Supplementary Material Available: ^{1}H and ^{13}C NMR data for compounds **1**–**4**, **10**–**27**, and **29**, and experimental procedures of the reaction of **3** and **7** and ozonolysis of the 1,4-γ-adduct **17** (11 pages). Ordering information is given on any current masthead page.

Direct Observation of Photochemical Cleavage of a Cyclopropylalkoxycarbene to an Alkyne

M. A. Kesselmayer and R. S. Sheridan*[1]

Departments of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
University of Nevada, Reno, Nevada 89557

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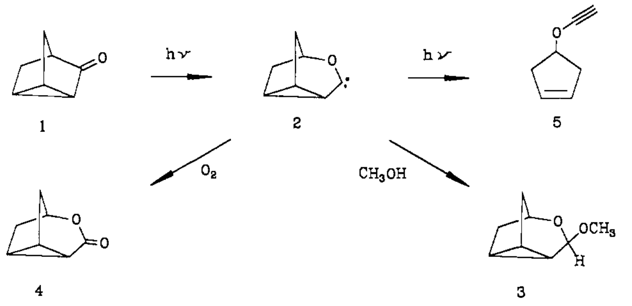
Alkoxycarbenes have drawn considerable interest in their relation to carbonyl photochemistry.[2] For example, the parent, hydroxymethylene, has been the subject of numerous theoretical studies vis-a-vis formaldehyde photochemistry.[3] Moreover, synthetic applications of photochemical carbonyl ring expansions to alkoxycarbenes have begun to appear.[4] We have recently published low-temperature spectroscopic investigations of methoxychlorocarbene[5] and phenoxychlorocarbene.[6] In these cases, however, the influence of the halogen on the spectroscopic and photochemical properties of the carbenes could not be easily separated from the oxygen perturbation of primary interest. We now wish to report the spectroscopic characterization of a nonhalogenated alkoxycarbene and its novel photochemistry.

Yates[2,7] has shown that irradiation of nortricyclanone (**1**) in solution gives products attributable to carbene **2**. For example, irradiation of **1** in MeOH solution gives acetal **3** and in the presence of O_2 gives lactone **4**. We have now found that irradiation (285 nm) of tricyclic ketone **1**, in an N_2 matrix at 20 K, leads to slow disappearance of the starting IR absorptions and the growth of new bands (Figure 1).[8] Subsequent broad-band irradiation (>270 nm) destroys a number of the new bands (labeled C), with concomitant growth in others (labeled A). Starting material is also observed to grow on broad-band photolysis. Unfortunately, the combination of the slow photolysis of **1** and the photolability of the initial photoproduct limits the obtainable intensity of the intermediate. A UV spectrum obtained on the same matrix indicates a broad band, with λ_{max} at 396 nm, growing and disappearing with the initial photoproduct IR bands.



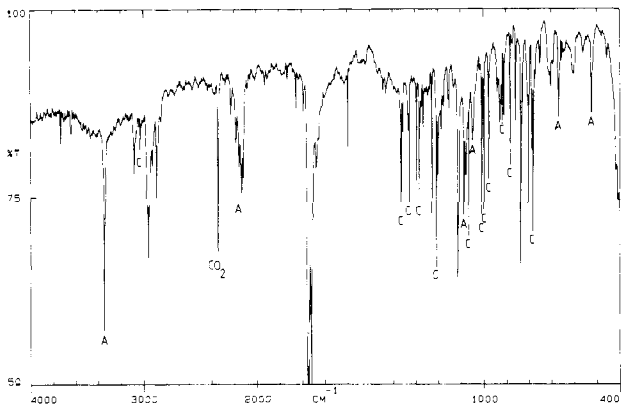
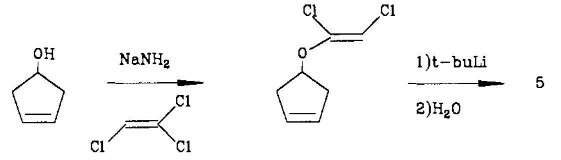


Figure 1. IR spectrum obtained on irradiation of N_2 matrix isolated **1** (1:800, 20 K) for 45 h at 285 ± 18 nm. Bands labeled C are assigned to carbene **2**, and those labeled A are assigned to acetylene **5**. Unlabeled bands are due to residual **1**.

