(13) Under the action of the four-ring flip ($\mathbf{M}_{11}$),[6] which is the presumed threshold mechanism,[14] *dl*- and *meso*-1 are each expected[12] to exhibit four C–CH_3, four *p*-OCH_3, and eight *o*-OCH_3 proton resonances. The number of signals observed at 92 °C was four, two and two, respectively, pointing to accidental isochrony in the OCH_3 resonances. The relative intensities of the C–CH_3 signals are consistent with the residual diastereoisomerism expected[12] for these systems under the action of the four-ring flip: three conformational *dl* pairs for *dl*-**1**, and one conformational *dl* pair plus two achiral forms for *meso*-**1**.

(14) By analogy with the lowering of the two-ring flip barrier in triarylmethanes which accompanies replacement of a mesityl by a 2-methyl-1-naphthyl group,[15] the four-ring flip barrier for 1 is expected to be slightly lower than the barrier of 17 kcal/mol found[6] for 1,2-dimesityl-1,2-bis(2,4,6-trimethoxyphenyl)ethane, and this process should therefore be fast on the NMR time scale at 92 °C.

(15) P. Finocchiaro, D. Gust, and K. Mislow, *J. Am. Chem. Soc.*, **96**, 2176 (1974).

(16) Attempts to distinguish between the alternatives (*dl*- vs. *meso*-**1**) by x-ray crystallography or by use of chiral auxiliary compounds (solvents or shift reagents) have so far been unsuccessful. These and similar[6,8] systems tend to form disordered crystals, and resonance doubling seems to be of a negligible magnitude.

(17) Rotations were recorded on a Cary 60 spectropolarimeter or on a Perkin-Elmer 141 polarimeter.

(18) The value of $[\alpha]^{22}_{350}$ +224.9° (*c* 0.05, $CHCl_3$) recorded[17] for (+)-α-pinene[19] is such that the presence of even minor quantities might contribute to a decrease in the value of the *negative* rotation of recovered **1**.

(19) The ORD curve of (+)-α-pinene in *cyclohexane* has been reported (A. I. Scott and A. D. Wrixon, *Tetrahedron*, **26**, 3695 (1970)).

(20) The strong absorption of **1** (λ_{max} (log ε): 324 (3.39), 289 (4.16), 225 (5.07), 213 (5.04) nm in acetonitrile) precluded penetration of the spectral region below 350 nm.

(21) For example, $[\alpha]^{27}_{350}$ ($CHCl_3$) was −6.2° after the fourth recrystallization.

(22) The four C–CH_3 proton resonances[13] coalesce to a singlet at ca. 145 °C, corresponding to two reversible diastereomerizations ($\Delta G^{\ddagger}_{145}$ = 21.5 kcal/mol for the highest energy process, by line shape analysis) in which all residual conformers are interconverted.[12] Since the rotation ($[\alpha]^{22}_{365}$ −6.4° (*c* 2.5, 1,2,4-trichlorobenzene)) of a sample of optically activated **1** remains unchanged after heating at 100 °C for 1 h, corresponding to ca. 10^4 half-lives for the above process, it follows that the observed rotation cannot be due to partial resolution of one or more of the residual conformational *dl* pairs[13] in either *dl*- or *meso*-1.

(23) We cannot rule out the formation of some *meso*-1 in the dimerization since the yield of isolated product (1) was less than quantitative (ca. 70%).

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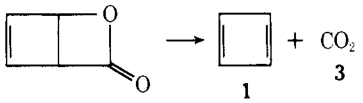
Cyclobutadiene. 3. Photolysis of Matrix-Isolated ^{13}C-Labeled Bicyclopyranones

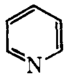
Sir:

Cyclobutadiene **1** has been generated and trapped in a variety of environments at cryogenic temperatures.[1-3a] The infrared spectrum of **1** is of substantial interest because of its relevance to the question of the geometry of the ring.[1-3a] Argon matrix-isolated bicyclopyranone **2** photodecomposes to **1** and carbon dioxide **3** showing bands in the infrared at 2340, 662, 1236, 653, and 573 cm^{-1}.[1a,b,2] Matrix-isolated carbon dioxide **3** as the sole guest shows absorption at 2340 and 662 cm^{-1}.



