

Photochemistry of Butatriene – Spectroscopic Evidence for the Existence of Allenylcarbene<sup>†</sup>Roman Wrobel,<sup>‡</sup> Wolfram Sander,<sup>\*,‡</sup> Dieter Cremer,<sup>\*,§</sup> and Elfi Kraka<sup>§</sup>*Lehrstuhl für Organische Chemie II der Ruhr-Universität, D-44780 Bochum, Germany, and Department of Theoretical Chemistry, Göteborg University, S-41296 Göteborg, Sweden**Received: November 12, 1999; In Final Form: February 17, 2000*

The photochemistry of butatriene (**2**), matrix-isolated in argon at 10 K, was investigated. UV irradiation (248 nm) produces vinylacetylene (**1**) and the dimer of acetylene and in addition methylenecyclopropene (**3**) as a major product. The photochemical **2** → **3** rearrangement is reversible, and on visible light irradiation ( $\lambda > 420$  nm) **3** is transformed back to **2**. The formation of **3** from **2** requires a [1,2]-H migration to allenylcarbene (**8**). According to MP2 and DFT calculations, **8** is a minimum on both the triplet (T) and the singlet (S) potential energy surface (PES). The comparison of measured and calculated infrared spectra suggests that two forms of **8** (either syn and anti form of S-**8** or a mixture of S-**8** and T-**8**) can be trapped at low temperatures in the matrix. The rearrangement **2** → **3** proceeds in a stepwise manner with S-**8** as intermediate on the S-PES (calculated heat of formation at 298 K,  $\Delta H_f^\circ(298) = 131.7$  kcal/mol) and T-**8** on the T-PES ( $\Delta H_f^\circ(298) = 129.0$  kcal/mol).

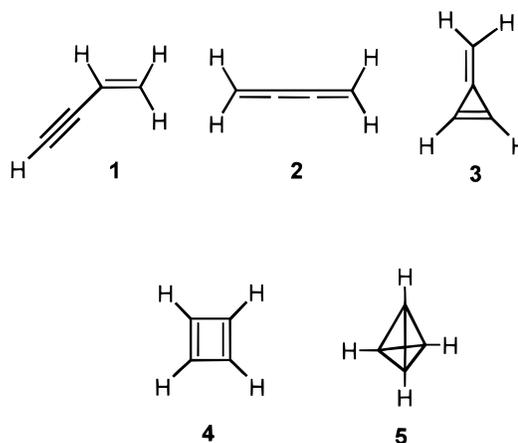
## Introduction

The C<sub>4</sub>H<sub>4</sub> potential energy surface (PES) is of special interest to organic chemistry and has been extensively investigated both experimentally<sup>1,2</sup> and theoretically.<sup>3,4</sup> Vinylacetylene (**1**) (see Chart 1) is the thermodynamically most stable C<sub>4</sub>H<sub>4</sub> isomer ( $\Delta H_f^\circ = 70.4$  kcal/mol),<sup>5,6</sup> followed by butatriene (**2**) lying 13 kcal/mol above **1**.<sup>6</sup> Of the three monocyclic isomers methylenecyclopropene (**3**), cyclobutadiene (**4**), and cyclobutynes, the first two could be isolated in low-temperature matrices.<sup>7,8</sup> Compound **3** was also synthesized in solution at low temperature (stable solutions below  $-75$  °C) and characterized by NMR spectroscopy.<sup>7,9</sup> So far, in addition to **1**–**4**, no other C<sub>4</sub>H<sub>4</sub> isomer has been isolated and especially the highly strained tetrahedrane (**5**) is still a challenge.

The photochemistry of some matrix-isolated C<sub>4</sub>H<sub>4</sub> molecules was reported by Chapman et al. in 1974 (Scheme 1).<sup>1</sup> Irradiation of methylenecyclobutenone (**6**) produced ketene (**7**) which, on subsequent shorter wavelength irradiation, gave **2** and **3**. Allenylcarbene (**8**) was postulated as the primary C<sub>4</sub>H<sub>4</sub> isomer which yields **2** and **3** via a [1,2]-H shift or a vinylcarbene–cyclopropene rearrangement, respectively. Prolonged irradiation finally results in the formation of **1** and acetylene (**9**). The formation of **1** as the main product of the irradiation of **3** was independently confirmed by Maier et al.<sup>2</sup>

Recently, we reported on the addition of matrix-isolated difluorovinylidene (**11**) to **9** and difluoroacetylene (**12**), which provides novel entries to C<sub>4</sub>H<sub>2</sub>F<sub>2</sub> and C<sub>4</sub>F<sub>4</sub> species, respectively (Scheme 2).<sup>10</sup> The thermal reaction of **11** with **12** yields allenylcarbene (**14a**) which is stable under the conditions of matrix isolation but, on irradiation, rearranges to tetrafluoromethylenecyclopropene (**13a**) (main product) and tetrafluorobutatriene (**16a**) (minor product). Thus, for the first time an

CHART 1



allenylcarbene as precursor of a methylenecyclopropene could be isolated and spectroscopically characterized. The fluorine substituent at the carbene center of **14a** stabilizes the closed shell singlet state, which now becomes the ground state, in contrast to carbenes **8** and **14b** with triplet ground states. In addition, the [1,2]-F migration in **14a** is prevented by a much higher barrier than the [1,2]-H migration in **8** and **14b**, and thus **14a** is perfectly stable under the conditions of matrix isolation.

