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Matrix Effect on the Photochemistry of Cyclopropyl Ketones. Photochemistry of the Triplet State of 2-Spirocyclopropyl-1-indanone at 77 K

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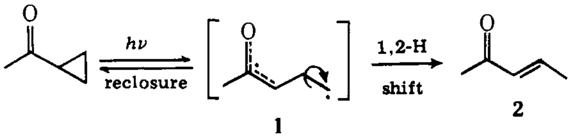
Abstract: The photochemistry of 2-spirocyclopropyl-1-indanone (spiro[cyclopropane-1,2′-[2*H*]inden]-1′(3′*H*)-one, **6**) was investigated in solution and in glass matrices at 77 K. Irradiation of **6** in methanol or benzene solution led to negligible reaction, while irradiation in methylcyclohexane or ethanol/methanol glasses at 77 K gave (*E*)-2-ethylidene-1-indanone. The decrease in the phosphorescence emission as a function of irradiation time and the quenching of both product formation and phosphorescence by piperylene indicated that the photoproduct is formed exclusively from the ^{3}n,π* state. The rate of disappearance of **6** was estimated from the change of the phosphorescence spectrum with time. This rate of disappearance during photolysis at 77 K was correlated with the incident light intensity and the process was found to be monophotonic. The luminescence of 2-spirocyclopropyl-1-indanone appears as multiplet phosphorescence with at least two components in methylcyclohexane, ethanol/methanol, or poly(methyl methacrylate) glasses at 77 K. In isopentane, on the other hand, the low-energy bands greatly predominated. These observations are attributed to emission from n,π* triplets held in various conformations.

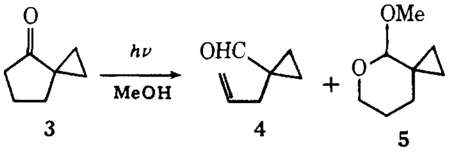
Introduction

The photochemical conversion of simple cyclopropyl ketones to propenyl ketones in the gas phase has been observed to occur from high vibrational levels of the singlet excited state.[1] Photoepimerization of cyclopropyl substituents via π*-assisted cyclopropane fission is also a well-established process,[2] occurring primarily from the triplet excited state. These transformations are accommodated mechanistically by invoking a biradical intermediate (**1**) as illustrated in eq 1. The biradical **1** can reclose to a cyclopropane with or without inversion of configuration at the radical centers or it can undergo a 1,2-hydrogen shift to give the conjugated acyclic ketone **2**.



(1)

The incorporation of the carbonyl group into a cyclic system as in spiro[2.4]heptan-4-one (**3**) can change the course of the photochemical reaction. Thus Crandall and Seidewand[3] showed that irradiation of **3** in methanol gave primary photoproducts **4** and **5** resulting not from isomerization of the cyclopropyl ring, but rather from α-cleavage at the other side of the carbonyl group. In spite of the fact that the geometry of the α-spirocyclopropyl and the carbonyl moieties might be expected to be optimal for interaction in **3**, no product from cyclopropyl ring fission was observed. Turro and co-workers[4,5] have made similar observations and have shown from rate and quantum yield measurements that the α-spirocyclopropyl substituent enhances the ring expansion of cyclopentanone. This was attributed to resonance stabilization of the acyl radical portion of the intermediate biradical leading to closer proximity of the alkyl radical center and the carbonyl oxygen.[6] The ring expansion was shown to occur exclusively from the triplet excited state.[4] Again no photoproduct due to cyclopropyl ring fission was observed.[7]



In the present study we have examined the photochemistry and spectroscopy of 2-spirocyclopropyl-1-indanone (**6**) in solution and in glass matrices. The objectives of the work were (1) to establish whether cyclopropyl ring fission will occur if α-cleavage at the other side of the carbonyl group is made difficult, (2) to assess the importance of the nature of the triplet state (n,π* vs. π,π*) in the π*-assisted cyclopropyl fission, and (3) to determine the effect of matrix isolation and low-temperature photolysis on the course of the chemical reaction.

