These results coupled with those of Chapman[9] indicate that photoisomerization of conjugated ketones to cyclopropanones may be a common path at room temperature as well as at low temperature.

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tion of cyclopropanones when irradiations were conducted using light of λ 300–360 nm.

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Generation of Pyridyl Radicals by Dissociative Electron Capture in Argon Matrices

Sir:

The matrix isolation technique consisting of the trapping of reactive species in a solid gas matrix at near liquid helium temperature, is generally thought to be applicable only to electrically neutral species. We have shown recently that photoirradiation of an argon matrix containing both electron-donating and electron-accepting species could lead to the generation of charged species effectively isolated within the matrix.[1,2] This technique has been successfully applied to generate singly ionized atomic species[1] as well as molecular anions.[2] In this communication we would like to report on the electron spin resonance spectra of 2-, 3-, and 4-pyridyl radicals generated within an argon matrix at near 4°K from the corresponding pyridyl halides by the process of dissociative electron capture. Generation of neutral radicals in a rare gas matrix through the process of dissociative electron capture demonstrates further utility of the electron-transfer techniques.

The design of the dewar and an X-band esr spectrometer system which allows the trapping of reactive species and measurement of their esr spectra has been previously described.[3] In this particular series of experiments, Na atoms were vaporized from a resistively heated stainless-steel cell and were trapped together with iodo- (or bromo-) pyridine in an argon matrix. The mole ratio of Na:pyridyl halide:argon was estimated to be roughly 1:10:1000. The matrix thus prepared was examined for its esr spectrum before and after the photoirradiation. A high-pressure mercury lamp (GE AH-6) combined with an appropriate filter was the light source and the irradiation lasted for 10 min.

Prior to the photoexcitation, the esr spectrum of the matrix consisted of a strong, sharp quartet due to Na atoms ($I = {}^3/_2$, $A \cong 330$ G) and a weak broad signal centered about the position corresponding to $g = 2.0$. Irradiation of the matrix using a sharp-cutoff filter (Corning 3-70) which cut off all the light below 5000 Å resulted in a complete disappearance of the Na signals, and a several-fold increase of the signal at $g = 2.0$. It should be emphasized that no change in the spectrum occurs when a matrix containing Na atoms or pyridyl halide alone is irradiated with such light. Figures 1–3 show the spectra obtained after the photoirradiation using 2-bromo-, 3-iodo-, and 4-iodopyridine, respectively. We propose that the following reaction sequence occurs under the photoexcitation,

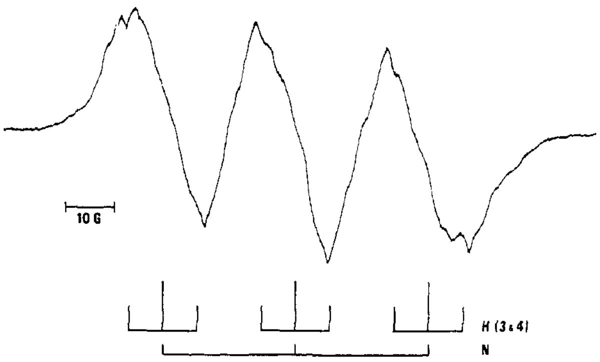

Figure 1. Esr spectrum observed after photoirradiation of an argon matrix containing Na atoms and 2-bromopyridine. Shown below is the spectrum pattern of 2-pyridyl radical calculated by INDO.

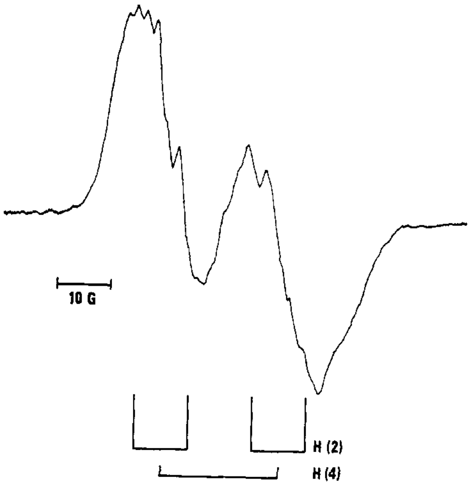

Figure 2. Esr spectrum observed after photoirradiation of an argon matrix containing Na atoms and 3-iodopyridine. Shown below is the spectrum pattern of 3-pyridyl radical predicted by INDO.