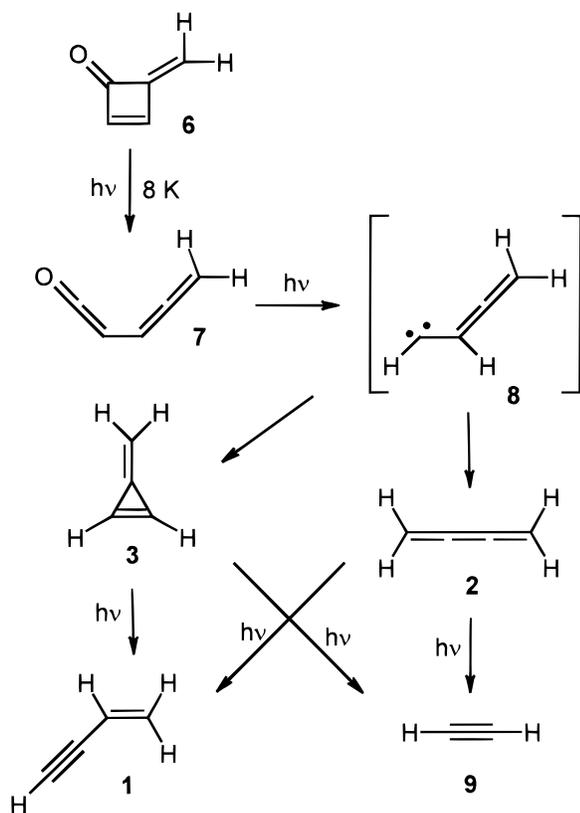
Visible irradiation of difluoromethylenecyclopropene (**13b**) produces difluorovinylacetylene (**15**) and small amounts of difluorobutatriene (**16b**). The formation of the latter product indicates that the cyclization of the allenylcarbenes **14** to **13** is reversible. In a review on cumulene photochemistry, Johnson stated that “among the most intriguing questions in butatriene photochemistry is the possible 1,2-hydrogen shift to allenylcarbene, followed by closure to methylenecyclopropene”.<sup>11</sup> Here we report on the photochemistry of **2** which produces **3**, among other products. The role of **8** as an intermediate in this photochemical rearrangement is discussed with the help of MP2 and DFT calculations.

<sup>†</sup> Part of the special issue “Marilyn Jacox Festschrift”.

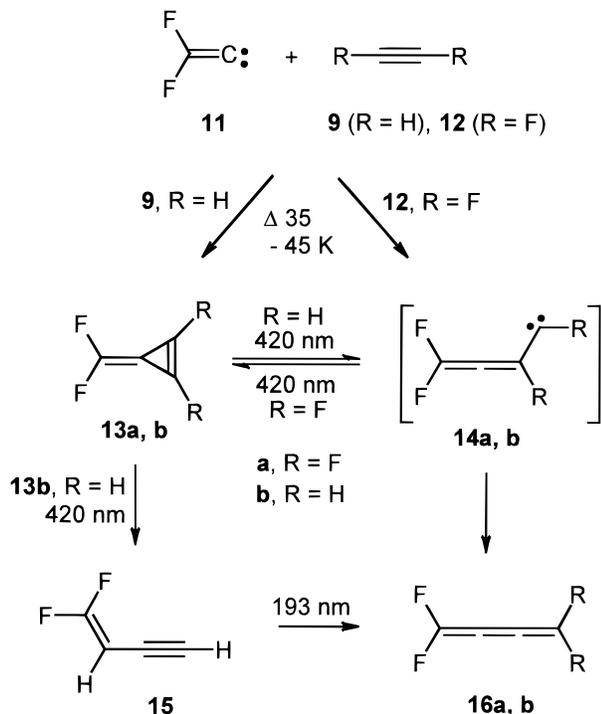
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## SCHEME 1



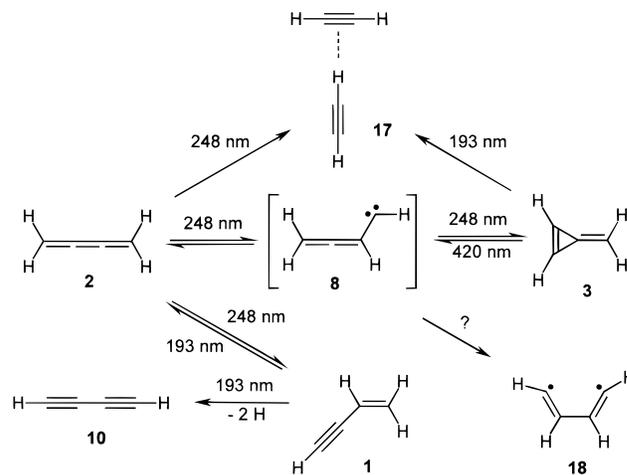
## SCHEME 2



## Results and Discussion

The IR spectrum of **2**, matrix-isolated in argon at 10 K, exhibits a very strong absorption at  $852\text{ cm}^{-1}$  ( $\text{CH}_2$  wagging) and strong absorptions at  $1367\text{ cm}^{-1}$  ( $\text{CH}_2$  scissoring) and  $1609\text{ cm}^{-1}$  (CC stretching). Several hours of irradiation with  $\lambda > 280\text{ nm}$  (mercury high-pressure arc lamp in combination with cutoff filters) does not result in any change of the spectrum. However, 15 min irradiation with  $\lambda = 248\text{ nm}$  (KrF excimer laser) results