The observed photochemistry and the IR and UV spectra suggest that the initially formed intermediate C in the matrix photolysis of **1** is alkoxycarbene **2**. Trapping experiments confirm this. Irradiation (285 nm) of a 50-K 3-methylpentane matrix containing **1** and MeOH (3-mp:MeOH:**1** = 20:5:1) generated the same products as in the N_2 experiments above, along with new IR bands identical with those of independently prepared acetal **3**. Warming the matrix to 90 K caused the disappearance of the bands due to **2** and the growth of the bands of **3**.

The strong IR band at 3350 cm^{-1} hints that the major photoproduct of carbene **2** contains a terminal acetylene (A in Figure 1). Absorptions at ca. 2200 and 670 cm^{-1} support this assignment. Alkyne **5** was independently synthesized from cyclopent-1-en-3-ol as shown below, and was shown to be identical with the photoproduct.[9]



It is interesting to note the carbene IR absorptions in the region of 1300 cm^{-1} for **2**. We have previously found that oxymethylenes exhibit anomalously high-energy C–O stretches near these frequencies.[5,6] We have attributed the associated unusual force constants to partial C–O double-bond character as predicted theoretically.[5b] Methylene scissoring deformations can also come at these frequencies, however, and this region in the IR is fairly complicated. The IR spectrum of ^{18}O labeled **2**, generated from the corresponding ketone, indicates that the band at 1369 cm^{-1} is a predominantly C–O stretch with an isotopic shift of 17 cm^{-1}.[10] Quinkert[11] has suggested that transient absorptions observed at ca. 360 nm in the irradiations of cyclobutanones in low-temperature glasses were attributable to the corresponding cyclic oxacarbenes. Although the absorption maximum observed for **2** is at somewhat lower energy, the difference might arise from conjugation with the adjacent cyclopropane. It should be noted that in the case of Quinkert,[11] however, no additional evidence sup-

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[1] Fellow of the Alfred P. Sloan Foundation, 1986–1988. Address correspondence to this author at the University of Nevada.

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[8] For general matrix isolation conditions and description of apparatus see ref 5b. Irradiations were performed with a Bausch and Lomb monochromator or with appropriate cut-off filters. The IR spectra were obtained on a Beckman 4250 spectrometer interfaced with an IBM XT computer for data storage and manipulation.

[9] Compound **5**: ^{1}H NMR (200 MHz, $CDCl_3$) 5.7 (br s, 2 H), 4.85 (t of t, 1 H, J = 5.1, 3.3 Hz), 2.68 (br s, 4 H), 1.52 (s, 1 H) ppm; IR (Ar, 10 K) 3350, 2145, 2140, 1195, 1115, 925, 695, 670, 605, 525 cm^{-1}.

[10] Labeled **1** was produced by hydrolysis of the corresponding ethylene glycol ketal with $H_2O(^{18}O)$.

[11] Quinkert, G.; Kaiser, K. H.; Stohrer, W.-D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 198.

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ported the assignment of the UV spectra to oxacarbenes. The UV spectrum of **2** compares favorably with that predicted theoretically for hydroxymethylene (392 nm).[3]

In our previous investigations of methoxychloro- and phenoxychlorocarbenes we observed photochemical C–O cleavage leading to decarbonylation or rearrangement to the corresponding acid chlorides.[5,6] Similarly, previous solution investigations of alkoxycarbenes have observed only C–O cleavages.[2] In the case of **2**, in contrast, either of two α-cleavages apparently occur: C–O or C–C. Here, the weaker nature of the cyclopropyl bonds likely plays a role in making C–C cleavage competitive. Thermal fragmentations of this nature in cyclopropylmethylenes are, in fact, well known.[12] Although cyclopropylmethylenes (triplet) have been spectroscopically observed before,[13] we believe this is the first exploration of their photochemistry. It is an open question whether or not the thermal and photochemical processes follow the same routes. The acetylene **5** has not been reported previously as a photoproduct of **1** either in solution[2,7] or in the gas phase.[14] We have found, however, that **5** is fairly unstable toward decomposition in solution and hence may have been lost in previous investigations. These questions as well as other aspects of oxymethylenes are being explored.