2 **1** **3**

Recently Maier[3a] has compared the spectra of the photoproducts from six independent precursors, **2** and **4–7**, of **1** and has failed to detect the 653-cm^{-1} band in those cases in which carbon dioxide is not a coproduct. Three of the precursors, **6a**, **6b**, and **7** extrude large, aromatic molecules which could, in principle, severely perturb the spectrum of neighboring cyclobutadiene **1**. A fourth, **4**, has previously been reported[2a] to lead to all three bands, 1245, 655, and 575 cm^{-1}, attributed to cyclobutadiene from studies of bicyclopyranone.



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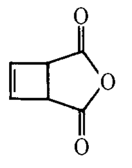

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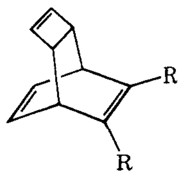
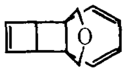
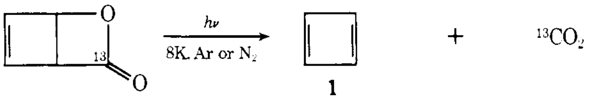


6a, R = CO_2CH_3
b, R–R = –COOCO–



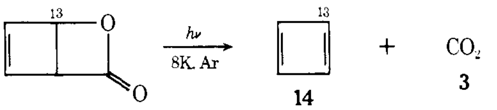
7

A verdict on the assignment of the 655-cm^{-1} band can be obtained from an analysis of the infrared spectrum of the photolysate of [2-^{13}C]bicyclopyranone **8**. If the ^{13}C label is localized in carbon dioxide it should have little effect on **1**, and cause only a shift in the bands related to the carbon dioxide fragment. If the 655-cm^{-1} band is an intrinsic property of the spectrum of **1** it should be unshifted by the substitution.



8 **1**

Ar: 1241, 575 cm^{-1} 636, 644 cm^{-1}
N_2: 1245, 575 cm^{-1} 639, 643 cm^{-1}



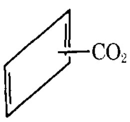
12 **14** **3**

1237 cm^{-1} 655 cm^{-1}
575 cm^{-1} 662 cm^{-1}

Irradiation of [2-^{13}C]bicyclopyranone **8** (90 atom % ^{13}C) gives rise to a product possessing two of the infrared bands (1241 and 575 cm^{-1})[4] that had been previously attributed to **1**. Bands at 662 and 655 cm^{-1} are present in the spectrum of photolysate, but they are ca. 10% as intense as an *identical pattern* of bands located at 644 and 636 cm^{-1}.[5] The weaker pair are undoubtedly derived from the residual 10% of **2** in starting pyranone. Hence both bands (662 and 655 cm^{-1}) are strongly shifted by the ^{13}C label and neither can be a property of cyclobutadiene **1** per se. Since pyridine (**4**) is a notably poorer precursor to cyclobutadiene, we must conclude that the band reported by Chapman[2] et al. (655 cm^{-1}) in the case of the photolysis of **4** must be due to an impurity or some product other than cyclobutadiene.

By comparison, photolysis of [6-^{13}C]bicyclopyranone (**12**) gives rise to bands at 662 and 655 cm^{-1} with no detectable absorption at 644 and 636 cm^{-1}. The most notable feature in this case is the slight shift of the 1241-cm^{-1} band of **1** to 1237 cm^{-1} in the spectrum of the ^{13}C-labeled species **14**, in accordance with the original assignment of this band to a predominately framework distortion of **1**. The signal at 575 cm^{-1} is independent of the ^{13}C-label.[6]

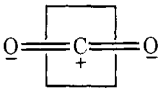
Maier, emphasizing the putative tendency of cyclobutadiene to undergo association with acceptor ligands,[3] views "a species of type **15** in which carbon dioxide functions as a ligand" to be responsible for the spectrum of photolyzed bicyclopyranone. It is also suggested that "formation of nonassociated cyclobutadiene would appear most likely on cycloreversion of the ether **7**."



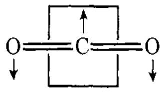
15

In fluid media, cleavage of a molecule to stable products results in molecular diffusion, and at low concentrations the fragments are generally without (spectroscopic) influence on each other. However cleavage of the matrix-isolated guest generates fragments which may be constrained to remain in 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]



A



B

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.

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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 $[^{13}\text{C}]$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.

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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