## SCHEME 3



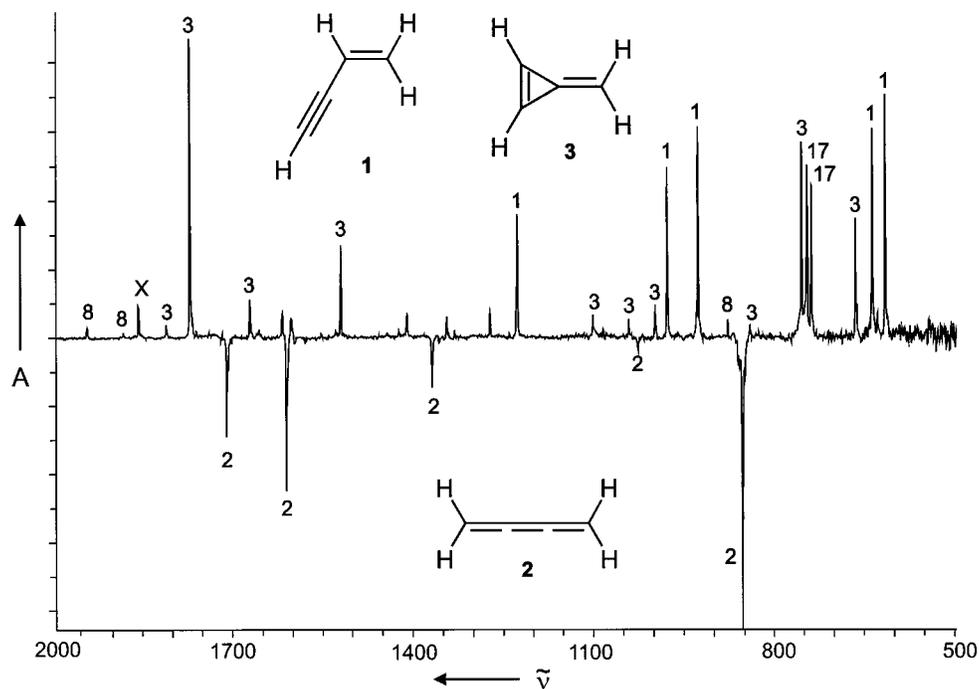
in a decrease of **2** and formation of **3**, **1**, and the van der Waals dimer of acetylene (**17**)<sup>12</sup> (Scheme 3, Figure 1). These photo-products are easily identified by comparison of the IR spectrum with literature data. Three additional weak absorptions at  $1942$ ,  $1881$ , and  $877\text{ cm}^{-1}$  could not be assigned to known compounds.

On irradiation of the product mixture described above with visible light ( $\lambda > 420\text{ nm}$ ), **3** rearranges to **1** and **2**, as it was described by Chapman et al. (Figure 2).<sup>1</sup> Several minutes of irradiation with  $\lambda = 193\text{ nm}$  (ArF excimer laser) results in a decrease of all absorptions of **1** and **3** and formation of more **2**. In addition, **17** and butadiyne (**10**) are formed (Figure 3).

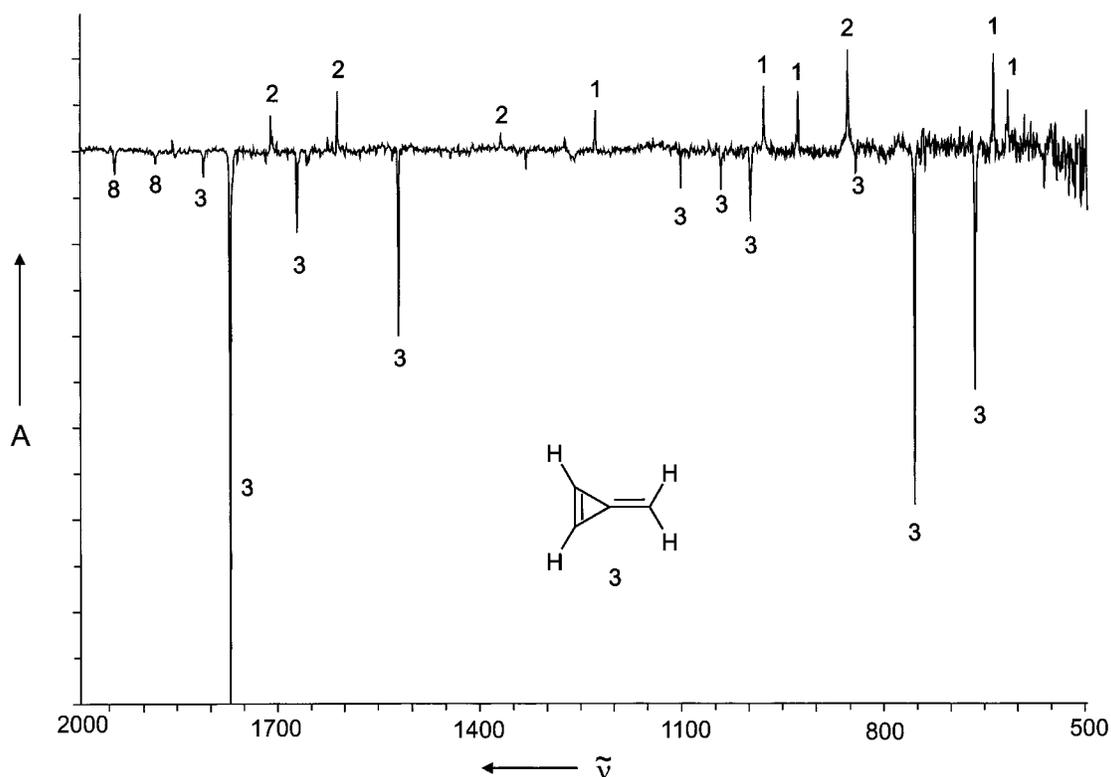
The structures, thermochemical data, and IR spectra of several  $\text{C}_4\text{H}_4$  isomers were calculated at the MP2 and DFT/B3LYP level of theory using a 6-311++G(3df,3pd) basis set.<sup>13</sup> The global minimum of the  $\text{C}_4\text{H}_4$  potential energy surface is **1** with a heat of formation  $\Delta H_f^\circ$  of  $70.4\text{ kcal/mol}$  determined by Roth et al.<sup>5</sup> The enthalpy of **2** is calculated to be  $81.9\text{ kcal/mol}$  (MP2, Table 1), in good agreement with experimental data ( $83.0\text{ kcal/mol}$ )<sup>6</sup> and previous theoretical predictions.<sup>4</sup> DFT exaggerates the stability of **2**, which is in line with its known tendency of exaggerating  $\pi$ -delocalization. Nevertheless, both the MP2 and B3LYP IR spectrum of **2** reasonably agree with the experimental IR spectrum.

