close proximity by the solid. Under these conditions weak interactions between stable products are potentially manifest.[7] A composite spectrum, constructed from spectra of the individually isolated components, need not be equivalent to the spectrum of the mixture photochemically generated under conditions of matrix isolation. Environmental influences on the spectra of matrix-isolated species are quite common.[7] Splitting of bands is a well-documented phenomenon.[7]

We believe that in all cases, **2**, **4-7**, photodecomposition leads to a pair of molecules in close proximity. We can offer at least two explanations for why the asymmetric bend of carbon dioxide could undergo an apparent splitting under the influence of the cofragment **1** without **3** being bound to **1**. With respect to nearest neighbor cyclobutadiene, the bending mode of **3** is nondegenerate. One arbitrary orientation of **1** and **3** is pictured below. In A, **3** bends perpendicular to the plane of **1**; in B, **3** bends in a plane parallel to **1**.[8]

In a second explanation for the twin bands, two different environments for **3** are envisaged. One, in which carbon dioxide is trapped in the same site as its cofragment ("intimate pair"); the other, corresponding to carbon dioxide occupying a site different from that of its cofragment ("host separated pair"). In the latter situation the spectrum of **3** should be less perturbed than in the former case. Two absorptions for the mode could thus arise. Hence, the controversial bands of photolyzed **2** are not uniquely rationalized by the proposal of a complex in which **3** serves as a ligand.[9,10]

It should be pointed out that a pair of bands in the 660-650-cm^{-1} region are a common feature of the spectrum of photolysate in which carbon dioxide has been generated by fragmentation, and are not unique to the bicyclopyranone system. We have observed such bands in a variety of studies including the photolyses of 1,3-oxazin-6-one[11a] **16** (in which hydrogen cyanide, acetylene, and carbon dioxide are produced) and vinylene carbonate **17**[11b] (in which ketene and carbon dioxide are among the products).

To date the bands at 1241 and 573 cm^{-1} are the only spectroscopic features unambiguously associated with matrix-isolated **1**.[1c,12-14] Although a number of interesting experiments[15-17] with derivatives of **1** possessing large, perturbing substituents have been described, these studies may have little bearing on the structure of the parent.[18] Since the singlet-triplet splitting of **1** is expected to be small[19] and subject to influences of substituents, conclusions concerning the structure of the parent **1**, extrapolated from studies of substituted cyclobutadienes, should be treated with reserve.

A clear expression of the properties of the parent should be derived from study of a species unencumbered by substituents, and free of the influence of neighboring molecules.

Acknowledgment. A Frederick Gardner Cottrell Grant from the Research Corporation, financial support from the National Science Foundation, from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from the research foundation of the State University of New York, and a NATO Senior Fellowship to A. Krantz are gratefully acknowledged.

References and Notes

(1) (a) C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972); (b) A. Krantz, C. Y. Lin, and M. D. Newton, *J. Am. Chem. Soc.*, **95**, 2744 (1973); (c) S. Masamune, M. Suda, H. Ona, and L. M. Leichter, *J. Chem. Soc., Chem. Commun.*, 1268 (1972).

(2) (a) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 614 (1973). (b) O. L. Chapman, D. De La Cruz, R. Roth, and J. Pacansky, *ibid.*, 1337 (1973). (c) Slight differences in calibration of spectrophotometers lead to slight differences in reported values. For example Maier[3] reports the 1245- and 575-cm^{-1} bands from the photolysis of pyridine as 1240 and 570 cm^{-1}.

(3) (a) G. Maier, H.-G. Hartan, and T. Sayrac, *Angew. Chem., Int. Ed. Engl.*, **15**, 226 (1976), and references therein; (b) G. Maier, W. Mayer, C. Haake, and R. Askani, *ibid.*, **12**, 1016 (1973).

(4) The band positions were measured using a Perkin-Elmer 180 spectrophotometer which has allowed us to make a more accurate determination than had been previously reported.

(5) In the gas phase ν_2 of carbon dioxide and [^{13}C]carbon dioxide absorb at 673 and 654 cm^{-1}, respectively. M. A. Pariseau, I. Suzuki, and J. Overend, *J. Chem. Phys.* **42**, 2335 (1965).

(6) Under high resolution conditions this band can be shown to consist of three absorptions. Upon annealing at 35 K two of these absorptions (575, 577 cm^{-1}) are invariant whereas the third (572 cm^{-1}) is replaced by a band at 568 cm^{-1}. Although the origin of these effects is still to be determined we note that the out-of-plane bending mode because of its larger amplitude of vibration should be more sensitive to environmental effects than the framework distortion at 1241 cm^{-1}.

