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PHOTOCHEMICAL RING EXPANSION OF TETRAMETHYLCYCLOBUTANONE REVISITED: ANGULAR DEPENDENCE OF ELECTRONIC ABSORPTION OF SINGLET CARBENES

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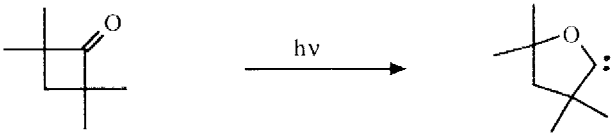
Abstract. Tetramethyltetrahydrofuranylidine, produced by the photochemical ring expansion of the corresponding cyclobutanone, has been characterized by IR and UV/Vis spectroscopy in a low-temperature N_2 matrix. The angular dependence of the UV/Vis spectra of this and related carbenes is explored by ab initio calculations

The photochemical ring expansion of cycloalkanones is a striking, yet incompletely understood reaction First observed by Yates in 1964,[2] this novel process appears to be restricted mainly to cyclobutanones and to a few strained larger-ring ketones.[3] Besides attracting the interest of mechanistic photochemists, these reactions have shown promise in organic synthesis.[4] Laser time-resolved solution studies of the oxacarbene intermediates have also begun to appear.[5] The bulk of the evidence supporting carbenes in this photochemistry still rests mainly on indirect solution trapping studies In 1974, however, Quinkert and coworkers[6] reported that irradiation of 2,2,4,4-tetramethylcyclobutanone (**1**) in an organic glass at 77 K produced a thermally labile intermediate that absorbed in the UV with a λ_{max} of approximately 360 nm This species, which disappeared on warming the glass to its softening point, was assigned as oxacarbene 2.

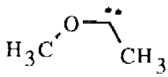


1 **2**

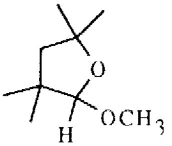
Over the past several years we have reported the low-temperature characterization of a number of oxygen-substituted carbenes. Our own results on alkyl substituted oxacarbenes, however, led us to question the previous assignment of the UV spectrum of **2** (and similar systems[6b]) For example, we have reported that photolysis of nortricyclanone (**3**) in a N_2 matrix at 10 K gave oxacarbene **4**, which was extensively characterized by IR, UV, ^{18}O labeling, and trapping.[7] Of particular note is the λ_{max} of **4** at 396 nm, considerably red shifted compared to that assigned to **2**. We have similarly studied **5**, formed on irradiation of the corresponding matrix isolated diazirine. The UV of **5** was centered at 385 nm (*cis* and *trans* isomer absorptions not resolved), again at a much longer wavelength than that suggested for **2**.[8] In hopes of resolving these discrepancies, we undertook a reinvestigation of the low-temperature photochemistry of **1**.


3


4


cis-5


trans-5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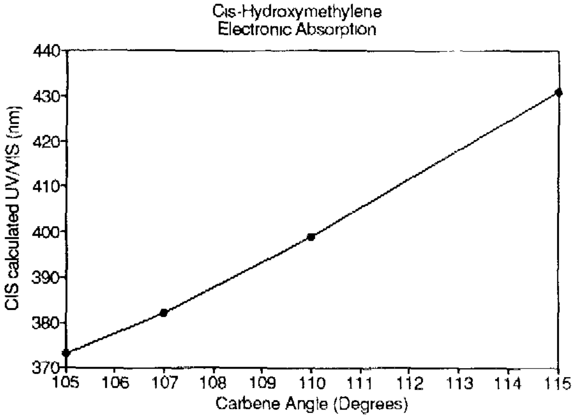
Irradiation of a N_2 matrix containing cyclobutanone **1** at 12 K with 284 nm light caused a decrease in the IR absorptions of starting material, and the production of a photolabile intermediate. Along with the IR bands of this new compound (strongest at 1343 and 1374 cm^{-1}),[9] absorptions were observed for fragmentation products CO, tetramethylcyclopropane, dimethylketene, and 2-methylpropene.[10] Subsequent irradiation of the matrix at 366 nm caused the destruction of the intermediate bands and concurrent increase in those of the other products, as well as those of starting material. Trapping experiments confirmed that the intermediate was oxacarbene **2**. Cyclobutanone **1** was irradiated at 284 nm in a 3-methylpentane matrix containing MeOH (5:1 3-MP:MeOH) at 30 K. The IR spectrum confirmed that the intermediate compound had been formed. Warming the matrix to 80 K caused the disappearance of the IR absorptions of carbene **2**, and the simultaneous appearance of IR bands for acetal **6**.[10]

During photolysis of the matrix containing ketone **1**, a broad band with λ_{max} at 360 nm in the UV/Vis spectrum could also be observed. This absorption grew and disappeared simultaneously with the IR bands assigned to carbene **2**, and also emulated the behavior of **2** in the MeOH trapping experiments. Finally, the "action spectrum" for photochemical destruction of the IR bands for **2** roughly matched the observed UV/Vis spectrum in the region of 420 - 320 nm.