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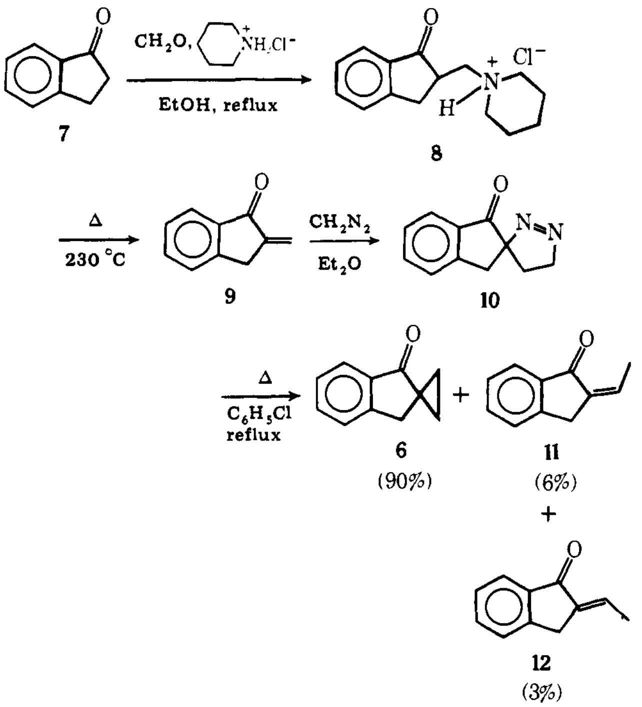
Scheme I



These studies have afforded answers to (1) and (3) but an answer to (2) awaits further work.

Experimental Section

All commercial chemicals employed were of reagent or spectral grade quality, and unless specified were used without further purification. Solution-phase irradiations were carried out in internally water-cooled quartz reactors at 25 °C with a Hanovia 450-W medium-pressure mercury lamp, and photolysis vessels were constructed of quartz. Glass matrix irradiations were carried out at 77 K; the photolysis vessels were thin quartz tubes immersed in a quartz Dewar flask filled with liquid nitrogen. The Dewar flask had quartz optical windows for irradiation with a 200-W high-pressure Xe lamp. All solutions were degassed and maintained under a nitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian T-60 NMR spectrometer; chemical shifts are reported in δ units downfield from tetramethylsilane as internal standard. Analytical gas chromatography was performed on a Perkin-Elmer F11 (hydrogen flame detector) chromatograph equipped with 6 ft × $\frac{1}{8}$ in. columns of 15% Carbowax 20M on 60-80 Chromosorb W (column A) or 5% poly 3A on Chromosorb W (column B). The optical absorption spectra were recorded on a Cary 17 spectrometer. The phosphorescence emission and excitation spectra were measured on a Perkin-Elmer MPF-4 spectrofluorimeter at 77 K, using the phosphorescence attachment equipped with rotating chopper; they were corrected with the Perkin-Elmer differential corrected spectra unit DCSU-2.

2-Spirocyclopropyl-1-indanone (6). This ketone was synthesized as shown in Scheme I.[8] 1-Indanone (**7**) was converted to 2-(piperidinomethyl)-1-indanone hydrochloride (**8**),[9] which on pyrolysis at 230 °C gave in good yield 2-methylene-1-indanone (**9**),[10] mp 22-24 °C (lit.[10] mp 22-24 °C). Treatment of **9** (6.00 g) in ether (100 mL) with ethereal diazomethane (from *N*-methyl-*N*-nitrosourea, ca. 2.0 g of CH_2N_2) until a permanent pale yellow coloration was obtained and evaporation of the solvent gave the pyrazoline **10** as a colorless solid in quantitative yield which was crystallized from ether/pentane: mp 57-58 °C; ν_{max} (CCl_4) 1710, 1600 cm^{-1}; $^{H}\delta$ 7.4-7.8 (m, 4 H), 4.68 (t, J = 7.5 Hz, 2 H), 3.62 (d, J = 17.5 Hz, 1 H), 3.15 (d, J = 17.5 Hz, 1 H), 1.9-2.4 (m, 2 H), 1.2-1.7 (m, 1 H). Pyrolysis of **10** in boiling chlorobenzene gave 2-spirocyclopropyl-1-indanone (**6**) in 90% yield, together with two byproducts, (*Z*)- and (*E*)-2-ethylidene-1-indanone (**11** and **12**)[11] (10%), in a 2:1 ratio. The ketone **6** was purified by chromatography on silica gel (100-200 mesh) with chloroform as eluent. The early fractions contained **11** and **12** followed by **6** which was crystallized from ether/pentane: mp 59-60 °C (lit.[8] mp 55-56 °C); ν_{max} (CCl_4) 1715 (sh), 1700 cm^{-1}; λ_{max} (methylcyclohexane) 350 nm (ϵ 10), 337 (20), 325 (40), 312 (53), 290 (2133), 281 (2588), 272 (2000); λ_{max} (methanol) 320 nm (ϵ 36), 292 (2615) 285 nm (2560); $^{H}\delta$ ($CDCl_3$) 7.3-7.8 (m, 4 H), 3.20 (s, 2 H), 1.2-1.4 (AA′BB′ m, 4 H). The purity of **6** was established by GLC analysis on both columns A and B.