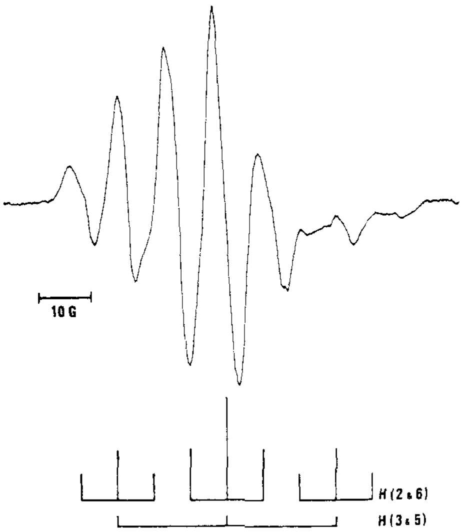

Figure 3. Esr spectrum observed after photoirradiation of an argon matrix containing Na atoms and 4-iodopyridine. Shown below is the spectrum pattern of 4-pyridyl radical predicted by INDO.

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and the spectra in Figures 1–3 are due to 2-, 3-, and 4-pyridyl radicals, respectively. The plausibility of the an-

$$\begin{array}{l} \mathrm{Na} + \mathrm{PyX} \xrightarrow[\lambda\ >5000\ \text{Å}]{h\nu} \mathrm{Na}^+ + [\mathrm{PyX}^-] \\ \hphantom{\mathrm{Na} + \mathrm{PyX} \xrightarrow[\lambda\ >5000\ \text{Å}]{h\nu} \mathrm{Na}^+ + [\mathrm{Py}}\downarrow \\ \hphantom{\mathrm{Na} + \mathrm{PyX} \xrightarrow[\lambda\ >5000\ \text{Å}]{h\nu} \mathrm{Na}^+ +{}} \mathrm{Py}\cdot + \mathrm{X}^- \end{array}$$

ion formation under the circumstance has been already demonstrated.[2] The splittings resolved in Figures 1–3, however, suggest hyperfine coupling interactions which are much larger than those expected for an anionic π radical. They can be easily understood if it were a σ radical, Py·, resulting from a spontaneous decomposition of the anion as indicated above.

Depicted below the observed spectra in Figures 1–3 are the spectral patterns of the pyridyl radicals calculated by the INDO molecular orbital theory.[4] The general agreement between the calculated pattern and the observed spectra strongly substantiates our proposed assignments. Thus the triplet pattern with a spacing of 27 G seen with 2-pyridyl radical (Figure 1) is attributed to the hyperfine structures (hfs) due to the ^{14}N nucleus, and the doublet pattern of 22 G separation observed with 3-pyridyl radical is assigned to the hfs with the 4 proton. As expected, the triplet-of-triplets pattern observed with 4-pyridyl radical (Figure 3) is very similar to that observed with phenyl radical.[5] The larger triplet with a spacing of 19 G is assigned to the hfs with the 3 and 5 protons, and the smaller triplet of 9 G to the 2 and 6 protons.

No explicit attempt to generate pyridyl radicals in order to examine their esr spectra has been reported previously. The esr signal detected in γ-irradiated solid pyridine was initially assigned to pyridine cations,[6,7] but was later reinterpreted as arising from 2-pyridyl radicals.[8] Our present result strongly supports the latter assignment.

