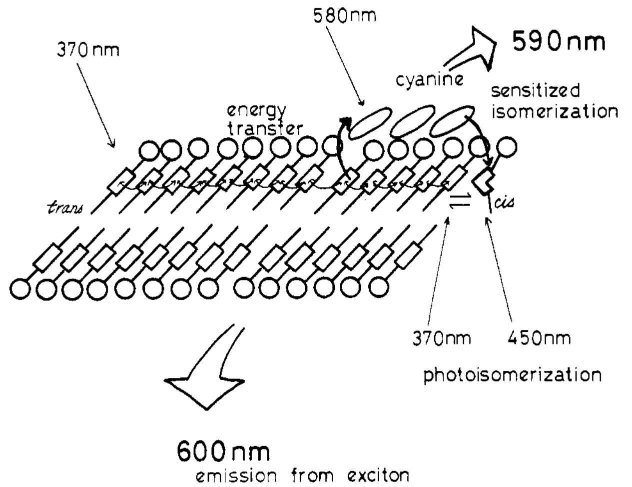

Figure 14. Schematic illustration of the photophysical and photochemical processes of an azobenzene-containing bilayer membrane.

will be formed instead of randomly distributed *trans*-azobenzenes, and efficient sensitization by the cyanine becomes possible.

Conclusion

Figure 14 summarizes schematically the photophysical and photochemical processes observed for the azobenzene bilayers with the $C_{12}AzoC_5N^+$ system as a typical example. Absorption at 370 nm produces an excitonic state which leads to isomerization directly or upon energy migration. The fluorescence emission at 600 nm also occurs from this state with enhanced quantum yield relative to that of the isolated species. Irradiation at 450 nm of the *cis*-azobenzene formed causes regeneration of the trans isomer. In the presence of bound cyanine dyes, the excitonic energy is transferred efficiently to the cyanine which subsequently fluoresces at 590 nm. Excitation of the cyanine at 580 nm results in the energy transfer to the *cis*-azobenzene and the consequent photoreversion to the trans isomer. The direct and sensitized photoreversions are contrasting in that the trans isomer is regenerated randomly in the former process, whereas it is regenerated in the cluster form in the latter case.

This scheme offers new possibilities in the construction of artificial photosynthetic systems. The photosynthetic system includes as major elements energy collection by antenna pigments, charge separation, and utilization of the charges for chemical reactions. The chromophore-containing bilayers can play the role of antenna pigments irrespective of whether the chromophores are bound to bilayers covalently or noncovalently. The charge separation can be accomplished when appropriate chromophores are introduced. We have shown that the positive hole created by photochemically induced electron transfer has an unexpectedly long lifetime in the case of a carbazole-containing bilayer.[38]

Monolayers and builtup multilayers have been used to prepare molecular systems that are capable of efficient transfer of energy and electron.[39,40] A large amount of work with planar lipid bilayers[41] and pigmented lipid bilayers also has been published.[42] It is clear that synthetic bilayer membranes provide molecular systems of similar capacity.[43]

Registry No. **3**, 17701-26-7; **2** (*n* = 16), 42187-36-0; **2** (*n* = 18), 14357-21-2; $C_{12}AzoC_5N^+Br^-$, 88683-86-7; $C_{12}AzoC_6N^+Br^-$, 88683-87-8; $C_{12}AzoC_4N^+Br^-$, 88683-85-6; $C_{10}AzoC_{10}N^+Br^-$, 88683-82-3; $C_8AzoC_{10}N^+Br^-$, 88774-98-5.

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Vinylidenecarbene: A New C_3H_2 Species

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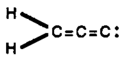
Abstract: It was found that photolysis of cyclopropenylidene in a matrix yields propargylene, which upon further irradiation is converted to a new C_3H_2 isomer. Comparison of the IR spectrum of this new isomer with the computed MP2/6-31G** IR spectrum of singlet vinylidenecarbene (ethenylidenecarbene, propadienylidene) confirms that this new C_3H_2 isomer has the structure $H_2C{=}C{=}C{:}$. The photolysis can be reversed by using shorter wavelength light to regenerate propargylene.

The experimental search for isomers on the C_3H_2 potential surface (e.g., **1**-**3**) began about 20 years ago with the trapping of the diphenyl derivative of cyclopropenylidene by dimethyl fumarate and dimethyl maleate.[1] The first C_3H_2 parent species identified by direct spectroscopic methods was triplet propargylene (**2**). In 1965 the ESR spectrum of **2** was published; and, based on the zero-field-splitting parameters, a linear or nearly linear structure was derived.[2] In 1972 a matrix-isolation study on the photolysis of diazopropyne and the IR spectrum of the same species was reported.[3] In 1974 **2** was identified as one of the products of the vacuum UV photolysis of matrix-isolated propyne and allene.[4] Some years later[5] the existence of a C_3H_2 species with a high proton affinity was claimed to be present in hydrocarbon flames on the basis of an ion cyclotron resonance study, but no


