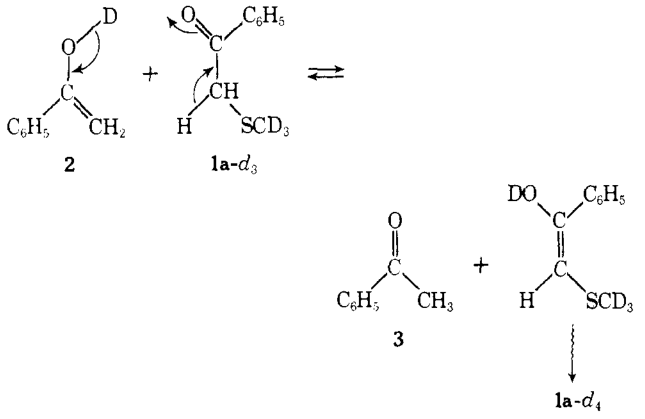
Scheme I



The nature of the excited state in the photolysis of **1a** and **1b** is not known, but it may be noted that if the triplet excited state is involved it must be very short-lived, since quenching by either oxygen or thioacetophenone was not observed.

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The Photochemistry of Bicyclo[3.2.0]hept-3-en-2-ones. Formation of 2-Cyclohexenecarboxylic Acid Derivatives[1]

Sir:

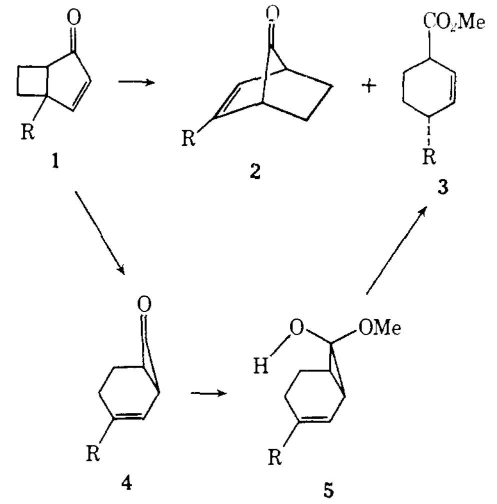
We have previously shown that irradiation of bicyclo[3.2.0]hept-3-en-2-one (**1a**) in pentane or in methylene chloride yields dimer(s) and 7-ketonorbornene **2a** and that the latter is formed *via* a nonconcerted path.[2] In this communication we report the conversion of bicycloheptenones **1a,b** into the methyl 2-cyclohexenecarboxylates **3a,b** as well as evidence which indicates the intermediacy of a cyclopropanone in this transformation.

Irradiation of **1a** (0.0672 *M* in methanol) gave **2a** (and the corresponding ketal), dimer(s), and **3a** (10–15%).[3] Identification of ester **3a** is based on its hydrogenation to methyl cyclohexanecarboxylate coupled with its nmr spectrum, which shows the presence of two vinyl hydrogens and differs from that of methyl 3-cyclohexenecarboxylate. Irradiation of **1b** (0.0156 *M* in methanol) gave **2b**, dimers, and **3b** (~15%). Ester **3b** was identified by comparison with an authentic sample of methyl *trans*-4-methyl-2-cyclohexenecarboxylate obtained from reduction of *p*-toluic acid.[4] No cis ester could be detected in the gas chromatogram of the product.

That esters **3a,b** do not arise from the 7-ketonorbornenes **2a,b** is inferred from the fact that (a) irradiation of **2a** in pentane or in methanol under the above conditions yields only recovered **2a**, and (b) addition of methanol to **2b** should give methyl 2- or 3-methyl-2-cyclohexenecarboxylate rather than **3b**. The stereospecific formation of **3b** is inconsistent with the intermediacy of a monocyclic ketene.

Irradiation of **1b** in deuteriomethanol containing a trace of deuteriosulfuric acid followed by dilution with ordinary water, extraction with pentane, and isolation by preparative glpc gave **3b** containing no deuterium (<5%).[6] Irradiation in ordinary methanol containing a trace of ordinary sulfuric acid, dilution with deuterium oxide, and isolation as above gave **3b** containing 23% of one deuterium at C-4, as evidenced by mass spectroscopy and partial collapse of the doublet at δ 0.97 to a singlet. These results require the intermediacy of a species containing one readily exchangeable hydrogen and may be accommodated in the following scheme: photoisomerization of **1** to the cyclopropanone **4**, immediate conversion of **4** to hemiketal **5** (attack on the less crowded face of the cyclopropanone),[7] and thermal isomerization of the hemiketal to the observed ester **3**.[8]

Efforts to firmly establish the intermediacy of **4** by irradiation of **2b** in pentane followed by addition of methanol and work-up, or by infrared spectroscopy using the technique of Chapman,[9] have been unsuccessful. Our efforts to isolate adducts of **4** are continuing.



a, R = H
b, R = CH_3

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[1] Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank the National Science Foundation for a grant toward the purchase of the mass spectrometer used in this work.

[2] R. L. Cargill, B. M. Gimarc, D. M. Pond, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Amer. Chem. Soc.*, **92**, 3809 (1970).