Irradiation of 2-Spirocyclopropyl-1-indanone (6) in Methanol or Benzene. A solution of **6** (100 mg) in methanol or benzene (10 mL) was irradiated in a quartz tube and monitored by GLC (column A, column temperature 185 °C). Every 3 h an aliquot was withdrawn and the mixture was analyzed by GLC. The progress of the reaction was also monitored by UV and NMR spectroscopy. The total irradiation time was 72 h. Ketone **6** failed to undergo significant reaction. During the course of the irradiation in methanol only 5% of the starting material was consumed to give insoluble polymeric material. No change in the starting material concentration was observed after irradiation for 72 h in benzene.

Irradiation of 2-Spirocyclopropyl-1-indanone (6) in MCH or E/M Glasses at 77 K. A 10^{-3} M solution of **6** (0.5 mL) in methylcyclohexane (MCH) or a 4:1 mixture of ethanol and methanol (E/M) was irradiated at 77 K for 2 h. Upon subsequent warming of the glass to room temperature the photochemical reaction was monitored by GLC (column A, column temperature 185 °C). GLC analysis revealed the formation of (*E*)-2-ethylidene-1-indanone (**12**), which had the same UV and NMR spectra and GLC retention time as an authentic sample of **12.**[11] When a 1.5 × 10^{-2} M solution of **6** in E/M that was 2 M in piperylene was irradiated (λ >300 nm) under similar conditions product formation was quenched to the extent of 90% (under these conditions 98% of the radiation was absorbed by **6**); in the absence of piperylene, **12** was again formed.

Irradiation of 2-Spirocyclopropyl-1-indanone (6) in Isopentane at 77 K. A solution (0.65 × 10^{-3} M) of **6** in isopentane was irradiated at 77 K for 2 h alongside a similar solution in E/M. Analysis of the photolysis reaction mixtures showed the formation of only a trace amount (<0.1%) of **12** in isopentane solution compared with a 3% conversion in E/M solution. The solubility of the ketone **6** in isopentane was limited and the sample became cloudy on cooling, owing to the occurrence of precipitation.

Results

Photochemistry of 2-Spirocyclopropyl-1-indanone (6). Irradiation of a dilute solution of **6** in methanol or benzene at 25 °C with light wavelength >250 nm for up to 72 h gave no detectable product, apart from a small amount (~5%) of polymeric material formed in methanol only. Quantitative GLC analysis indicated no change in the starting ketone concentration during the course of irradiation in benzene. Similarly, irradiation of **6** in purified cyclohexene resulted in the formation of bicyclohexenyl and other products characteristic of sensitized triplet reactions of cyclohexene; however, the concentration of **6** was unchanged.

In order to obtain information on the excited state or states involved in this energy-wasting process and their reactivity the photochemistry and luminescence spectrum of **6** were examined in several glasses at 77 K. Glassy solutions of **6** in methylcyclohexane (MCH) or a 4:1 mixture of ethanol/methanol (E/M) were irradiated with light of wavelength >250 nm at 77 K. The area illuminated became slightly colored. When the solutions were subsequently warmed to room temperature, GLC analysis showed the formation of (*E*)-2-ethylidene-1-indanone (**12**). The GLC traces of an irradiation mixture and an authentic sample of **12** showed that **12** had the same retention time as the photochemical product. The progress of the photochemical reaction was also followed by UV spectroscopy. Figure 1 shows the UV absorption of **6** in E/M glass before irradiation and after irradiation at 77 K. Increased absorption in the 300-380-nm wavelength region corroborated the formation of an α,β-unsaturated ketone. Formation of this product was quenched by 2 M piperylene. Irradiation of **6** at 77 K in isopentane, which gives a much less viscous matrix compared to MCH or E/M, gave only trace amounts of **12.**