$H_2C{=}C{=}C{:}$

1

$H-C\equiv C-\ddot{C}-H$

2

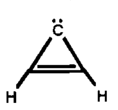


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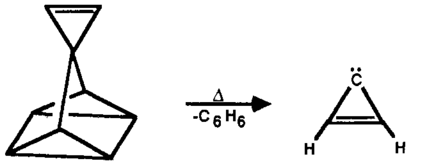
Table I. Calculated Optimum Geometries of Singlet and Triplet Vinylidenecarbene[a]

state	bond length or angle[b]	SCF/ STO-3G[c]	SCF/ 4-31G	SCF/ 4-31G**	UMP2/ 6-31G**
singlet	C_1–C_2	1.304	1.306	1.310	1.333
	C_2–C_3	1.282	1.280	1.277	1.292
	C_1–H	1.092	1.075	1.077	1.084
	∠HCH	114.7	116.4	117.2	116.6
triplet	C_1–C_2	1.386	1.364	1.369	1.363
	C_2–C_3	1.256	1.258	1.248	1.216
	C_1–H	1.084	1.073	1.075	1.076
	∠HCH	117.4	117.8	118.6	118.8

[a] Both are computed to have C_{2v} symmetry. [b] In ångstroms or degrees. [c] Reference 10a.

structure could be given. In 1984 we were able to prepare a second parent C_3H_2 isomer, namely cyclopropenylidene (**3**), by high-vacuum flash pyrolysis of the polycyclic precursor **4** and to isolate it in an argon matrix.[6] Its identification was based on the excellent agreement of the experimental and calculated[7] IR frequencies and intensities and on the fact that **3** could be converted photochemically to propargylene (**2**).[6] The interest in C_3H_2 isomers gained a new dimension in 1985 when the rotational spectrum of cyclopropenylidene (**3**) produced by acetylene/helium discharge was measured, and when it was found that certain ubiquitous but previously unassigned interstellar lines are due to rotational transitions of cyclopropenylidene.[8] The authors claimed that **3** may be one of the most abundant molecules in molecular clouds. From the millimeter wave spectra of the ^{13}C and D_1 isotopomers, the complete structure of cyclopropenylidene (**3**) could be derived.[9] Because of the large dipole moment (3.4 D) **3** has a strong rotational spectrum and can easily be detected by microwave spectroscopy.



4 **3**

Theoretical studies have predicted that there should be another C_3H_2 isomer with an even larger dipole moment (4 D)[10,11]: singlet vinylidenecarbene (**1**, ethylidenecarbene, propadienylidene). Unlike **2** which is predicted to have a triplet ground state **1** is predicted to be a singlet.[10-12] On a careful reexamination of our IR spectra of the photoproducts of cyclopropenylidene taken in 1984,[6] we noticed that besides the bands of propargylene (**2**), there was a tiny new absorption near 1950 cm^{-1}, the expected region for the antisymmetric C=C=C stretching vibration of allene-type molecules. This observation was the first hint of the existence of vinylidenecarbene (**1**), though substituted vinylidenecarbenes are known.[13] Here we report the photochemistry of cyclopropenylidene (**3**), prepared by thermal degradation of di-*tert*-butyl 2-cyclopropene-1,1-diperoxycarboxylate (**10**), which leads to a third C_3H_2 isomer, vinylidenecarbene.

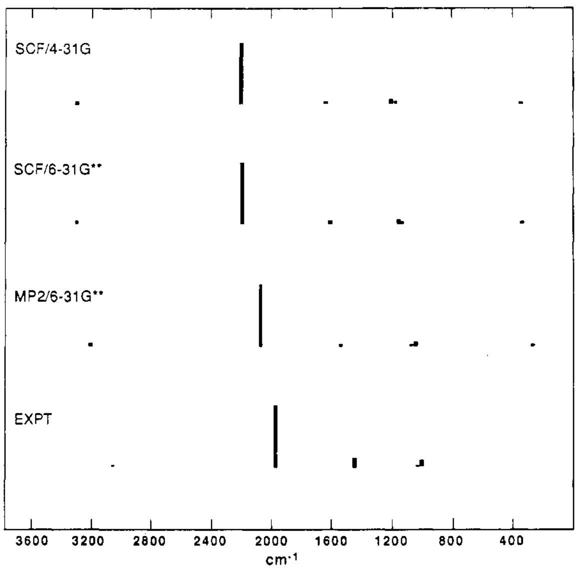
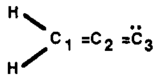


Figure 1. Comparison of experimental and theoretical infrared spectra of singlet vinylidenecarbene. Positions of bands are represented by bars whose heights give the intensity relative to the strongest band. Very low intensities are somewhat exaggerated (see Table III for exact intensities); bands of relative intensity less than 0.005 are not shown. MP2 intensities were obtained from the combination of MP2 normal modes and SCF dipole moment derivatives (see text). The observed spectrum was plotted by summing the intensities of matrix-split pairs for each absorption (see text).