The photochemical interconversion of **3** and **2** requires a [1,2]-migration of one hydrogen atom. Obviously, carbene **8** is the key intermediate in this rearrangement and is linked to **2** via a [1,2]-H shift and to **3** via a vinylcarbene–cyclopropene rearrangement. Two conformations of triplet carbene T-**8** ( $^3A''$ ) were located at both the UMP2/6-311++G(3df,3pd) and the UB3LYP/6-311++G(3df,3pd) level of theory, *s-syn*-T-**8** and *s-anti*-T-**8**, both possessing  $C_s$  symmetry (Figure 4). Since DFT contrary to MP2 leads to reliable S–T splittings in the case of carbenes, UB3LYP results were considered to give a reliable description of the various states and conformations of **8**. The *syn* and *anti* forms possess the same stability while vibrational corrections lead to an enthalpy difference of  $0.2\text{ kcal/mol}$  in favor of the *anti* form (Table 1). The best estimate for the heat of formation of *s-syn*-T-**8** is  $129.2\text{ kcal/mol}$ , which suggests an enthalpy difference of  $46\text{--}47\text{ kcal/mol}$  with regard to **2** (using either the experimental or the MP2 value of  $\Delta H_f^\circ(298)$ , Table 1). The *syn* and *anti* form are separated by a rotational barrier of  $3.4\text{ kcal/mol}$  so that interconversion is prevented under the conditions of matrix isolation, but easily possible at higher temperatures.

The closed shell S state of carbene **8** with the electron configuration  $\sigma^2\pi^0$  possesses four  $C_1$  symmetrical minima,



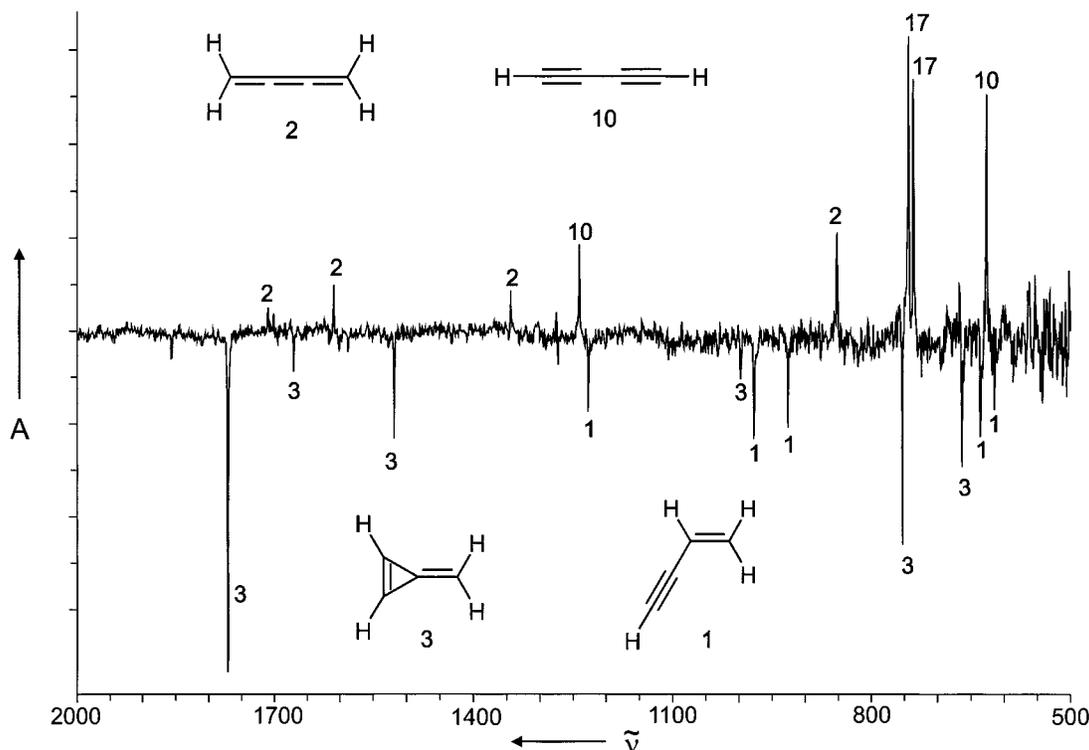
**Figure 1.** Difference IR spectrum showing the 248 nm photochemistry of butatriene **2** in argon at 10 K. Bands pointing downward: IR absorptions disappearing after 15 min irradiation with  $\lambda = 248$  nm (10 Hz, 150 mJ/pulse). Bands pointing upward: new absorptions of methylenecyclopropene **3**, vinylacetylene **1**, and acetylene dimer **17**.