(7) (a) B. M. Chadwick, *Spec. Period. Rep., Mol. Spectrosc.*, **3**, 281 (1975); (b) B. Meyer, "Low Temperature Spectroscopy", American Elsevier, New York, N.Y., 1971; (c) H. E. Hallam, Ed., "Vibrational Spectroscopy of Trapped Species", Wiley, London, 1973.

(8) The splitting of the 1241-cm^{-1} band in the case of photolyzed **5** can also be rationalized by such effects. For example cyclobutadiene can be viewed as occupying either the inside or outside of a sandwich composed of carbon dioxide, carbon monoxide, and **1**.

(9) The absence of evidence indicative of a strong interaction between **3** and **1** does not mean, of course, that there are no interactions between the pair as it is entirely possible that weak van der Waals molecules are formed.

(10) Rather than being due to an attraction between **3** and **1**, the splitting could conceivably result from a repulsion.

(11) (a) A. Krantz and B. Hoppe, *J. Am. Chem. Soc.*, **97**, 6590 (1975); (b) R. G. S. Pong, unpublished results.

(12) Although absorption in the visible spectrum at λ_{max} 410 nm has been noted during the photolysis of **2**, this band is still observed in matrices heavily doped with oxygen, under conditions where cyclobutadiene bands are not detectable: C. Y. Lin, unpublished observations.

(13) Previously reported[1c,14] values for the electronic spectrum of **1** cannot be reproduced using noble gas matrices[3a] as host for **1**.

(14) G. Maier and B. Hoppe, *Tetrahedron Lett.*, 861 (1973).

(15) (a) S. Masamune, N. Nakamura, M. Suda, and H. Ona, *J. Am. Chem. Soc.*, **95**, 8481 (1973); (b) L. T. Delbaere, M. N. G. James, N. Nakamura, and S. Masamune, *ibid.*, **97**, 1973 (1975).

(16) G. Maier and A. Alzerreca, *Agnew. Chem., Int. Ed. Engl.*, **12**, 1015 (1973).

(17) H. Kimling and A. Krebs, *Angew. Chem., Int. Ed. Engl.*, 11, 932 (1972).

(18) See also the very interesting study of the tetrafluoro species by M. J. Gerace, D. M. Lemal, and H. Ertl, *J. Am. Chem. Soc.*, **97**, 5584 (1975).

(19) See M. J. S. Dewar and H. W. Kollmar, *J. Am. Chem. Soc.*, **97**, 2933 (1975), and references therein.

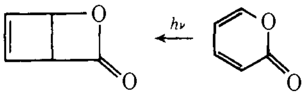
R. G. S. Pong, B.-S. Huang, J. Laureni, A. Krantz*
Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794

Received September 28, 1976

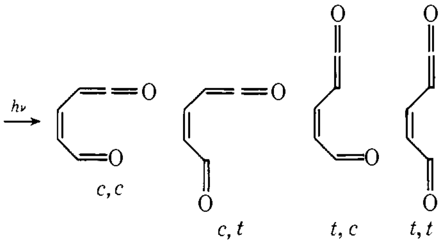
A Degenerate Process in the Photoirradiation of Matrix-Isolated α-Pyrone

Sir:

Studies of α-pyrone **1** have yielded a rich harvest of interesting chemistry.[1-8] Corey[1] recognized the potential of α-pyrone (**1**) as a means of entry, through its photoisomer bicyclopyranone (**3**), to the cyclobutadiene system. Rapidly reversible ring opening of 2-pyrones can be induced photochemically[2,6b] or thermally;[3,5] at high temperatures, 2-pyrones bearing hydrogen at the 6 position exchange substituents between the 3 and 5 positions. Pirkle has presented evidence which strongly supports the notion that the exchange reaction involves reversible [1,5]sigmatropic shifts of the aldehydic hydrogen of aldoketene intermediates.[3,5] Argon matrix-isolated **1** undergoes photochemical conversion to a set of four aldoketene conformers[6-8] (**2**) which relax thermally, to a new ratio,[7] at temperatures as low as 35 K. α-Pyrone[6a,7] has also been described as a precursor to bicyclopyranone (**3**) under conditions of matrix isolation at cryogenic temperatures, although the photoconversion is not strictly quantitative owing



3 **1**



2

to the presence of residual aldoketenes and products derived from them. Apparently, a photostationary state between α-pyrone and aldoketene conformers is set up which is eventually displaced in favor of the bicyclopyranone.[6,9]