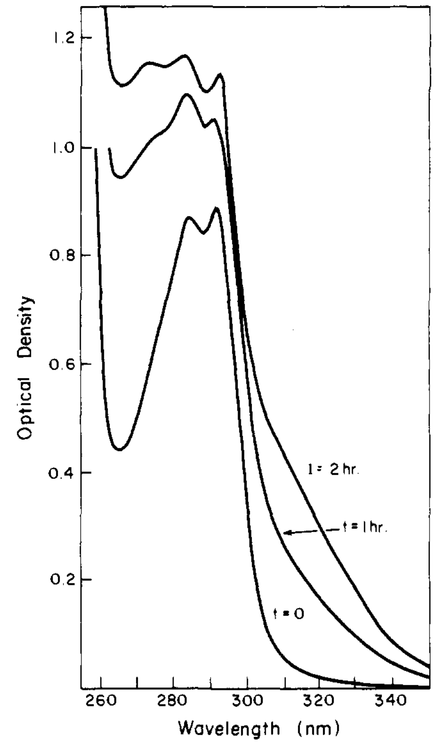


Figure 1. The ultraviolet absorption of **6** in alcohol before and after irradiation in glass at 77 K.

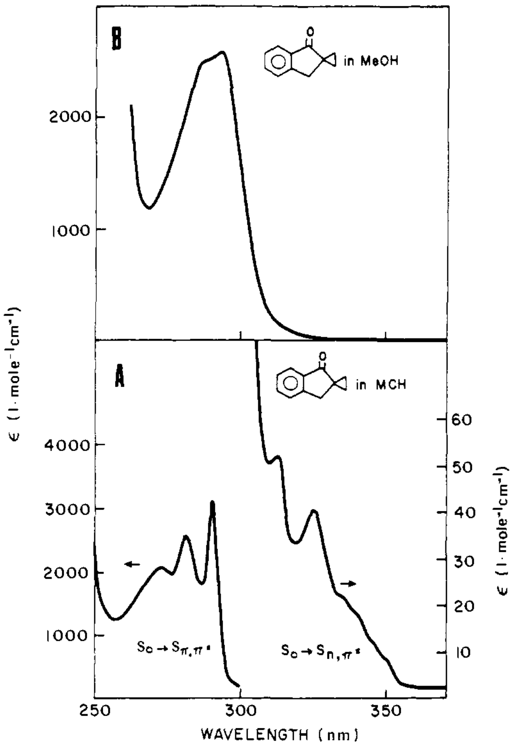
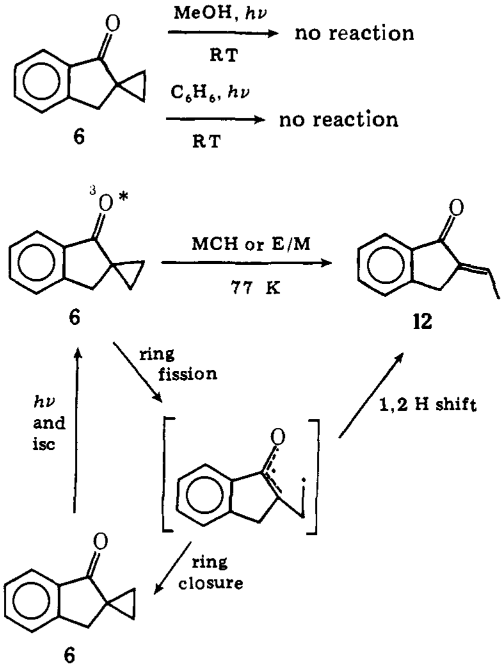


Figure 2. Absorption spectra of 2-spirocyclopropylindan-1-one in MCH (A) and MeOH (B).

Scheme II



The origin of the photochemical product, whether homogeneous sample or aggregate, is uncertain since some precipitation of the ketone unavoidably occurred on cooling.

Scheme II summarizes the results on the solution phase and glass matrix (77 K) photochemistry of **6**.