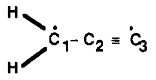
To aid in the spectroscopic identification of **1** we calculated IR frequencies and intensities of this species. Such calculated vibrational spectra can be of great use in the identification of unusual and reactive chemical species.[14]

Computed Vibrational Spectrum of Vinylidenecarbene (1)

To be sure that the ground state of vinylidenecarbene is a singlet, vibrational spectra were computed for both the singlet of **1** (S1) and its triplet (T1). Optimized geometries of S1 and T1, both of which have C_{2v} symmetry, are given in Table I and their computed energies in Table II for several basis sets. From Table II it is seen that whereas the SCF/STO-3G calculations[10a] favor the triplet state by about 26 kcal/mol, the extension of the basis set decreases this difference; and the inclusion of electron correlation by MP2 reverses the order of stabilities to favor the singlet state by about 35 kcal/mol. Hehre and collaborators[10a] also reported the singlet–triplet energy differences with larger basis sets (at optimum STO-3G geometries). Their 4-31G and 6-31G* results of −8.2 and −1.5 kcal/mol are very close to ours in Table II. Kenney and collaborators[12] arrived at a singlet–triplet energy splitting of 48.7 kcal/mol by computing the D-MBPT (8) energies with a DZ basis set augmented by a single set of d-functions on the terminal carbon atom. For both the singlet and triplet they assumed the same geometry with the two CC bonds equal to 1.32 Å. As our UMP2 results in Table I show, these assumed bond lengths are more realistic for the singlet state than for the triplet state. Hence this assumption may lead to the overestimation of the singlet–triplet energy gap by several kcal/mol. Finally DeFrees and McLean found the singlet to be 40 kcal/mol more stable than the triplet at the MP4/SDTQ level.[11] Given these results it appears very likely that the ground state of vinylidenecarbene **1** is a singlet.



S1



T1

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Table II. Energies of the Optimum Vinylidenecarbene Structures

singlet state		triplet state		$E_{\text{triplet}} - E_{\text{singlet}}$ (kcal/mol)
method	energy (au)	method	energy (au)	
RHF/STO-3G[a]	−113.13793	UHF/STO-3G[a]	−113.17866	−25.6
RHF/4-31G	−114.425897	UHF/4-31G	−114.439104	−8.3
RHF/6-31G**	−114.595219	UHF/6-31G**	−114.597743	−1.6
MP2/6-31G**	−114.968255[b]	UMP2/6-31G**	−114.912057[b]	+35.3

[a] Reference 10a. [b] Full active space (no frozen core).

Table III. Calculated and Observed Vibrational Frequencies (cm^{-1}) of Singlet Vinylidencarbene and Its Dideuterio Derivative[a]

		$H_2C{=}C{=}C{:}$				$D_2C{=}C{=}C{:}$	
	mode	SCF/4-31G	SCF/6-31G**	MP2/6-31G**	experiment	MP2/6-31G**	experiment
B_1	CCC out-of-plane bend	337 (10)	303 (17)	225 (15)		217 (12)	
B_2	CCC in-plane bend	340 (294)	339 (122)	262 (126)		242 (103)	
B_1	CH wagging	1210 (926)	1164 (781)	1051 (772)	999.5 (0.10)	840 (519)	800.3 (0.06)
					1004.8 (0.05)		803.2 (0.06)
B_2	CH rock	1183 (172)	1139 (172)	1080 (160)	1025.0 (<0.01)	866 (157)	829.2 (0.02)
							832.6 (0.01)
A_1		1251 (40)	1247 (15)	1152 (5)		995 (20)	950.8 (0.01)
A_1	coupled CC stretches and scissoring	1643 (494)	1615 (534)	1542 (310)	1446.9 (0.14)	1267 (140)	1208.7 (0.08)
					1449.3 (0.05)		
A_1		2204 (15776)	2188 (16700)	2075 (16970)	1952.2 (1.00)	2049 (14820)	1933.4 (1.00)
					1963.2 (0.32)		1944.4 (0.80)
A_1	CH symm stretch	3300 (543)	3302 (488)	3206 (457)	3049.5 (0.02)	2350 (2650)	2200.5 (0.07)
					3059.6 (<0.01)		2212.5 (0.08)
B_2	antisymm CH stretch	3382 (118)	3389 (64)	3304 (64)		2462 (60)	

[a] IR intensities are in parentheses, calculated intensities are absolute values in cm^{-2} L mol^{-1}, experimental intensities are relative to the strongest band.

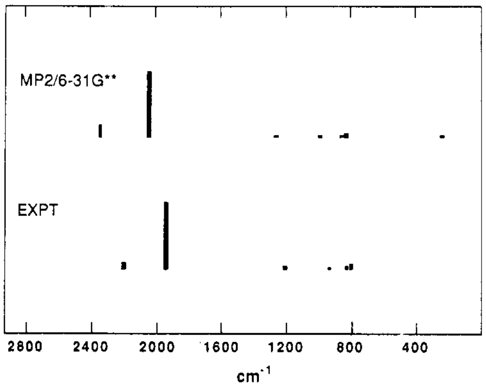


Figure 2. Observed and MP2/6-31G** infrared spectra for dideuteriovinylidenecarbene. (Notes in the caption to Figure 1 also apply to this figure.)