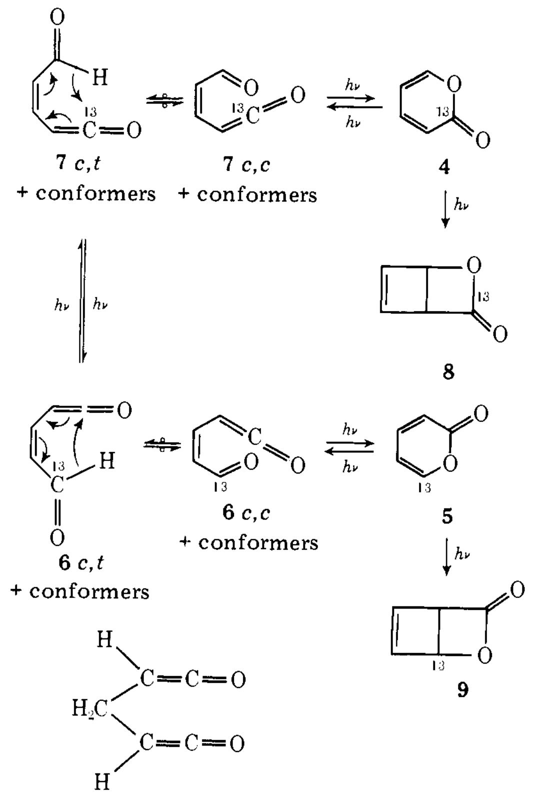
In this context we wish to point out our observations with matrix-isolated [2- and 6-^{13}C]-α-pyrone, **4** and **5**, respectively. [2-^{13}C]-α-Pyrone **4** was synthesized by the method of Nakagawa et al.,[10] using [1-^{13}C]vinylacetic acid prepared[11] from [^{13}C]carbon dioxide (90 atom % ^{13}C) and allylmagnesium bromide. [6-^{13}C]-α-Pyrone **5** was synthesized by the same sequence with [^{13}C]paraformaldehyde (90 atom % ^{13}C, purchased from Merck and Co. Inc., Teterboro, N.J.) as the source of the label. When either of the isomers **4** or **5** was irradiated at 8 K in argon with ultraviolet light (λ = 2750-3200 Å), the preparation of a specifically labeled bicyclopyranone was sabotaged by redistribution of the ^{13}C label between the 2 and 6 positions of the ring. Chapman et al.,[9b] on the other hand, have claimed that specifically labeled monodeuterio and vicinal dideuteriobicyclopyranones were prepared from the corresponding α-pyrones, but their photolytic conditions were not specified. In our hands, the four aldoketene conformers ($\nu_{C={}^{13}C=O}$ 2068, 2074, 2081 and 2089 cm^{-1}) initially generated from **4**, are rapidly equilibrated photochemically with an additional set of four absorbing at $\nu_{C=C=O}$ 2121, 2129, 2133 and 2136 cm^{-1}.

For the aldoketenes, the relative rate of redistribution of the ^{13}C label to ring closure (α-pyrone formation) is a wavelength dependent process, related perhaps to the concentration and photochemical reactivity of aldoketene conformers *c, c* and *c, t*. With light of λ = 2350-2700 Å, redistribution of the label in α-pyrone is demonstrably less rapid than in the aldoketenes, but apparently occurs faster than equilibration of the label between the 2 and 6 positions of bicyclopyranone.

The photochemical events which give rise to the spectroscopic phenomena described above are depicted in Scheme I. The direct conversion of **7** to **8** (or **6** to **9**) as a major process is incompatible with the rates of equilibration of the ^{13}C label observed for the components of this system. Initially, bicyclopyranones reflect the degree of equilibration of the label in α-pyrone and not that observed in the aldoketenes. Equilibration of the label between aldoketenes **6** and **7** is probably mediated by a 1,5-hydrogen shift, which shuttles the aldehydic hydrogen between the terminal carbon atoms,[12] there being no evidence for the alternative path involving successive [1,3]sigmatropic shifts of hydrogen, and the bisketene (**10**).

Irradiation of [2-^{13}C]-α-pyrone[13] **4** in ether at −10 °C using Corey's procedure,[1] produces specifically labeled bicyclopyranone **8**. Similarly **9** is produced from **5**. Unlike the matrix-isolated case, equilibration of the label does not intrude upon the α-pyrone framework. This finding has precedent in the preparation of specifically deuterated *3-d-* and *5-d-*bicyclopyranones from the correspondingly deuterated 2-pyrones.[2] Evidently the very rapid thermal reversion of aldoketenes to α-pyrone[6b] takes place before a photochemically induced 1,5-hydrogen shift can intervene.