Optical Absorption and Emission Spectra. Figure 2 shows the absorption of 2-spirocyclopropyl-1-indanone (**6**) in MCH and methanolic solution. As can be seen from the figure, the weak, structured n,π^* transition band is apparent in MCH; however, it merges with the strong π,π^* transition band in methanolic solution. In general, the spectra are similar to those of 2,2-dimethylindanone and indanone.[12] The phosphorescence emission and excitation spectra of **6** in E/M and MCH glasses at 77 K are shown in Figure 3. The appearance of the emission spectrum is very similar in both solvents. The luminescence of **6** appears as multiple phosphorescence with at least two components in both solvents. There was no change in relative intensities of the various components as a function of rotating chopper speed, indicating that all have decay times (τ) greater than 1 ms. The dependence of this multiple phosphorescence on the viscosity of the matrix[13] was investigated in methylcyclohexane, ethanol/methanol, poly(methyl methacrylate) (PMMA), and isopentane. The 0-0 bands appeared at 376 and 405 nm for the two components in MCH, E/M, or PMMA and the entire spectra displayed vibrational structure with a spacing of 1650 cm^{-1}. This compares well with the stretching frequency of 1700 cm^{-1} found in the infrared spectrum of **6**. The excitation spectrum in both MCH and E/H was identical with the absorption spectrum of **6** and was independent of the monitoring wavelength. The phosphorescence of **6** in isopentane at 77 K, on the other hand, exhibited predominantly the low-energy part of the spectrum with the 0-0 band at 404 nm; a very weak contribution from the high-energy spectrum was still present.

Dependence of Phosphorescence Emission Intensity on Irradiation Time. The phosphorescence spectrum of **6** (10^{-2} M) in MCH at 77 K excited at 325 nm was monitored as a function of irradiation time, maintaining the spectrofluorimeter conditions constant. Figure 4 shows the dependence of the phosphorescence emission intensity of **6** in MCH glass at 77 K on the time of irradiation. A remarkable decrease in the phosphorescence intensity of **6** as a result of continuous irradiation was observed. Similar results were obtained by irradiation at 280 nm and also in an E/M polar glass. Phosphorescence, like product formation, was quenched by 2 M piperylene.

Light Intensity Dependence. The relative rate of disappearance of ketone **6** in the photolysis in a glass matrix was estimated by measuring the emission intensity as a function of irradiation time. The rate of disappearance of **6** at 77 K was found to be directly dependent on the light intensity (I_0). A reduction of the light intensity by a factor of 5 reduced the rate

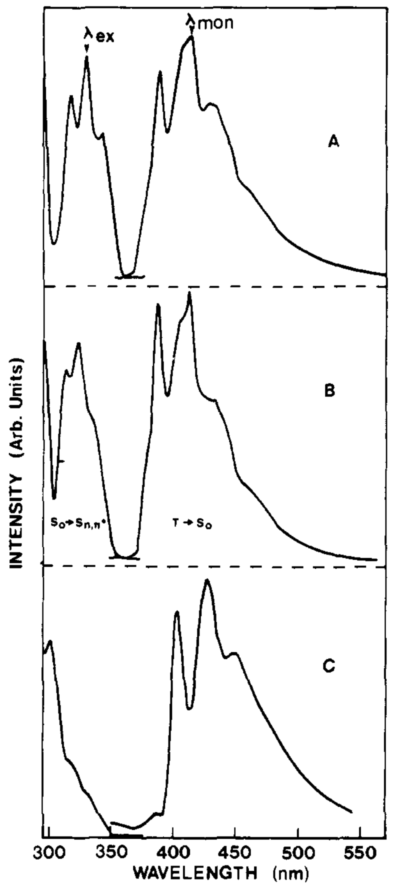


Figure 3. Phosphorescence emission and excitation of 2-spirocyclopropylindan-1-one at 77 K in MCH (A), a 4:1 mixture of ethanol/methanol (B), and isopentane (C).