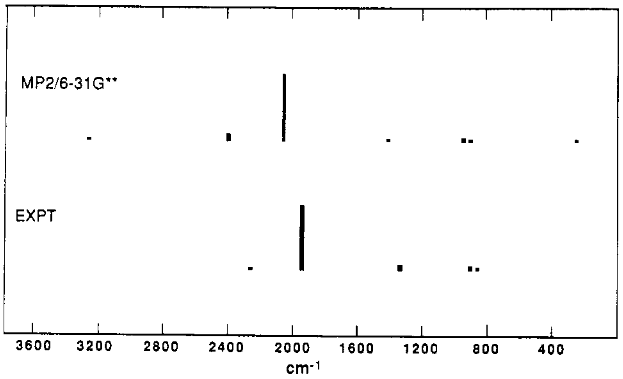


Figure 3. Observed and MP2/6-31G** infrared spectra for monodeuteriovinylidenecarbene. (Notes in the caption to Figure 1 also apply to this figure.)

Computed vibrational frequencies and IR intensities of **1** and its dideuterio derivative are given in Table III, and those of the monodeuterio derivative in Table IV. These theoretical spectra are plotted in Figures 1–3. A dominant feature of the spectra of the singlets is a strong band at about 2100 cm^{-1}. The high intensity of this band is understandable because it belongs to an "antisymmetric" CC stretching mode oscillating between the two limiting structures and is therefore associated with a large change

Table IV. Calculated and Observed Vibrational Frequencies (cm^{-1}) of Singlet Monodeuteriovinylidenecarbene[a]

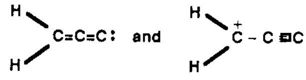
	mode	MP2/ 6-31G**	experiment
A″	CCC out-of-plane bend	222 (14)	
A′	CCC in-plane bend	251 (113)	
A″	CH(D) wagging	905 (133)	865.4 (0.03)
			868.8 (0.02)
A′	CH(D) rock	951 (645)	904.0 (0.03)
			909.8 (0.03)
A′	CCC symm stretch	1139 (24)	
A′	CH(D) scissoring	1413 (223)	1331.6 (0.07)
			1335.5 (0.05)
A′	CH(D) rock and CCC antisymm stretch	2064 (16063)	1940.6 (1.00)
			1953.1 (0.49)
A′	CD stretch	2401 (1254)	2254.5 (0.02)
			2266.5 (0.02)
A′	CH stretch	3259 (196)	

[a] IR intensities are in parentheses, calculated intensities are absolute values in cm^{-2} L mol^{-1}, experimental intensities are relative to the strongest band.

Table V. Calculated Vibrational Frequencies (cm^{-1}) of Triplet Vinylidenecarbene[a]

	mode	MP2/6-31G**
B_2	CCC in-plane bend	406 (22)[b]
B_1	CCC bond out-of-plane bend	483 (131)
B_1	CH wagging	709 (2424)
B_2	CH rock	1076 (39)
A_1	coupled CC stretches	1150 (390)
A_1	scissoring	1528 (2)
A_1	coupled CC stretches	2072 (130)
A_1	CH symm stretch	3280 (68)
B_2	antisymm CH stretch	3394 (5)

[a] IR intensities in cm^{-2} L mol^{-1} are in parentheses. [b] Intensities are MP2 intensities obtained with GAUSSIAN 82 (Revision K).



in dipole moment. Finally, the computed frequencies and intensities of the triplet of vinylidenecarbene are given in Table V

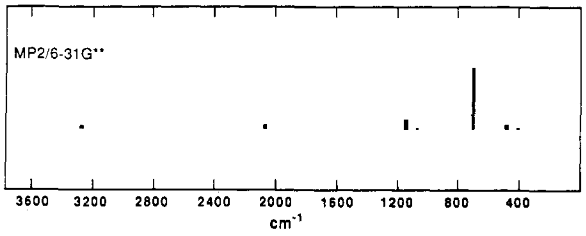
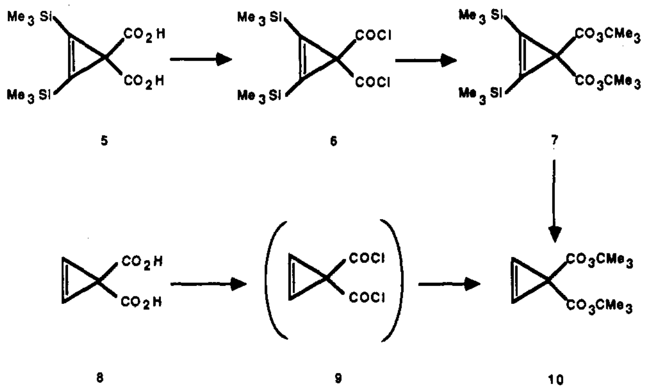


Figure 4. Calculated MP2/6-31G** infrared spectrum for triplet vinylidenecarbene obtained with GAUSSIAN 82 (Revision K). These are rigorous MP2 intensities (see text).