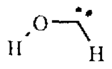
Our results thus confirm the assertion of Quinkert and coworkers[6] that the UV absorption of oxacarbene **2** has a maximum at 360 nm. The question that remains, however, is why is the UV spectrum of **2** so different from those of the other oxacarbenes, **4** and **5**, which are closer to 400 nm? A possible solution might lie in the different geometries of these carbenes. We reason that the carbenic carbon might be subject to angular deformation from the different steric requirements in the various carbenes. The lowest energy absorption for these singlet carbenes corresponds to a σ^2 to σ^1p^1 transition. Gleiter and Hoffmann[11] have pointed out that the energy difference between the σ^2 and σ^1p^1 configurations of singlet carbenes should be a sensitive function of the angle at the carbenic center. Smaller angles imply more s-character in the σ orbital, which should lower the lone-pair energy, increase the energy gap, and thus decrease the wavelength of absorption. Conversely, larger carbene angles should correlate with longer wavelengths.

To explore this possibility, we have carried out ab initio molecular orbital calculations of the first excited states of *cis*-hydroxymethylene (*cis*-7) as a function of carbene angle.[12] Geometries of *cis*-7 were optimized at the 6-31G* level, with the HCO angle constrained to three different values in addition to the 107° angle predicted from full optimization. The first excitation wavelengths were then calculated at these geometries with the CIS method (configuration interaction with singles) in Gaussian 90.[12] The results, illustrated graphically in Figure 1, confirm the expected correlation between carbene angle and UV/Vis absorption.

Figure 1



trans-7



cis-7

The geometries of the experimentally characterized oxacarbenes were also optimized at the 6-31G* level. These calculations give carbenic CCO angles of 107.6, 111.5, and 113.6° for **2**, **4**, and *cis*-**5**, respectively. Although we were previously unable to instrumentally resolve the UV/Vis absorptions of *cis*- and *trans*-**5**, we presented evidence[8] that the *cis* isomer absorbed at longer wavelengths than the *trans*, we estimate a λ_{max} in the range of 390 - 410 nm for *cis*-**5**.[13] It is tempting to also include in the series *trans*-**5**, for which the ab initio calculations give a CCO angle of 108° (370 nm estimated λ_{max}[8]). *Trans* isomers are expected to have different lone-pair interactions than the *cis* carbenes, however, and have longer wavelength absorptions at the same CCO angles. For example, CIS/6-31G* calculations predict λ_{max} = 405 nm for *trans*-hydroxymethylene (*trans*-**7**) constrained at the 107° HCO angle of *cis*-**7** (λ_{max} = 380 nm).

It can thus be seen that the highest energy absorbing carbene, **2**, *does* have the smallest CCO angle. It must be noted, however, that the carbene spectra obviously depend on other factors. For example, the difference in λ_{max} between **4** and *cis*-**5** is not as large as we would expect for the predicted difference in bond angles. Other geometric differences, such as the COC angles (calculated to be 117.9, 120.7, and 126.3° for **2**, **4**, and *cis*-**5**, respectively) may also play a role. Carbenes with a broader range of geometric constraints will need to be examined before a full understanding of this issue emerges. The variability and geometric dependence of the electronic spectra of singlet carbenes, however, may need to be considered in future attempts to characterize these reactive species in solution by laser techniques.[14,15]

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12. Ab initio calculations were carried out with Gaussian 90, Revision J: Frisch, M J.; Head-Gordon, M , Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb. M ; Binkley, J S , Gonzalez, C ; Defrees, D. J , Fox, D. J ; Whiteside, R. A ; Seeger, R ; Melius, C F , Baker, J ; Martin, R. L ; Kahn, L. R ; Stewart, J. J. P.; Topiol, S ; Pople, J. A. Gaussian, Inc , Pittsburgh PA, 1990 Vibrational analyses indicated that all optimized geometries (except for **7**) represented true local minima at this level of calculation.

13. Our conformational assignment has also been confirmed by ab initio calculations by others. Hess, B A , Jr ; Smentek-Mielczarek, S. *J Mol Struct.* **1991**, *227*, 265 Geometries were also calculated therein for *cis* and *trans*-**5** at the MP2/6-31G* level, and are nearly identical to those found in this study at the 6-31G* level.

14 The geometry of the parent tetrahydrofuranylidine has been calculated previously at the 3-21G level: Hopkinson, A. C.; Lee-Ruff, E., Lien, M H. *Tetrahedron* **1988**, *44*, 6815

15. CIS calculations on the 6-31G* optimized geometries predict UV/Vis absorptions that also roughly follow the trend of the carbenic bond angle: 346, 357, 369, and 397 nm for **2**, *trans*-**5**, **4**, and *cis*-**5**.

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