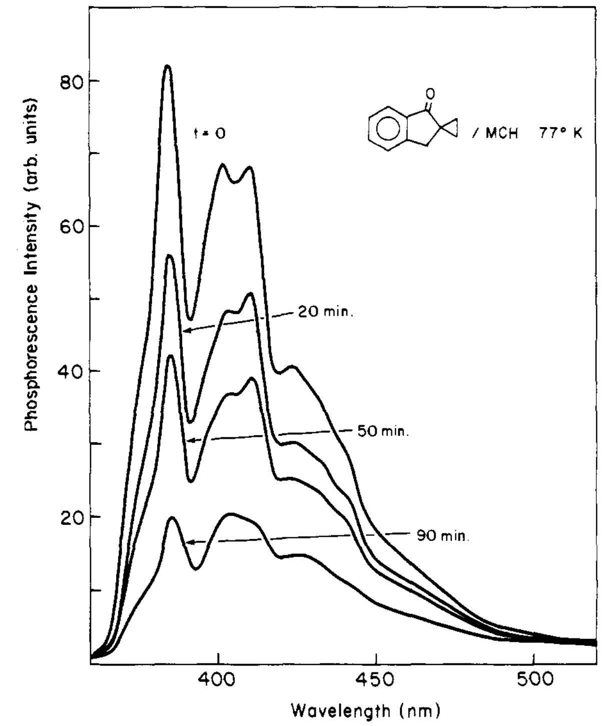


Figure 4. The phosphorescence emission of **6** in MCH at 77 K as a function of irradiation time (λ_{ex} 325 nm).

of disappearance of **6** by a factor of 4.6. Thus the photochemical reaction of **6** is taking place via a one-photon process from the lowest excited n,π^* triplet state.

Discussion

Perhaps the most striking finding is the observation of the photochemical conversion of 2-spirocyclopropyl-1-indanone to (*E*)-2-ethylidene-1-indanone in glass matrices but not in a solution. Few studies have been made of the photochemistry of ketones at low temperature,[14,15] but interest in photochemical reactions occurring from upper excited states has been mounting.[16]

Recently, it has been reported that benzaldehyde, acetophenone, and benzophenone undergo wavelength-dependent photochemistry in solid matrices at 77 K[15] and in the vapor phase,[17] but not in solution. The reactions in solid matrices take place via higher excited triplet states, formed by a biphotonic process, leading to α-cleavage. Similarly, photochemical reactions of naphthalene derivatives from upper triplet states populated by biphotonic excitation in rigid glasses at 77 K have also been reported.[18,19] In the present study we followed the rate of reaction of **6** during photolysis in a glass matrix at 77 K by monitoring the phosphorescence intensity (see Figure 4). First, the quenching of both the phosphorescence of **6** and the formation of **12** in an E/M glass by piperylene and second, the decrease in phosphorescence intensity of **6** as a function of irradiation time indicate that the emitting triplet is a precursor in the photochemical reaction, but do not eliminate the participation of an upper excited triplet formed from the emitting one. However, the direct dependence of the rate of reaction of **6** on light intensity shows that the photolysis of **6** in the solid matrix occurs from the lowest emitting, n,π^* triplet state via a monophotonic process. This conclusion is supported by the fact that the reaction rate is wavelength independent. These results are thus in contrast to previous work on ketones and aromatic molecules in solid matrices, where reactions occur from upper triplet states populated via biphotonic processes.

We now turn to the question of why **6** undergoes facile photoconversion to the α,β-unsaturated ketone **12** in a glass matrix while it is unusually photostable in solution. In order to assess the alternative consequences of excitation of **6** let us examine the relative energies of the triplet involved and the strength of potentially reactive bonds. The triplet energy of **6** determined from the phosphorescence 0–0 band is 75.9 kcal/mol, the carbonyl-phenyl bond strength is 97 kcal/mol, while the carbonyl-cyclopropyl bond strength is 82 kcal/mol. On the other hand, the energy required for cyclopropyl bond fission is 61 kcal/mol. Therefore, energetically one of the possible avenues for excitation energy dissipation is transfer to the cyclopropyl ring leading to bond rupture. The preferred conformation of **6** retains the favorable orthogonality of the carbonyl and cyclopropyl planes, but in the excited state the torsional angle is modified such that the π system overlaps efficiently with only one of the radial cyclopropyl bonds, It is thus possible that the cyclopropyl group is important in the chemistry of the majority of molecules that are excited, but the excitation energy is dissipated without chemical consequence. The epimerization studies by Zimmerman[2] demonstrate the potential reversibility of the ring-cleavage step. The relative rate of ring fission determines whether any competing reaction such as ring expansion will occur, and the rate of ring closure determines whether epimerization will result. The incorporation of an α-spirocyclopropyl substituent in cyclopentanone had no effect on the total quantum yield of the photochemical reaction of cyclopentanone,[4] indicating that the rate of cyclopropyl ring fission in this case must be less than $5 \times 10^8\ s^{-1}$, allowing efficient α-cleavage at the other side of the carbonyl group to occur in the normal fashion. The only effect the spirocyclopropyl ring has is stabilization of the acyl radical leading to formation of ring expansion product. In the present case, with all possible competing reactions eliminated on structural grounds ring fission probably occurs in solution, but the rate of ring closure is rapid, and the biradical returns to the starting material without any chemical consequence. Thus this material is a potential UV photostabilizer since it channels radiation energy efficiently to thermal energy without chemical change.[20]