Scheme I



and plotted in Figure 4. Our SCF/6-31G** vibrational frequencies for both the singlet and triplet are very similar to the SCF/6-31G* (unscaled) frequencies reported by DeFrees and McLean.[11] They reported no IR intensities.

Preparation of Cyclopropenylidene (3)

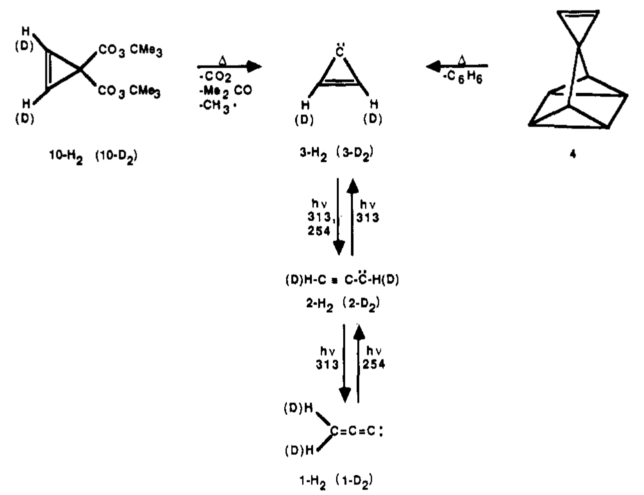
Perester **10** can more easily be prepared than the quadricyclane derivative **4** and is the best candidate for the preparation of cyclopropenylidene (**3**).[15] The synthesis of **10** is outlined in Scheme I. 2,3-Bis(trimethylsilyl)-2-cyclopropenedicarboxylic acid (**5**)[16] can be converted via dichloride **6** into diperester **7**. The trimethylsilyl protecting groups may be removed by H_2O/KF or D_2O/KF, yielding the precursors **10**-H_2 or **10**-D_2. Diperester **10**-H_2 can also be prepared starting with the unsubstituted 2-cyclopropene-1,1-dicarboxylic acid (**8**) via the dichloride **9**.[16] The peresters **10**-H_2 and **10**-D_2 were pyrolyzed in high vacuum and the products cocondensed with a large excess of argon on a CsI window held at 12 K. A complete conversion was reached at 480 °C. The IR spectra showed the expected products: acetone, CO_2, methyl radical, and cyclopropenylidene (**3**).

This observation proves that geminal diperesters can be used as carbene sources in cases where standard procedures (fragmentation of salts of tosylhydrazones, diazocompounds, etc.) cannot be applied.

The very intense absorptions of acetone and CO_2 made it difficult to register the bands of the other compounds formed. But fortunately all products except **3** are stable during the following photolysis, and therefore most of the bands could be eliminated by subtracting the spectra at various stages of the photolysis. These difference spectra turned out to be a good tool not only for monitoring the spectral changes caused by irradiation but also for picking out the bands of the photoprecursor and its photoproducts.

Photoisomerization of Cyclopropenylidene (3)

Scheme II



On irradiation of the argon matrix containing **3**-H_2 with 313-nm light the 4 IR bands of cyclopropenylidene (**3**) at 1278.6, 1277.7 (doublet), 1063.6, 887.1, and 787.8 cm^{-1} decrease, and the absorptions of triplet propargylene (**2**) (3293.0, 3266.0, 408.8, 402.6, 259.9, 245.9) grow. The bands are obviously split (matrix effects) into "doublets" which indicates that there are primarily two different matrix sites. (This "splitting" of the bands differs from experiment to experiment and can be changed irreversibly by annealing the matrix to 30 K. After this procedure the higher component of the doublets disappears completely.) Two additional bands at 582.4 and 547.2 cm^{-1} are seen. They have also been observed on irradiation of both cyclopropenylidene (**3**) prepared from precursor **4**[6] and diazopropyne.[3] The intensities of these two bands with respect to the other bands of propargylene do not remain exactly constant at different stages of the photolysis. Therefore they cannot rigorously be assigned to propargylene.

After irradiation of **3**-H_2 for 2.5 h a conversion of about 75% is achieved. In this early stage of the photolysis a pair of bands at 1963.2 and 1952.2 cm^{-1} can already be observed. They are the strongest absorptions of a set of bands (3059.6, 3049.5, 1963.2, 1952.2, 1449.3, 1446.9, 1025.0, 1004.8, and 999.5 cm^{-1}) which, on further irradiation, grow in proportion to the decrease of the first set of bands assigned to **2** (including the absorptions at 582.4 and 547.2 cm^{-1}). After 20 h the bands of cyclopropenylidene (**3**) are barely detectable (<4% of the initial intensity), and only traces of propargylene (**2**) are left. As discussed below, the new set of bands can be ascribed to vinylidenecarbene (**1**) which is formed by a photochemically induced 1,3-hydrogen shift along with a change in multiplicity.

