	−9.2	−9.3	10.2	5.4	0.73	0.27	108	126	119	1.08	1.29	1.07	1.07
$H_2N\dot{N}H$[c] 4-31G	−14.2	−6.1	−6.4	10.8	3.7	0.79	0.21	108	124	116	1.01	1.36	0.990	0.987
$H_2N\dot{N}H$[d] STO-3G	−19.1	+4.6	+22.2	10.6	8.4			102	110	107	1.06	1.44	1.04	1.04

[a] The methyl groups were constrained to be tetrahedral and the optimized CH bond length is 1.12 Å. [b] Average hfs for the three methyl protons. [c] The hfs and spin densities were calculated by INDO using the geometry predicted by 4-31G. [d] The hfs were calculated by INDO using the geometry predicted by STO-3G; the radical is nonplanar with $\delta = 106°$ and the $H_1N_1N_2H_3$ dihedral angle = 165°.

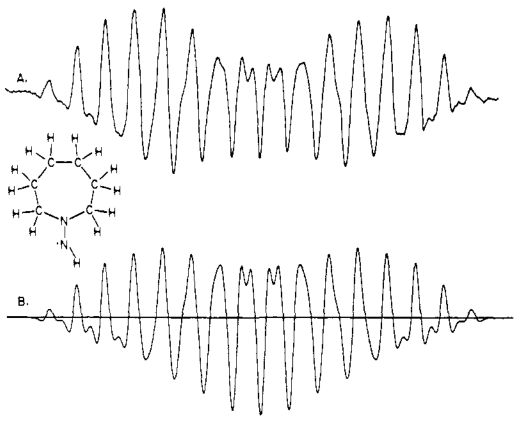

Figure 1. Second derivative epr spectrum of the radical from *N*-aminohexamethylenimine in adamantane at room temperature (A) and its computer simulation (B).

β-picrylhydrazyl) is a stable free radical, its nonaromatic derivatives are presently known only as unstable transients in gas-phase electrodeless discharge,[2] in molecular beam reactions of hydrazines with oxygen and hydrogen atoms,[3] and most recently in aqueous-phase pulse radiolysis.[4] Alkylhydrazyl radicals represent an extremely interesting species from the point of view of molecular orbital theory since they possess both a three electron π bond and a lone pair on nitrogen. They are also isoelectronic with hydrazine cation radicals and aminoalkyl radicals. It is interesting to note that whereas the tetraalkylhydrazine cation radicals[5] and the aminoalkyl radicals[6] are apparently nonplanar, the parent hydrazine cation radical $H_2NNH_2^+$ is thought to be planar.[7] The present results are significant because they not only give direct experimental information concerning the structure of hydrazyl radicals but also yield information on decomposition mechanisms of hydrazines in condensed phases.

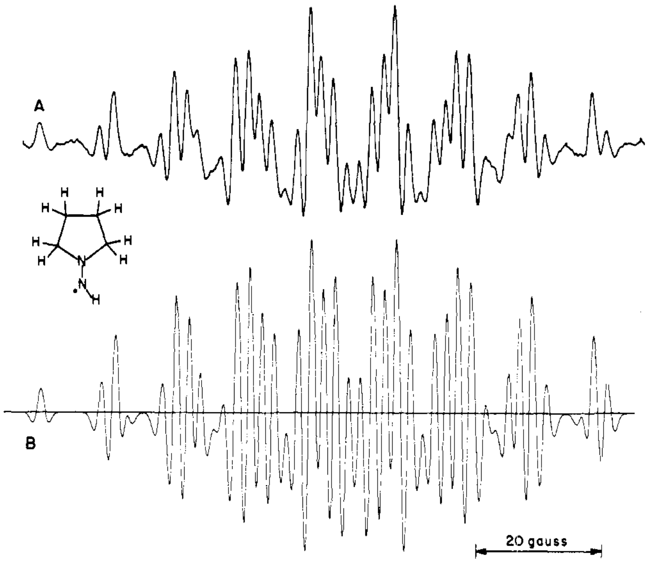

Figure 2. Second derivative epr spectrum of the radical from *N*-aminopyrrolidine in adamantane at −34° (A) and its computer simulation (B).

Experimental epr spectra (A) from *N*-aminohexamethylenimine and *N*-aminopyrrolidine in adamantane are compared with their computer simulations (B) in Figures 1 and 2 (see Table I). The *g* values of these radicals at room temperature are all the same as that of DPPH (2.0036). The five- and seven-member ring radicals have four equivalent β protons with large temperature dependencies; this is indicative of rapid ring inversion. The smaller value for the seven-member ring is a result of its preferred conformation giving less overlap of the β protons with the orbital on N_2. This explanation is suggested by consideration of models for the two cases. The six-member ring radical (not included in Table I) exhibits line-width alternation as a result of its greater barrier to inversion than the others. The temperature dependence of the β protons in the UDMH radical is an order of magnitude less than in the ring radicals indicating free rotation of the methyl groups. However, all of these radicals exhibit large temperature dependencies in their ^{14}N hfs. This result contrasts sharply with the relative lack of temperature dependence found for arylhydrazyl radicals.[8]

Energy optimizations of the parent hydrazyl radical

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(3) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **53**, 4377 (1970).