**Figure 2.** Difference IR spectrum showing the 420 nm photochemistry of methylenecyclopropene **3** in argon at 10 K. Bands pointing downward: IR absorptions disappearing after 30 min irradiation with  $\lambda > 420$  nm. Bands pointing upward: absorptions of vinylacetylene **1** and butatriene **2** formed during the irradiation.

which are arranged in enantiomeric pairs, namely one pair with a syn and one with an anti conformation of the terminal CH group (*s-syn-S-8* and *s-anti-S-8*, Figure 4). Both conformers of **T-8** are planar, while the **S-8** conformations are slightly distorted from a planar arrangement of the C atoms (Figure 4), which

seems to be a result of the fact that allyl resonance is no longer possible for the **S-8** forms. For example, the formal (H)C—C(H) single bond in **S-8** (1.407 and 1.416 Å, Figure 4) is clearly longer than in **T-8** (1.373 and 1.371 Å, Figure 4). The four  $C_s$  symmetrical **S-8** forms are transition states for the interconver-



**Figure 3.** Difference IR spectrum showing the 193 nm photochemistry of methylenecyclopropene **3** and vinylacetylene **1** in argon at 10 K. Bands pointing downward: IR absorptions disappearing after 10 min irradiation with  $\lambda = 193$  nm (1 Hz, 150 mJ/pulse). Bands pointing upward: absorptions of butatriene **2**, acetylene dimer **17**, and butadiyne **10** formed during the irradiation.

**TABLE 1: Energies of C<sub>4</sub>H<sub>4</sub> Isomers Calculated at the B3LYP/6-311++G(3df,3pd) Level of Theory<sup>a</sup>**

molecule	method	state	$\Delta E$	$\Delta\Delta H(298)$	$\mu$	$\Delta H_f^\circ(298)$	$\omega_1$
<b>1</b>	MP2	<sup>1</sup> A, C <sub>s</sub>	-154.38933	-154.32249	0.54	(70.4)	219
	DFT		-154.79540	-154.72900	0.42		226
<b>2</b>	MP2	<sup>1</sup> A <sub>g</sub> , D <sub>2h</sub>	11.5	11.5	0.0	81.9 (83.0)	227
	DFT		3.4	2.9	0.0		225
<b>3</b>	DFT	<sup>1</sup> A <sub>1</sub> , C <sub>2v</sub>	22.4	21.9	2.13	92.3	361
	MP2	<sup>3</sup> A'', C <sub>s</sub>	79.8 (0)	79.9(0)	0.45		221
s-syn-T- <b>8</b>	DFT		61.0 (0)	58.8(0)	0.76	129.2	207
	MP2	<sup>3</sup> A'', C <sub>s</sub>	80.9 (1.1)	80.6(0.7)	0.67		244
s-anti-T- <b>8</b>	DFT		61.0 (0)	58.6(-0.2)	0.74	129.0	206
	DFT	<sup>1</sup> A, C <sub>1</sub>	63.4 (2.4)	61.3(2.5)	2.86	131.7	163
s-syn-S- <b>8</b>	DFT	<sup>1</sup> A, C <sub>1</sub>	64.9 (3.9)	62.4(3.6)	252	132.8	158
<b>9</b>	DFT	<sup>1</sup> A <sub>1</sub> , C <sub>2v</sub>	43.6	41.1	0.32	111.5	31
	DFT	<sup>1</sup> A <sub>g</sub> , D <sub>∞h</sub>	44.4	41.2	0.0	111.6 (108.6)	653

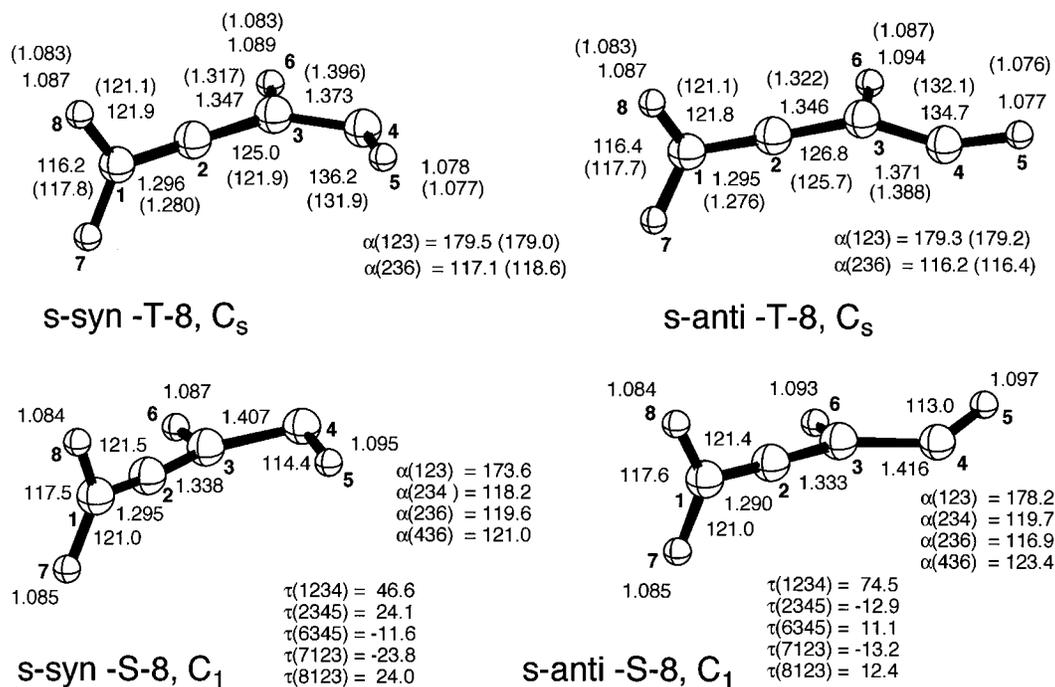
<sup>a</sup> Absolute energies and enthalpies for **1** in hartree, relative energies  $\Delta E$  and enthalpies  $\Delta H$  in kcal/mol, dipole moments in Debye. Energies  $\Delta E$  in parentheses give the S-T splittings or syn-anti differences relative to s-syn-T-**8**. The smallest frequency [cm<sup>-1</sup>] is given to verify the nature of the stationary point. Heats of formation are given relative to  $\Delta H_f^\circ(\mathbf{1}) = 70.4$  kcal/mol and are based on the best calculational result obtained. Experimental  $\Delta H_f^\circ$  values (in parentheses) are taken from ref 6.

sion of the enantiomeric pairs, which requires just 0.5 (syn) and 0.2 kcal/mol (anti), respectively. The S-**8** minima are located 2.5 and 3.8 kcal/mol above the corresponding T-**8** forms.