On changing the excitation wavelength to 254 nm (mercury low pressure lamp) a rather rapid back reaction occurs. After 2 h, the bands of **1** and the absorptions of cyclopropenylidene are completely missing, and the propargylene absorptions (including the bands at 582 and 547 cm^{-1}) are of high intensity. By a repeated photolysis of the newly formed **2** with 313-nm light the complete reversibility of the isomerization can be demonstrated. After 20 h of irradiation at this wavelength a set of bands that are identical with those previously assigned to **1** reappears, and they reach the same intensity as before. Even a small amount of cyclopropenylidene (**3**) can be detected. The same photochemical cycle (Scheme II) is performed if the dideuteriocyclopropenylidene (**3**-D_2) prepared by pyrolysis of perester **10**-D_2 is treated in the same way.

Identification of Vinylidenecarbene (1)

Because of the reversible transformation (313 nm) of propargylene into the new photoisomer **1** and in part to cyclopropenylidene, this new species must have the formula C_3H_2. Its characterization as vinylidenecarbene proves to be straightforward when the observed and theoretical spectra (C_3H_2, C_3HD and C_3D_2) are compared. In Figures 1 and 2 the C_3H_2 and C_3D_2 experimental spectra of this new photoisomer are plotted along with the computed theoretical spectra of vinylidenecarbene. The discussion will be limited to comparison of the experimental and

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(15) We also tried to use a microwave discharge in argon/allene mixtures[9] in order to produce matrix isolated **3**, but we got only traces of cyclopropenylidene besides large amounts of acetylene, diacetylene, ethylene, and methane.

(16) Maier, G.; Wolf, B. *Synthesis* **1985**, 871.

MP2 spectra since the MP2 method should be the most reliable of the three used, although in the present case there are no major differences between the three sets of computed spectra. The most intense band of the observed spectrum ($\sim$1950 cm^{-1}) is in good agreement with the prediction that the most intense band of vinylidenecarbene should occur at 2075 cm^{-1}. Upon dideuteriation this intense band is shifted by only 19 cm^{-1}, and this agrees well with a predicted shift of 26 cm^{-1}. Upon monodeuteriation this band is observed to shift by 12 cm^{-1} in even better agreement with the predicted shift of 11 cm^{-1}. Examination of the computed normal mode of this band indicates that it is primarily the "antisymmetric" A_1 stretching of the two carbon–carbon double bonds, although there is significant coupling with CH_2 scissoring. Further support for this assignment comes from the fact that this is the region where allene-type molecules typically give rise to an antisymmetric stretch that is known to be barely affected by a substituent. Only one C–H stretch could be observed (3049.5 and 3059.6 cm^{-1}). This is likely to be the A_1 symmetric stretch since, although both the A_1 and B_2 C–H stretches are predicted to be of low intensity, the former is computed to have an intensity of seven times that of the latter. Again, comparison of this absorption with that of allene (3000 cm^{-1}, Ar, 12 K) lends further support to the allene-like structure of this new photoisomer. Of the remaining two A_1 bands, one is predicted to be of very weak intensity and the other to be of weak intensity. The band observed at 1446.9 cm^{-1} is assigned to this second A_1 band (1542 cm^{-1}) of weak intensity. The computed normal mode indicates that it is predominantly a CH_2 scissoring. The computed shifts of 129 and 275 cm^{-1} on mono- and dideuteriation compare favorably with the experimental values of 115 and 238 cm^{-1}.

Two additional bands are observed near 1000 cm^{-1}. Three weak absorptions are predicted to fall into this region, the very weak A_1 (1152 cm^{-1}) band, the CH rock (1080 cm^{-1}), and the CH wagging (1051 cm^{-1}). On the basis of the difference in the intensities of the two observed bands we tentatively assign the pair of experimental frequencies (999.5, 1004.8 cm^{-1}) to the CH wagging (B_1) and the less intense absorption found at 1025 cm^{-1} to the CH rock (B_2) vibration. On dideuteriation both are shifted by about 200 cm^{-1} to lower frequencies, in good agreement with the calculated spectra. The fourth expected A_1 band cannot—due to the extremely low intensity—be detected in the case of **1**-H_2, but in the spectrum of **1**-D_2 the band at 950.8 cm^{-1} may originate from this mode. The calculations show that this absorption should be more intense for the dideuteriated species.

Comparison of the observed and computed spectra of C_3HD is done in Table IV and Figure 3. All observed bands are easily assigned by comparison with the computed spectrum.

Taking into account that calculated frequencies are normally found to be too high, the agreement between calculated and experimental spectra for the **1**-H_2, **1**-D_2, and **1**-HD isotopomers is striking and leaves little doubt that the new C_3H_2 isomers are indeed the vinylidenecarbenes (**1**-H_2, **1**-D_2, and **1**-HD). The theoretical spectra also show that vinylidenecarbene has a singlet ground state since the theoretical IR spectrum of the triplet species looks completely different (see Table V and Figure 4). This conclusion based on distinct differences in computed IR spectra is much sounder than one based on the computed energy differences of Table II since these vary greatly with the method of computation. Following the photolysis of **3** by ESR spectroscopy also confirms that **1** has a singlet ground state. The argon-matrix isolated pyrolysis products of **10** exhibit only a very intense ESR signal arising from methyl radicals. On irradiation with 313-nm light the known absorption of triplet propargylene[2] appears, but it decreases again together with the IR bands of **2** upon long time photolysis. These results indicate that **1** possesses a singlet ground state.