In solid matrices little change is to be expected in the rate of ring fission since this is primarily dependent on the overlap between the chromophore (CO) and the acceptor cyclopropyl bond. Thus, irradiation should lead to the formation of the biradical at almost the same rate as in solution. For any process to compete with ring closure in the solid matrix it either should have an intrinsically lower activation energy or its activation energy must be lowered in the matrix owing to favorable conformations of the rigid molecules. The reaction involved here is 1,2 hydrogen migration. If this reaction had an intrinsically lower activation energy than ring closure, some migration product should have been observed at room temperature. The absence of such product formation in photolyses at room temperature could be explained if it is assumed that there is a much smaller Arrhenius factor for 1,2 hydrogen migration than for ring closure, which is not unreasonable to expect. The other possible explanation is that the molecules are frozen in conformations in the solid matrix that favor 1,2 hydrogen migration. Efficiency studies, stereochemical probes, and the temperature dependence of the rate of reaction should provide information regarding this possible rationalization for the difference in reactivity of **6** in solution and in solid matrices.

A point of spectroscopic importance concerns the observation of multiple phosphorescence from 2-spirocyclopropyl-1-indanone in several glass matrices. This molecule has no enolizable α hydrogen, which in this case eliminates Lim's proposal[12] of emission due to enol formation. Wagner and co-workers[13] reported dual phosphorescence from alkyl aromatic ketones, which was attributed to emission from $^3n,\pi^*$ excited states frozen in the ground-state conformation and from conformationally relaxed excited states. In evidence it was shown that the emission intensities of the various components are viscosity dependent. Similarily the phosphorescence of **6** in rigid glasses such as MCH, E/M, or PMMA at 77 K exhibited multiple emission, while in a less rigid glass (isopentane) it exhibited predominantly the low-energy part of the spectrum, in analogy with Wagner's observations.

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Carbanions, Electron Transfer vs. Proton Capture. 6. Determination of the Effect of Ion Pairing on the Electron-Transfer Equilibrium between Fluoradenide Ion and Nitrobenzene

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Abstract: Fluoradenide ion in methanol reacts with nitrobenzene in an endoergic electron-transfer equilibrium which is followed by a rate-determining, second-order loss of nitrobenzenide ion. The rate constant for the second process has been determined by directly measuring the decay rate of photochemically produced nitrobenzenide using ESR spectrometry. Combination of K_a measurements with rate constants for loss of fluoradenide and loss of nitrobenzenide allows calculation of the effect of reaction variables on the electron-transfer equilibrium constant. This method has been used to show that ion pairing, which can be detected spectroscopically for the carbanion, stabilizes this carbanion more than nitrobenzenide ion, driving the equilibrium toward carbanion. A similar effect is observed for the proton-transfer equilibrium. The phenomenon is explained in terms of competition between ion pairing and hydrogen bonding as a mode of carbanion stabilization in this protic, polar solvent.

In previous work, we have studied the competition for 9-methoxyfluorenide ion between $PhNO_2$ and methanol as a function of counterion.[1] In an attempt to remove the kinetic complications inherent in this system of low steady-state carbanion concentrations, we decided to study a stable carbanion for which proton capture was not a factor in determining electron-transfer efficiency. We were fortunate to find that the fluoradenide ion, FD^-, not only gives an electron-transfer re-

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