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Cycloheptatrienylidene Singlet–Triplet Energetics: Theory Responds

Curtis L. Janssen and Henry F. Schaefer III*

Department of Chemistry, University of California
Berkeley, California 94720

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Some time ago Radom, Vincent, and one of us (RSV)[1] predicted that the cyclic allene

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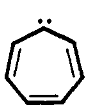
lies energetically ~16 kcal/mol below the isomeric C_7H_6 carbene cycloheptatrienylidene stationary point



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It was concluded that the observed[2] lowest energy structure (previously identified as **2**) in this sphere of the C_7H_6 potential energy hypersurface "is better named cycloheptatetraene". This prediction was confirmed 2 years later in Chapman's laboratory[3] at UCLA. RSV also estimated that singlet cycloheptatrienylidene lies energetically below the triplet electronic state having a qualitatively similar planar stationary point geometry.[1]

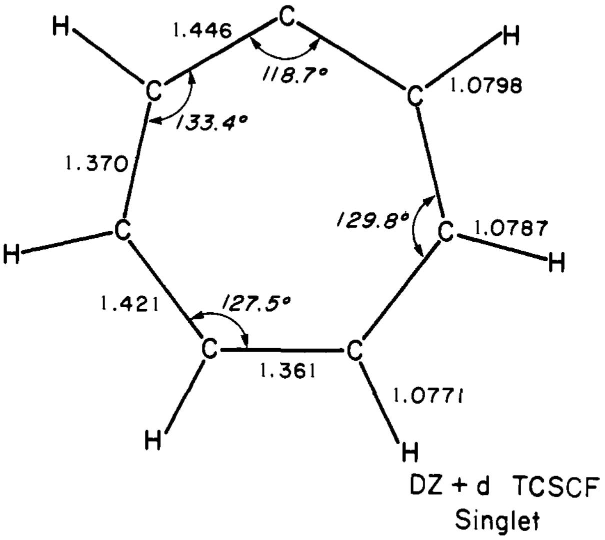

Figure 1. Theoretical structure for the lowest singlet state of planar cycloheptatrienylidene. A double ζ plus carbon d function (DZ + d) basis set was used in conjunction with two-configuration self-consistent-field theory (TCSCF).

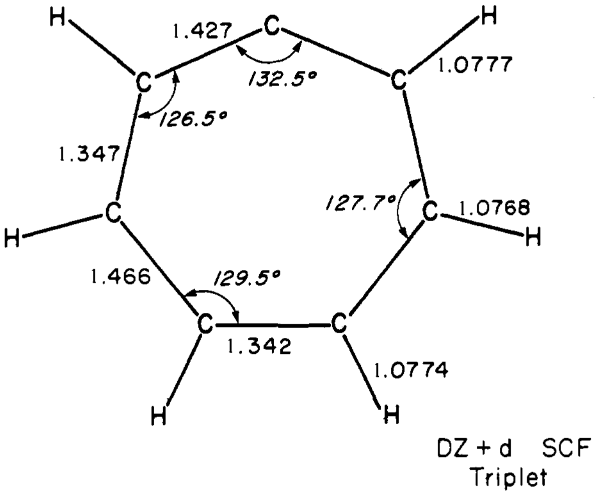

Figure 2. Ab initio equilibrium geometry for the lowest triplet state of planar cycloheptatrienylidene. All bond distances are in Å.

Very recently McMahon and Chapman[4] have presented experimental results which appear to challenge the latter prediction from theory. Specifically, they report that cycloheptatrienylidene produces an intense ESR signal. McMahon and Chapman state[4] that "observation of the ESR signal of cycloheptatrienylidene implies that the triplet state is either the ground state or within several calories per mole of the ground state". They then conclude that "the triplet ground state of cycloheptatrienylidene necessitates a re-evaluation of both qualitative arguments... and the calculations".

An independent experimental communication (appearing a few months later) by Kuzaj, Lüerssen, and Wentrup[5] states less dogmatically that "one intriguing possibility is that (cycloheptatrienylidene) has a triplet ground state", again based on ESR observations. It is significant that the EPR parameters D and E assigned by Chapman[4] to **2** are rather different from those assigned by Wentrup[5] to the same molecule. It would appear that one of the ESR assignments is incorrect.

In this communication we confirm that the theoretical predictions of RSV are correct and suggest that they are indeed consistent with the very recent experiments of McMahon and

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