Finally, the high dipole moment of **1** (4.06 D in the 6-31G** basis) should be mentioned. This is even greater than the computed 3.39 D (6-31G**) moment of cyclopropenylidene (**3**) which has been observed in interstellar space. Since we have shown that vinylidenecarbene can be formed from cyclopropenylidene, vinylidenecarbene might also be present and detectable there.

Computational Methods

The calculations were performed by three standard quantum chemical ab initio methods,[17] SCF/4-31G, SCF/6-31G**, and MP2/6-31G**, for which the merits and pitfalls of the calculated vibrational spectra are relatively well understood.[14] Optimum geometries were obtained by standard options of the program GAUSSIAN 82.[18] Force constants were obtained differently at SCF and MP2 levels. At the SCF level a set of structures was generated, each of which was distorted from the equilibrium structure along symmetry-adapted internal coordinates ΔS_i. These displacements were chosen to make a distortion of each bond involved in ΔS_i equal to ±0.02 Å and bond angle changes equal to ±3°. For each structure the energy gradient and the dipole moment were computed by the program HONDO.[19] The gradients obtained in cartesian coordinates were transformed to symmetry-adapted coordinates. Numerical differentiation of the gradient and the dipole moments yielded force constants and dipole moment derivatives, as advocated by Pulay.[20] Force constants and dipole moment derivatives in the A_1 symmetry block were obtained by averaging the data given by $+\Delta S_i$ and $-\Delta S_i$. The vibrational frequencies were computed by the Wilson GF method, and IR intensities were obtained from the dipole moment derivatives as described elsewhere.[14] For singlet structures, force constants at the MP2 level were computed numerically, i.e., directly from the MP2 energies. Diagonal force constants were obtained by a three-point harmonic fit to $-\Delta S_i$, 0, and $+\Delta S_i$ points, and the off-diagonal force constants were obtained from $(+\Delta S_i)(+\Delta S_j)$ and $(-\Delta S_i)(-\Delta S_j)$ distortions. ΔS_i corresponded again to changes of 0.02 Å or 3°. It should be pointed out that our MP2 intensities are not computed in an entirely consistent way. Since neither GAUSSIAN 82 (Revision H) nor HONDO, which were used for all but the triplet MP2 calculations, computes dipole moments for MP2 wave functions, we computed SCF/6-31G** dipole moment changes along the MP2/6-31G** normal modes to approximate the MP2 intensities. The MP2 energies for the distorted singlet structures were computed by the program HONDO 5/MP2.[21] The frozen-core approximation was used for MP2 vibrational calculations on the singlets, though it was not used in the MP2 optimum structures in Table I nor the MP2 energies in Table II.

The newer GAUSSIAN 82 (Revision K) was used for the triplet MP2 calculations in Table V and Figure 4. This version does compute MP2 dipole moments and hence exact MP2 IR intensities. First derivatives were computed analytically and second derivatives numerically. The frozen core approximation was not used. Trial calculations on cyclobutadiene[22] indicate that results from these two methods (i.e., that used for singlets and that for the triplet) of computing MP2 intensities differ very little.

Experimental Section

A. Matrix Isolation Equipment. Cryostat: A Displex closed cycle refrigerator CSA 202 (Air Products) was used. **Spectrometers**: FT IR spectrometer IFS 85 (Bruker) with CsI optics (IR spectra were taken with a resolution of 1 cm) and an EPR spectrometer E 4 (Varian) were used. **Light Sources**: A mercury high-pressure lamp HBO 200 (Osram) with a monochromator (Bausch & Lomb) (band width 20 nm) and a mercury low-pressure lamp "Flächenstrahler 75 W" (Gräntzel) were used. **Flash Pyrolysis/Matrix Isolation**: A homemade oven with an inner quartz tube (i.d. 8 mm, length of heated zone 5 cm), which could be heated with a heating wire up to 1000 °C, surrounded by a water cooled metal jacket was used. The oven was directly flanged to the cryostat. Precursors **10**-H_2 and **10**-D_2 were warmed to 50–60 °C and slowly (4–5 h) sublimed through the quartz tube (480 °C) and cocondensed with a

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[22] Hess, B. A., Jr.; Čársky, P.; Schaad, L. *J. Am. Chem. Soc.* **1983**, *105*, 695, and further unpublished results.

high excess of argon on a CsI window (IR) or a copper rod (EPR) at 12 K.