Rotation of the CH group of S-**8** leads to the corresponding open-shell S state <sup>1</sup>A'' ( $\sigma^1\pi^1$ ) via surface crossing. We did not investigate this state further, but ROSS-DFT calculations indicate that it should be 14–15 kcal/mol higher in energy than the T state <sup>3</sup>A''.<sup>14</sup> Again, the C<sub>s</sub> symmetrical forms of the <sup>1</sup>A'' state are transition states, which, however, does not exclude more stable minima.

It was possible to locate the transition state for the [1,2]-H shift in **2** on both the S- and the T-PES. According to B3LYP/6-311++G(3df,3pd) calculations, the S transition state is 63.6 kcal/mol above the S-**2** while the T transition state is 52.2 kcal/mol above T-**2**, which in turn is calculated to be 32 kcal/mol above the ground state and which is characterized by an orthogonal arrangement of the terminal CH<sub>2</sub> groups. The total

activation enthalpy on the T-PES is 84.4 kcal/mol and, by this, 20 kcal/mol larger than the activation enthalpy on the S-PES. The energy of the laser light used is about 148 kcal/einstein at  $\lambda = 193$  nm and by this much larger than either S- or T-barrier so that one could assume an equal chance of generating S-**8** or T-**8**. However, one has to consider the lifetime of T-**2**, which is probably much too small to make any reaction with a barrier of 52 kcal/mol likely on the T-PES. Therefore, the rearrangement from **2** to **8** should predominantly take place on the S-PES. On the way to carbene S-**8**, S-PES and T-PES cross and there is the possibility of an intersystem crossing of C<sub>4</sub>H<sub>4</sub> to the T-PES and the formation of T-**8**.<sup>14</sup> Calculations show that the rearrangement **2** → **8** implies an electron jump from a p<sub>x</sub> orbital at the carbene C to the corresponding p<sub>y</sub> AO to form the electron configuration  $\sigma^2\pi^0$  of the carbene. The change in the orbital angular momentum resulting from the electron jump is com-



**Figure 4.** Calculated geometries of triplet carbene T-8 (above) and singlet carbene S-8 (below) optimized at the UB3LYP and UMP2 levels of theory employing the 6-311++G(3df,3pd) basis set. Bond lengths in Å, angles in deg. MP2 results in parentheses.

compensated by an electron spin flip, thus conserving the total angular momentum.

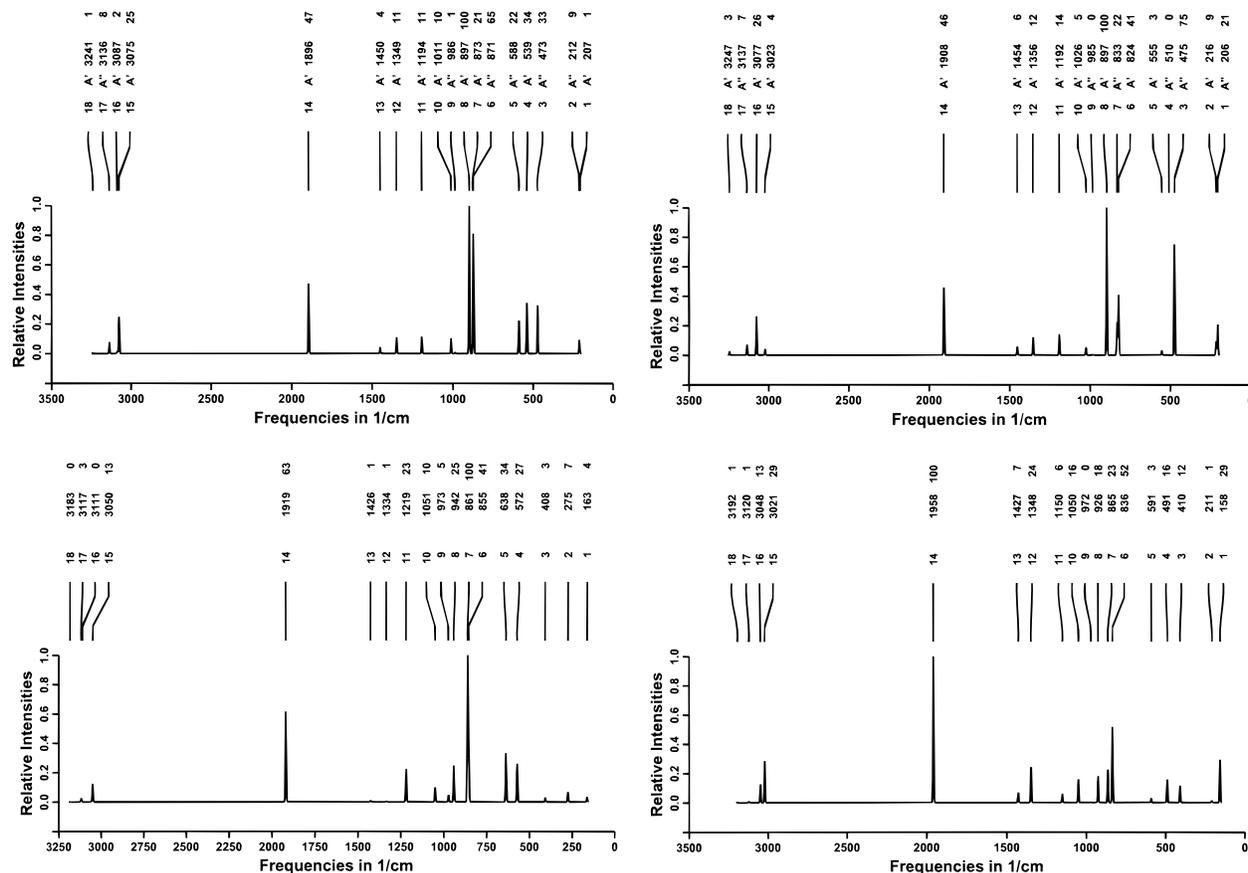
Considering that intersystem crossing will take place to some extent, both S-8 and T-8 should be formed. It is known that a carbene in an excited state rapidly relaxes to its ground state and this may also be true in the case of carbene 8. We tested this possibility by assuming a vertical transition from one of the four possible S-8 equilibrium forms to the corresponding T-8 form; however, we found that in all cases a vertical transition leads to a T geometry significantly higher in energy (the T state requires a planar geometry at the carbene C while the S state is stabilized in a nonplanar geometry). This suggests that once S-8 is formed in the matrix it may stay in the S state until continued irradiation leads to rearrangement of S-8 to another molecule. The calculated geometry of the S transition state of the rearrangement  $2 \rightarrow 8$  indicates that because of steric and overlap reasons the anti form should be preferentially formed, although this is less stable than the syn form in the case of the S-8.