[3] (a) Changing the irradiation solvent from pentane to methanol had no significant effect on the yields of 2 and dimer. (b) These irradiations were carried out with a Hanovia 450-W mercury arc or with "blacklights" in Pyrex vessels and were worked up by dilution with water, extraction with pentane, drying, solvent distillation, and preparative glpc. The isolated yield of **3a** was 8.5%.

[4] The details of this two-stage reduction (lithium–ammonia) will be described in a full paper. Both cis and trans isomers of **3b** are obtained and are separable. Assignment of stereochemistry is based on catalytic hydrogenation of **3b** to the known *trans*-4-methylcyclohexanecarboxylic acid.[5]

[5] A. A. B. Kleis, A. A. Massier, D. Medema, P. E. Verkada, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **80**, 595 (1961).

[6] Irradiation of **1b** in methanol containing sulfuric acid followed by the described work-up gave **2b**, **3b**, and dimer(s) in the same yields obtained in the absence of the acid.

[7] N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

[8] The analogous intramolecular hydrogen transfer in the carene series, $\Delta H^{\ddagger}$ 27 kcal/mol, $\Delta S^{\ddagger}$ −17 eu, has been discussed: (a) G. Ohloff, *Tetrahedron Lett.*, 3795 (1965); (b) K. Gollnick, *ibid.*, 327 (1966); and K. Gollnick and G. Schade, *Tetrahedron*, **22**, 123 (1966).

[9] L. L. Barber, O. L. Chapman, and J. D. Lassila, *J. Amer. Chem. Soc.*, **91**, 3664 (1969). Chapman has noted the rapid photodecarbonyla-

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.

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-iodo-

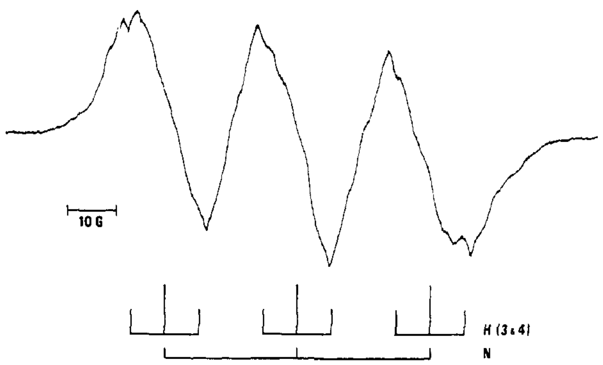

Figure 1. Esr spectrum observed after photoirradiation of an argon matrix containing Na atoms and 2-bromopyridine. Shown below is the spectrum pattern of 2-pyridyl radical calculated by INDO.

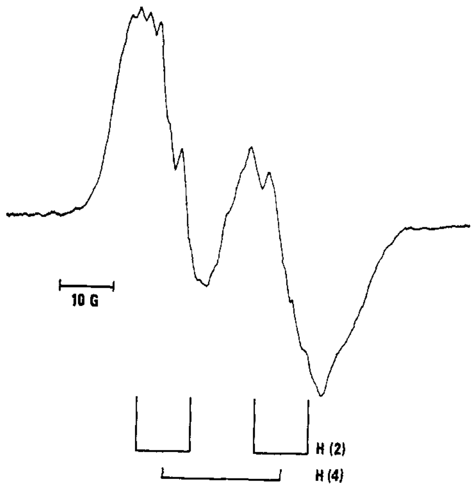

Figure 2. Esr spectrum observed after photoirradiation of an argon matrix containing Na atoms and 3-iodopyridine. Shown below is the spectrum pattern of 3-pyridyl radical predicted by INDO.

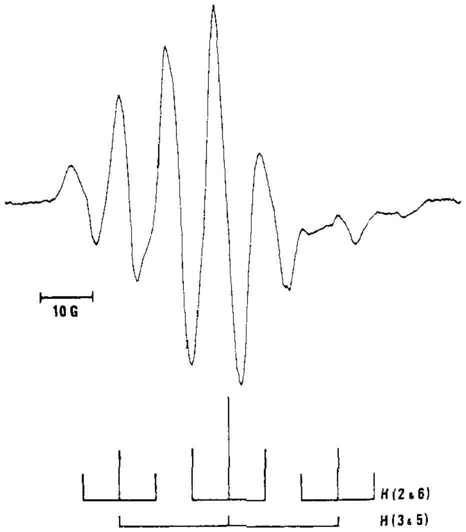

Figure 3. Esr spectrum observed after photoirradiation of an argon matrix containing Na atoms and 4-iodopyridine. Shown below is the spectrum pattern of 4-pyridyl radical predicted by INDO.

pyridine, respectively. We propose that the following reaction sequence occurs under the photoexcitation,

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(1) P. H. Kasai, *Phys. Rev. Lett.*, **21**, 67 (1968).

(2) P. H. Kasai and D. McLeod, *J. Chem. Phys.*, **51**, 1250 (1969).

(3) P. H. Kasai, E. B. Whipple, and W. Weltner, Jr., *ibid.*, **44**, 2581 (1966).