In our earlier attempts to generate pyridyl radicals by direct uv photolysis (λ <4000 Å) of pyridyl iodides, we observed only the radicals which can only result from a process involving a rupture of the aromatic ring. Corresponding irradiation of a matrix containing pyridyl radicals generated by the photoelectron transfer process led to disappearance of the spectrum reported here and appearance of the spectrum identical with that obtained by direct photolysis. Thus the rupturing of the ring appears to be a result of a photolytic process imposed on pyridyl radicals. Detailed analysis of the esr spectra of the pyridyl radicals and their photolysis sequence under uv irradiation will be reported soon.

Acknowledgments. We thank Dr. L. Skattebøl for his synthesis of 4-iodopyridine used in this study.

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A New Quenching Mechanism of the (π–π*) Ketone Triplet State

Sir:

We herein wish to describe some unusual observations encountered during a photochemical study of 1-benzoyl-8-benzylnaphthalene (**1**).[1] Photolysis (366 nm)[2] of **1** ($\epsilon_{366\ \mathrm{nm}}$ 140) in degassed[3] benzene solution (9.5×10^{-2} *M*) gave, in an extremely clean reaction, a 1.4:1 mixture of the alcohols **2** (mp 110–115°) and **3** (mp 147–148°), respectively (91% isolated yield).[4] A quantum yield of 0.30 was obtained for the reaction at 7% conversion.[5] The structures of **2** and **3** were confirmed not only by their well-defined nmr and mass spectra but also by their facile acid-catalyzed dehydration into the hydrocarbon 1,2-diphenylacenaphthylene.[6]

Ketone **1** sensitizes the isomerization of *trans*- to *cis*-stilbene. In addition, the photoreaction of **1** (formation of **2** and **3**) is quenched by *trans*-stilbene as well as by oxygen. Using the benzophenone-sensitized isomerization of *trans*-stilbene as a standard,[7] the intersystem crossing efficiency of **1** was found to be unity. Stern–Volmer treatment of **1** using *trans*-stilbene as the quencher gave a linear plot with a slope of 5.4×10^4 M^{-1} (Figure 1). A limiting value of 9.3×10^4 sec^{-1} for k_r was determined from the expression $\Phi_0/\Phi_Q = [k_q/k_r][Q] + 1$, assuming $k_q = 5 \times 10^9$ l./mol sec.[8] This low value for k_r rules out reaction from either the excited singlet state of **1**[9] or a higher triplet state of **1**.[10]

Phosphoresence spectra of **1** have been measured at 77°K in several solvents.[11] A small bathochromic shift (characteristic of π–π* triplet states)[12] was observed for the 0–0 band of **1** on changing from methylcyclohexane to EPA glass. The spectra of **1** closely resemble those (recorded in the same solvents)[11] of 1-naphthyl phenyl ketone, a substance whose triplet state has been assigned the π–π* configuration.[13] Irradiation of ketone **1** at 77°K in either methylcyclohexane or EPA glasses leads to the formation of alcohols **2** and **3**. These data strongly suggest that the lowest

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(2) A water-cooled Hanovia Type L 450-W medium-pressure lamp fitted with Corning color filters 0-52 and 7-54 was employed as the 366-nm light source.

(3) All reactions were run in sealed Pyrex tubes degassed by four freeze–thaw cycles at 10^{-5} Torr.

(4) All melting points are uncorrected. Satisfactory analyses and spectral data were obtained for all new compounds.

(5) The actinometer used for these measurements was the 0.1 *M* benzophenone-sensitized isomerization of 0.1 *M trans*-stilbene. Several different quantum yields have been reported for this actinometer. We have chosen the value $\Phi = 0.56$ reported by H. A. Hammond, D. E. DeMayer, and J. H. R. Williams, *J. Amer. Chem. Soc.*, **91**, 5180 (1969). The same quantum yield was obtained for the photoconversion of 1 into 2 and 3 when methanol was used as the reaction solvent.

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(11) Luminescence spectra determinations were carried out at the Eastman Kodak Company Research Laboratories.

(12) For examples, see (a) H. McConnell, *J. Chem. Phys.*, **21**, 700 (1952); (b) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

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