Scheme I



10

The distinction between the course of reaction in the two phases is illustrative of a condition which distinguishes photochemistry at cryogenic temperatures from the corresponding conventional gas and liquid phase studies. This distinction could place limits on mechanistic correlations drawn by comparing reactions carried out in such widely disparate media. A priori, there are at least two ways that unimolecular photoreactions in inert gas matrices can differ from photochemistry in other phases. It is often the case that reactions in the latter mode at normal temperatures give rise to species which are unstable at the ambient temperatures. This situation is formulated in eq 1.

$$A \xrightarrow{h\nu} B \xrightarrow{\Delta} C \text{ (room } T) \qquad (1)$$

Species such as B, when photochemically generated at cryogenic temperatures may be stabilized by the matrix environment (eq 2). A further photochemical reaction may ensue converting the trapped species B to products which are distinct from those obtained in the case described in eq 1.

$$A \xrightarrow{h\nu} B \xrightarrow{h\nu} D + \ldots \text{ (cryogenic } T) \qquad (2)$$

A second, more intriguing situation, involves the generation of vibrationally hot molecules which are slow to transfer their excess energy to the host lattice. This situation may obtain when the "hot" molecule possesses a small number of atoms, and vibrational modes which are poorly matched to the phonon bands of the host lattice. The lifetime of such a molecule in a vibrationally excited state may be prolonged in the matrix, compared to its lifetime in the excited state in other condensed phases. Hence the matrix isolated species may have opportunities to probe regions of a potential energy surface that are not accessible to it in environments that function as more efficient energy traps. One possible scheme is formulated below where an asterisk and cross signify electronically and vibrationally excited species respectively.

$$A \xrightarrow{h\nu} A^* \rightarrow B^\ddagger \rightarrow B \quad \begin{matrix}\text{(conventional}\\ \text{environment)}\end{matrix} \qquad (3)$$

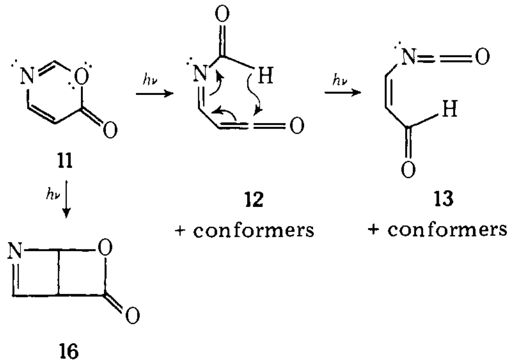
$$A \xrightarrow{h\nu} A^* \rightarrow B^\ddagger \rightarrow C^\ddagger \rightarrow C \quad \begin{matrix}\text{(cryogenic } T,\\ \textit{rare gas matrix})\end{matrix} \qquad (4)$$

Stabilizing B requires efficient energy transfer from $B^\ddagger$ to the matrix, a requirement which is not met in this hypothetical scheme (eq 4).

Thus, depending upon the situation the matrix environment could have a stabilizing or "destabilizing" effect on photochemically generated species.

In the present case, it is clear that at least two discrete photochemical steps are responsible for producing **6** from **4** (or **7** from **5**). Specifically labeled aldoketene **7**, a primary photochemical product of **4**, is in turn converted to **6**, if the conformational requirements are met, as a result of a further photochemical event.

During the irradiation of the 1,3-oxazin-6-one **11**[14] we have observed a band at 2250 cm^{-1} due to a species which appears to be interconvertible with the ketenes **12.** A 1,5-hydrogen shift from **12** would give rise to an aldoisocyanate **13,** which would be expected to absorb near ν 2250 cm^{-1}.[15] Thus the photoreactions of the oxazinone **11** appear to be analogous to the α-pyrone system.[14]



Studies designed to uncover further degenerate processes such as sigmatropic shifts of oxygen across the cyclobutene framework of **9** and hypothetical condensation of carbon dioxide **14** with [^{13}C]cyclobutadiene **15** are in progress.

Acknowledgment. A Frederick Gardner Cottrell Grant from the Research Corporation, financial support from the National Science Foundation, from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and from the Research Foundation of the State University of New York, and a NATO Senior Fellowship to A. Krantz are gratefully acknowledged.