In Figure 5, the B3LYP IR spectra of s-syn-T-8 (Figure 5a), s-anti-T-8 (5b), s-syn-S-8 (5c), and s-anti-S-8 (5d) are shown, which turn out to be more reliable than the corresponding MP2 spectra, because MP2 calculations do not provide a reliable description of the S carbene and underestimate, in the case of the T carbene, the allyl resonance, thus predicting a too short  $\text{C}=\text{C}=\text{C}$  double bond and a too high  $\text{C}=\text{C}=\text{C}$  stretching frequency (UMP2: 2158, 2106; UB3LYP: 1896, 1908  $\text{cm}^{-1}$ , Figure 5a,b). Hence, the following discussion is exclusively based on the DFT results. The four most intense IR bands in the region down to 700  $\text{cm}^{-1}$  are predicted to be at 1919 ( $\text{C}=\text{C}=\text{C}$  stretch), 861 ( $\text{CH}_2$  wag), and 855  $\text{cm}^{-1}$  ( $\text{C}-\text{H}$  bend) for s-syn-S-8 and 1958, 865, and 836  $\text{cm}^{-1}$  for s-anti-S-8, 1896, 897, and 871 for s-syn-T-8 and 1908, 897, and 833 for s-anti-T-8, which agree with those IR bands that could not be assigned to known compounds (1942, 1881, 877, 855, 850  $\text{cm}^{-1}$ ; Figure 1).

Clearly, in the experimental IR spectrum two different  $\text{C}=\text{C}=\text{C}$  stretching vibrations (1942 and 1881  $\text{cm}^{-1}$ ) can be

distinguished, indicating two different forms of 8. Experiment does not provide any information whether these are the syn and anti S-8 or T-8 conformations or a mixture of both. Both DFT and MP2 predict, independent of the basis set used, that syn and anti conformation lead to allenyl stretching bands separated by about 10  $\text{cm}^{-1}$  and probably difficult to distinguish in the experimental difference spectrum. Also, the calculated absolute IR intensities of these lines are about a factor 10 smaller than the corresponding intensities calculated for the S-8 forms. The fact that two typical allenyl stretching bands of different intensities separated by 61  $\text{cm}^{-1}$  are found (Figure 1) can be explained that the band at 1881  $\text{cm}^{-1}$  results from one or both T-8 conformations and the band at 1942  $\text{cm}^{-1}$  from s-anti-S-8 (calculated differences 50 and 62  $\text{cm}^{-1}$ ; for s-syn-S-8 the differences with the T-8 forms are too small (23, 11  $\text{cm}^{-1}$ )). Other explanations for the observation of two IR bands in the region of the allenyl stretching vibration are also possible and have to be investigated in future work. In any case, the comparison of the experimental with the calculated spectra strongly indicates that allenylcarbene 8 is formed and stabilized in the matrix as a photochemical rearrangement product of 2. There is evidence that both S-8 and T-8 forms are present in the matrix.

Three mechanisms have to be discussed to account for the formation of the van der Waals dimer 17 from 2: (i) The direct cleavage of the central bond of 2 to produce two molecules of vinylidene, which subsequently rearrange to acetylene. Since vinylidene is 46 kcal/mol higher in energy than 9,<sup>14</sup> and two molecules of 9 are 17 kcal/mol higher than 2, the formation of two molecules of vinylidene from 2 is predicted to be endothermic by 117.6 kcal/mol. Since the 248 nm irradiation corresponds to an excitation of 115 kcal/mol, this pathway is not possible. (ii) An alternative intermediate is the butadienediyl biradical (18), which was introduced by Maier et al.<sup>12</sup> to explain the formation of 1 by 248 nm irradiation of 17. The formation of 18 from 2 requires two consecutive [1,2]-H shifts with carbene S-8 as an intermediate. (iii) The third mechanism is the cleavage of 3 to acetylene and vinylidene, which rapidly