B. Synthesis of Precursors 10-H_2 and 10-D_2. 2,3-Bis(trimethylsilyl)-2-cyclopropene-1,1-dicarboxylic Acid Dichloride (6). Diacid **5**[16] (800 mg, 2.94 mmol) was stirred for 4 h at room temperature with 10 mL of thionyl chloride. The excess of $SOCl_2$ was removed (oil pump vacuum) and the residue extracted with pentane. Evaporation of the solvent gave dichloride **6** (892 mg, 96%) as pale waxy yellow crystals: mp (after distillation) 31 °C dec; IR 1845, 1805, 1775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.40 (s); ^{13}C NMR ($CDCl_3$) δ 170.2, 125.2, 29.5, −1.8. Anal. Calcd for $C_{11}H_{18}Cl_2O_2Si_2$: C, 42.73; H, 5.86. Found: C, 43.08; H, 5.92.

Di-*tert*-butyl 2,3-Bis(trimethylsilyl)-2-cyclopropene-1,1-diperoxycarboxylate (7). To a solution of *tert*-butyl hydroperoxide (80%) (875 mg, 7.78 mmol), absolute pyridine (615 mg, 7.78 mmol) and 40 mL of pentane were added dropwise over 3 h a solution of dichloride **6** (892 mg, 2.88 mmol) in 25 mL of pentane at −30 °C. After the mixture was stirred at −30 °C for 50 h the pyridinium salt was filtered off and the filtrate washed with an aqueous solution of $NaHCO_3$ (10%), H_2SO_4 (10%), and water. The usual workup and recrystallization from hexane gave diperester **7** (544 mg, 45%) as colorless crystals: mp 84 °C dec; IR 1762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (s, 18), 1.35 (s, 18); ^{13}C NMR ($CDCl_3$) δ 169.2, 122.8, 83.7, 28.4, 25.3, −1.7. Anal. Calcd for $C_{19}H_{36}O_6Si_2$: C, 54.77; H, 8.71. Found: C, 54.50; H, 8.63.

Di-*tert*-butyl 2-Cyclopropene-1,1-diperoxycarboxylate (10-H_2). From **7**: A solution of diperester **7** (135 mg, 0.32 mmol) and 6 mL of acetonitrile was treated for 3 h at room temperature with KF (70 mg, 1.21 mmol) and dibenzo-18-crown-6 (67 mg, 0.17 mmol). After filtration the solvent was evaporated and the residue dissolved in ether. After filtration through a short silica gel column to separate the crown ether, final chromatography (silica gel, ether) gave pure perester **10**-H_2 (67 mg, 77%). From **8**: Diacid **8**[16] (400 mg, 3.12 mmol) was stirred for 5 h at 40 °C with an excess of $SOCl_2$. After removal of the unreacted $SOCl_2$ (oil pump vacuum) the crude dichloride **9** was used directly for the preparation of the diperester. A solution of dichloride **9**, 10 mL of pentane, and 2 mL of ether was dropped slowly into a solution of absolute pyridine (500 mg, 6.33 mmol), *tert*-butyl hydroperoxide (80%) (675 mg, 6.32 mmol), and 20 mL of pentane at −30 °C under an argon atmosphere. A brownish precipitate of pyridinium chloride was formed. After 12 h of additional stirring at −30 °C the reaction mixture was filtered and the filtrate washed with water, 10% sulfuric acid, 10% $NaHCO_3$ solution, and again with water and finally dried with $MgSO_4$. Evaporation of the solvent and recrystallization from hexane yielded diperester **10**-H_2 (45 mg, 8%) as colorless crystals: mp 89 °C (detonation); IR 1775 cm^{-1}; ^1H NMR δ 1.36 (s, 2), 6.95 (s, 9); ^{13}C NMR 167.6, 102.3, 84.4, 31.2, 26.1; mass spectrum (70 eV), *m/e* 155 ($M^+ - O\text{-}t\text{-}Bu - CO_2$), 126 ($M^+ - 2\,O\text{-}t\text{-}Bu$), 82 ($M^+ - 2\,O\text{-}tBu - CO_2$). Active O. Calcd 23.50%; found (iodometric) 23.44%.

Di-*tert*-butyl [2,3-$^2H_2$]-2-Cyclopropene-1,1-diperoxycarboxylate (10-D_2). To a solution of diperester **7** (352 mg, 0.83 mmol) and 10 mL of [$^2H_3$]acetontrile was added dry KF (186 mg, 3.27 mmol), which was moistened with D_2O, and dibenzo-18-crown-6 (175 mg, 0.44 mmol). After 3 h of stirring at room temperature and workup as described above, diperester **10**-D_2 (146 mg, 64%) (contaminated with ≈10–20% of the monodeuteriated isotopomer) was isolated as colorless crystals: mp 86 °C (detonation); IR 1776 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (s); ^{13}C NMR ($CDCl_3$) δ 167.8, 84.6, 26.9, 25.9 (olefinic deuteriated C atoms not detectable). Anal. Calcd for $C_{13}D_2H_{18}O_6$: C, 56.92; H, 7.34. Found: C, 57.13; H, 7.19.

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