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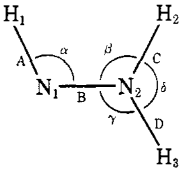
(5) S. F. Nelsen and P. J. Hintz, *ibid.*, **93**, 7105 (1971).

(6) D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **53**, 3932 (1970).

(7) O. Edlund, A. Lund, and Å. Nilsson, *ibid.*, **49**, 749 (1968); C. L. Marquardt, *ibid.*, **53**, 3248 (1970); M. H. Reilly and C. L. Marquardt, *ibid.*, **53**, 3257 (1970).

(8) M. Erö-Gécs and M.-M. Hegyhâti, *ibid.*, **55**, 2561 (1971).

by both INDO[9] and 4-31G[10] and of the UDMH radical by INDO yield planar geometries. However, STO-3G[11] predicts a nonplanar hydrazine-like structure with a 6 kcal/mol barrier at the optimized planar geometry (I and Table II).



I

The planar species are π radicals with the unpaired electron in an antibonding orbital unequally shared by N_1 and N_2 and with essentially zero spin density in the in-plane lone-pair orbital on N_1. The nonplanar radical predicted by STO-3G is also a π radical but with the unpaired electron localized in a p orbital of N_1; this results in the much longer NN bond length and the positive hfs of H_2 and H_3 which is characteristic of β protons. The calculated hfs for the protons in the planar radicals are in good agreement with the experimental values, but the large difference predicted for N_1 and N_2 is not observed. The nonplanar STO-3G geometry, however, yields ^{14}N hfs values in much better agreement with experiment.

Large vibronic interactions in the neutral alkylhydrazyl radicals are suggested by the temperature dependencies of the ^{14}N hfs and by the appearance of C_{2v} symmetry on the epr time scale. Thus, the observed equivalence of the β-proton hfs requires either vinylic inversion[12] of H_1 or rotation of H_1 about the N–N bond plus rapid inversion at N_2 if nonplanarity exists at that site. However, experimental measurements on more alkylhydrazyl radicals and particularly on the parent hydrazyl radical must be made before the geometric and electronic structure can be stated with assurance.

Our observation of hydrazyl radicals rather than amino radicals upon the X irradiation of hydrazines indicates that a different mechanism operates for the decomposition of hydrazines in the condensed phase under ionizing radiation, where there is N–H bond scission, than in gas-phase flash photolysis,[13] electrodeless discharge,[2] or very low pressure pyrrolysis[14] where N–N bond scission primarily occurs. This difference may be partially the result of a cage effect causing recombination to be preferred over diffusion apart of the amino radicals resulting from possible N–N bond scission. However, recent evidence has been obtained that the hydrazyl radicals are formed by dissociation of the cation radicals of the hydrazine precursors which are actually the initial species formed in the radiation damage.[15]

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A Novel Photochemical Rearrangement of Aryl-6,7-dioxabicyclo[3.2.2]nona-3,8-dien-2-one into Tricyclic Lactone[1]

Sir:

Recently much interest has arisen in the photochemistry of 2,5-dienone (enone–π-methane) compounds. We wish to report a new photochemical rearrangement of 1- and 3-aryl-6,7-dioxabicyclo[3.2.2]-nona-3,8-dien-2-ones (II and II′), dioxy analogs of bicyclo[3.2.2]nona-3,6-dienone, into tricyclic lactones (III and III′, respectively), in which either the enone–π interaction or the cleavage of the O–O bond in II and II′ is considered to initiate the reaction. The rearrangement discovered in this study may be interesting not only in connection with enone–π-methane[2–5] but also for epidioxide chemistry.[6–8]

In contrast to the fact that I[9] did not give a clean photoproduct, photolysis of an acetone solution of a mixture of IIa and IIa′ (2.2:1)[10] with a high-pressure mercury lamp through a Pyrex filter[11] under a nitrogen atmosphere, followed by silica gel chromatography, afforded a crystalline compound IIIa,[12] mp 169°, in 15.3% yield, and a trace of IIIa′. The structure of IIIa was assigned on the basis of the following evidence: ν_{CO} (KBr) 1783 cm^{-1}; λ_{max}^{EtOH} (log ε) 267 (4.26) mμ;

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(1) A part of this work was presented at the 3rd International Congress of Heterocyclic Chemistry, Sendai, Japan, Aug 1971; Abstracts, p 167.

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(10) A mixture of epidioxides II and II′ was obtained by the sensitization reaction of oxygen with 2-aryltropone in quantitative yield. The structure of the epidioxides was confirmed by comparison of spectral data with I[9] and VI.[14] The ratio of II and II′ in the mixture was estimated by the proton areas of H_3 for II and H_1 for II′ in the nmr spectrum.

(11) The Pyrex filter used in this study transmits light at a longer wavelength than 2800 Å. In one photolysis run of a mixture of IIa and IIa′, ethanol was used as a solvent, in which the same tricyclic lactone (IIIa) was obtained. We consider that the energy transfer from the excited acetone to II and II′ is not a necessary factor for the reaction.

(12) All new crystalline compounds in this communication gave satisfactory elemental analyses.