References and Notes

(1) E. J. Corey and J. Streith, *J. Am. Chem. Soc.*, **86**, 950 (1964).
(2) W. H. Pirkle and L. H. McKendry, *J. Am. Chem. Soc.*, **91**, 1179 (1969).
(3) W. H. Pirkle, H. Seto, and W. V. Turner, *J. Am. Chem. Soc.*, **92**, 6984 (1970).
(4) W. H. Pirkle and M. Dines, *J. Am. Chem. Soc.*, **90**, 2318 (1968).
(5) (a) W. H. Pirkle and W. V. Turner, *J. Org. Chem.*, **40**, 1617 (1975); (b) *ibid.*, 1644 (1975).
(6) (a) C. Y. Lin and A. Krantz, *J. Chem. Soc. Chem. Commun.*, 1111 (1972); (b) A. Krantz, *J. Am. Chem. Soc.*, **96**, 4992 (1974).
(7) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 244 (1973).
(8) R. G. S. Pong and J. S. Shirk, *J. Am. Chem. Soc.*, **95**, 248 (1973).
(9) (a) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 614 (1973); (b) O. L. Chapman, D. DeLa Cruz, R. Roth, and J. Pacansky, *ibid.*, 1337 (1973).
(10) M. Nakagawa, M. Tonozuka, M. Obi, M. Kuichi, T. Hino, and Y. Ban, *Synthesis*, 510 (1974).
(11) W. G. Dauben, J. C. Reid, and P. E. Yankwich, *Anal. Chem.*, **19**, 828 (1947).
(12) Thermal sigmatropic shifts of order [1,5] are well-established reactions; see R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970, p 123. It is unclear whether the 1,5-hydrogen shifts in the present study take place in an excited state or from a vibrationally excited form of aldoketene.
(13) Details of the synthesis will be published elsewhere.
(14) A. Krantz and B. Hoppe, *J. Am. Chem. Soc.*, **97**, 6590 (1975).
(15) L. Bellamy, "The Infra-red Spectra of Complex Molecules", 3rd ed, Wiley, New York, N.Y., 1975, p 298.

B.-S. Huang, R. G. S. Pong, J. Laureni, A. Krantz*
Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794
Received August 28, 1976

Studies of Mitochondrial Monoamine Oxidase. Inactivation of the Enzyme by Isomeric Acetylenic and Allenic Amines Yielding Mutually Exclusive Products

Sir:

Monoamine oxidases (MAO), [EC 1,4,3.4], the mitochondrial membrane-bound flavin-linked class of enzymes whose members metabolize putative neurotransmitters and play a role in controlling levels of diverse exogenous and endogenous amines,[1] have been the object of recent intense interest.[2-8] Studies of the chemical inactivation of MAO by active-site directed reagents are potentially useful in defining the modes of reactivity of the enzyme. The inhibitory action of β,γ-acetylenic amines, substances which have been exploited clinically to control depression and hypertension,[9] has been a point of focus.[2]

Abeles, Singer, and coworkers have studied the inactivation of bovine liver MAO **2a** with 3-dimethylaminopropyne (**1,** R_1 = CH_3) and have assigned the flavocyanine Ia as the most probable structure of the irreversibly formed adduct between **1** and the enzyme.[2] Their conclusion exploits the finding that the electronic spectrum of the inactivated enzyme is very similar to that of the flavocyanine Ib, a photoproduct of **1** with 3-methyllumiflavin **2b** which possesses an unusually intense absorption band at 391 nm (ϵ 25 500, pH 7.0).[10-12]

Three mechanisms (Scheme I) have been advanced to explain the formation of Ia upon inactivation of the enzyme.[2] Path a features attack on the oxidized form of the flavin of a resonance stabilized, formally, carbanionic species. Another, path b, views the adduct as a consequence of the union of flavin and oxidized substrate. A third, path c, involves generation of a radical-pair complex between flavin and substrate, which collapses to form a new, stable covalent bond. From a different mechanistic standpoint, Rando[7] has emphasized the possible role of allenes in the inhibition of MAO by β,γ-acetylenic amines, and has categorized the latter substances as enzyme-suicide inhibitors, after the example provided by Bloch.[8]

In this context we wish to report our findings with a pair of inhibitors of monoamine oxidase. *N*-But-2-ynyl-*N*-benzylmethylamine[13] (**3a**) and *N*-2,3-butadienyl-*N*-benzylmethylamine[14] (**4**) are related as tautomers, and it might be expected that, if their respective reactions with the enzyme followed any of the paths outlined in Scheme I, the identical flavocyanine, **5a,** would be produced in both cases (Scheme II). This point is illustrated for path a and is based on the assumption that intermediate enamines would be rapidly converted by proton transfer to a common flavocyanine.

When a sample of the bovine liver MAO (15.6 mg of protein/mL, specific activity 2.56 μmol/min mg of protein),[15,16] purified according to Salach's procedure,[2,17] is made 10^{-4} M in **3a,** loss of enzymatic activity is accompanied by dramatic