**Figure 5.** Unscaled UB3LYP/6-311++G(3df,3pd) infrared spectra of s-syn-T-8 (a), s-anti-T-8 (b), s-syn-S-8 (c), and s-anti-S-8 (d).

rearranges to a second molecule of acetylene. In view of an estimated enthalpy increase of 62 kcal/mol for the latter process, reaction ii is more likely. Investigations are presently in progress to clarify this point.<sup>14</sup>

## Conclusions

We have demonstrated that methylenecyclopropene **3** is a direct product of the irradiation of butatriene **2**. The rearrangement  $2 \rightarrow 3$  takes place predominantly on the S-PES where the most plausible pathway is a two-(or multi)-step mechanism involving a [1,2]-H migration followed by a vinylcarbenecyclopropene rearrangement, which involves allenyl carbene S-**8** as the key intermediate and requires a calculated activation enthalpy of 64 kcal/mol. A comparison of measured and calculated IR spectra suggests that either S-**8** in its syn and anti conformation or a mixture of S-**8** and T-**8** conformations exists at low temperatures in the matrix.

After this work was finished, Aycard and co-workers<sup>22</sup> published an IR spectroscopic study on the photolysis of matrix-isolated allenylketene intended to find experimental evidence for allenylcarbene **8**. However, **8** could not be detected by the authors.

## Experimental Section

Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Messer-Griesheim, 99.9999%) or xenon (Air Products, 99.99%) on top of a CsI window with a rate of approximately 0.15 mmol/min. Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 0.5  $\text{cm}^{-1}$  in the range of 400–4000  $\text{cm}^{-1}$ .

Irradiations were carried out with use of an KrF ( $\lambda = 248$  nm) or ArF excimer laser ( $\lambda = 193$  nm; Lambda Physik COMPex 100) or Osram HBO 500 W/2 mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the arc lamps was absorbed by a 10-cm path of water. Schott cutoff filters were used (50% transmission at the wavelength specified) in combination with dichroic mirrors.

**Butatriene 2.** The labile **2** was prepared according to a procedure described by L. Brandsma and H. D. Verkruisje<sup>15</sup> and purified by sublimation (3 times) at low temperature. Matrix isolation was achieved by slow sublimation at  $-125$  °C and deposition with a large excess of argon or xenon on top of a cold window at 30 K. After deposition the matrix was cooled to 7–10 K. IR (Ar, 10 K): 2996 (5), 2924 (6), 1708 (21), 1609 (43), 1439 (7), 1367 (15), 1228 (4), 1030 (5), 1022 (5), 977 (3), 852 (100)  $\text{cm}^{-1}$  (rel intensity).

**Products of the Photochemistry of 2. Methylenecyclopropene 3.** IR (Ar, 10 K): 1809 (5), 1770 (100), 1670 (14), 1519 (31), 1100 (9), 1041 (8), 997 (12), 841 (7), 754 (65), 664 (42)  $\text{cm}^{-1}$  (rel intensity).

**Vinylacetylene 1.** IR (Ar, 10 K): 3327 (100), 3315 (95), 1227 (38), 977 (74), 926 (86), 636 (76), 615 (98)  $\text{cm}^{-1}$  (rel intensity).

**Dimer of Acetylene 17.** IR (Ar, 10 K): 3285 (94), 3269 (51), 2059 (3), 750 (15), 745 (100), 737 (90)  $\text{cm}^{-1}$  (rel intensity).

**Butadiyne 10.** IR (Ar, 10 K): 3333 (55), 2019 (5), 627 (100)  $\text{cm}^{-1}$  (rel intensity).

**Computational Methods.** Standard restricted MP2 (RMP2) for closed-shell molecules and unrestricted MP2 (UMP2) calculations were carried out with the 6-311++G(3df,3pd) basis set.<sup>13</sup> The choice of the basis has to be seen on the background of a more complete quantum chemical exploration of the C<sub>4</sub>H<sub>4</sub> PES, which will include, in addition to typical closed-shell

molecules, also loose transition states and van der Waals complexes such as **17**.<sup>14</sup> Also, the 6-311++G(3df,3pd) basis represents a VTZ+P basis set, for which the DFT basis set limit is almost reached and, accordingly, basis set truncation error and basis set superposition error turn out to be small.

The description of S biradicals requires a two- or multi-configurational approach. We have avoided this problem by retreating to restricted open shell theory for low-spin (ROSS) cases as it was discussed by Andrews, Murray, and Handy<sup>16</sup> for Hartree–Fock and second-order perturbation theory. At the ROSS–DFT level,<sup>17</sup> the two-configurational problem is reformulated in a way that one can essentially remain within the realm of single-configuration theory at the cost of building up a more complicated Fock matrix. Also, a new exchange correlation (XC) functional has to be constructed for the ROSS case.<sup>17</sup> For the purpose of employing a consistent description of S and T biradicals, the latter were calculated at the restricted open-shell DFT (RODFT) level of theory. Hence, DFT calculations were performed at four different levels, namely at the RDFT, UDFT, RODFT, and ROSS–DFT level of theory to adequately describe closed-shell molecules, T excited states, and biradicals in the S or T state. In all calculations the B3LYP hybrid functional<sup>18</sup> was applied, which leads to the most accurate ROSS–DFT results.<sup>17</sup>

For each molecule and transition state investigated, vibrational frequencies were obtained to verify the nature of the corresponding stationary point and to determine absolute enthalpies H(298). In the case of RDFT calculations, the internal and external stabilities of the R solution were investigated with the help of appropriate stability tests.<sup>19</sup> In the case of an external instability, the corresponding U solution was determined. Calculations were performed with COLOGNE 99<sup>20</sup> and *Gaussian 94* program packages.<sup>21</sup>

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