

## 2-Vinylmethylenecyclopropane/3-Methylenecyclopentene Rearrangement: Matrix-Infrared Spectroscopic Identification of 4-Methylene-2-pentene-1,5-diyl (1,2'-Bisallyl Diradical)

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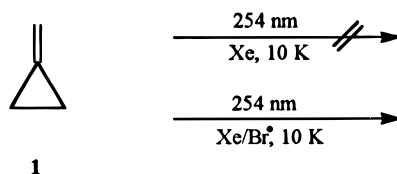
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**Abstract:** triplet-4-Methylene-2-pentene-1,5-diyl (**T-4t**) has been generated upon irradiation of 2-vinylmethylenecyclopropane (**6**) in a bromine-doped xenon matrix and characterized by means of IR spectroscopy for the first time. Conclusions for the thermal isomerization of **6** to 3-methylenecyclopentene (**7**) are discussed. All experimental results indicate that this isomerization probably proceeds via the diradical **S-4** as an intermediate.

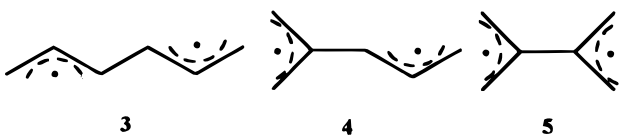
### Introduction

Recently, we<sup>1</sup> were able to demonstrate that trimethylenemethane (**2**) can be formed by the irradiation of methylenecyclopropane (**1**) in a halogen-doped xenon matrix with  $\lambda = 254$  nm. The characteristic feature of this new method for the formation of reactive species is the irradiation with wavelengths which the organic precursor does *not* absorb. The energy of the irradiation is first absorbed by the halogen atoms which are embedded in the xenon matrix and subsequently transferred to the organic molecules. It has to be emphasized that both, the



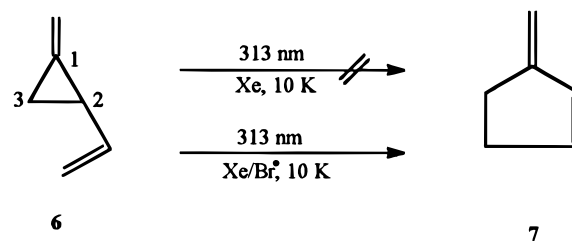
bromine atoms as well as the organic molecules, are matrix isolated. As a consequence, the energy transfer cannot proceed via a direct interaction between the molecules and the bromine atoms. Therefore, the solid xenon acts as the medium for the transfer of the absorbed energy. Thus, the reactions which can be observed are not the result of a *direct* photolysis; they are only photochemically induced.

The object of this investigation was to examine whether 4-methylene-2-pentene-1,5-diyl (**4**) can be formed from 2-vinylmethylenecyclopropane (**6**) by using the new method described above. By this means we hoped to be able to draw some conclusions concerning the mechanism of the thermal isomerization of **6** to 3-methylenecyclopentene (**7**).



In 1968, 2-vinylmethylenecyclopropane (**6**) was first prepared by Shields, Billups, and Lepley<sup>2</sup> who also reported the thermal

isomerization of **6** to 3-methylenecyclopentene (**7**). Even at 80 °C, more than 90% of the 2-vinylmethylenecyclopropane (**6**) rearranged within 13 h. This remarkable thermal lability of **6** was used as an argument against the intermediacy of a diradical in the course of the rearrangement and in favor of a concerted process. The isomerization of **6** to **7** can be conceived as either a [3,3] sigmatropic reaction in analogy to the Cope rearrangement or as a [1,3] sigmatropic reaction similar to the vinylcyclopropane to cyclopentene rearrangement<sup>3</sup> with inversion at the migrating center.<sup>4</sup>



Subsequently Billups et al.<sup>5</sup> determined the activation energy of the isomerization **6** → **7** ( $E_a$  (gas phase) = 25.8 ± 1.4 kcal mol<sup>-1</sup>). They intended to use the activation energy as an experimental evidence against the intermediate formation of diradicals. Unfortunately, the bond energy of 27 kcal mol<sup>-1</sup>, which they estimated for the C2–C3 bond in **6** differed less than 2 kcal mol<sup>-1</sup> from the experimentally determined activation energy. Therefore, no unequivocal conclusions concerning the mechanism of the thermal isomerization could be drawn.

None of the studies<sup>5,6</sup> which have been performed so far furnishes definite proof for the formation of a diradicaloid intermediate in the 2-vinylmethylenecyclopropane (**6**) to 3-methylenecyclopentene (**7**) rearrangement.

The special interest in diradical 4-methylene-2-pentene-1,5-diyl (**4**) is not solely based upon its possible intermediacy in the isomerization **6** → **7**. The structural features of **4** are of

(2) Shields, T. C.; Billups, W. E.; Lepley, A. R. *J. Am. Chem. Soc.* **1968**, *90*, 4749–4751.

(3) (a) Overberger, C. G.; Borchert, A. E. *J. Am. Chem. Soc.* **1960**, *82*, 1007–1008. (b) Flowers, M. C.; Frey, H. M. *J. Chem. Soc.* **1961**, 3547–3548.

(4) Maier, G. *Valenzisomerisierungen*; Verlag Chemie: Weinheim, 1972.

(5) Billups, W. E.; Leavell, K. H.; Lewis, E. S.; Vanderpool, S. *J. Am. Chem. Soc.* **1973**, *95*, 8096–8102.

(6) Gilbert, J. C.; Higley, D. P. *Tetrahedron Lett.* **1973**, 2075–2078.

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(1) (a) Maier, G.; Reisenauer, H. P.; Lanz, K.; Tross, R.; Jürgen, D.; Hess, B. A., Jr.; Schaad, L. J. *Angew. Chem.* **1993**, *105*, 119–121; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 74–76. (b) Maier, G.; Jürgen, D.; Tross, R.; Reisenauer, H. P.; Hess, B. A., Jr.; Schaad, L. J. *Chem. Phys.* **1994**, *189*, 383–399.

interest per se. On one hand, **4** is a non-Kekulé<sup>7</sup> hydrocarbon of the trimethylenemethane series (the vinyllog to trimethylenemethane (**2**)), and on the other hand, it can be characterized as 1,2'-bisallyl diradical. Therefore, in addition to *triplet*-1,3,5-hexatriene (**3**) (1,1'-bisallyl diradical) and tetramethylenethane<sup>8</sup> (**5**) (2,2'-bisallyl diradical), the diradical **4** is the third member (1,2'-bisallyl diradical) of the series of bisallyl derivatives. These species are fully conjugated diradicals,<sup>9</sup> which can formally be obtained by the combination of two allyl radicals under hydrogen abstraction.

### Matrix Experiments

In a xenon matrix, 2-vinylmethylenecyclopropane (**6**), consisting of a mixture of the *s-trans*- and *s-cis*-conformer, was exposed to light of the wavelength  $\lambda = 313$  nm. Even after 19 h we could not observe any new absorptions in the IR spectrum. The only significant change in the spectrum was a variation of the band intensities. We attribute these alterations to a partial conformational isomerization of the *s-cis*- to the *s-trans*-conformer of **6**. Especially eye-catching was a decrease in intensity of an absorption at  $916.5\text{ cm}^{-1}$ . This observation is in total accordance with the calculation of the IR spectra (B3LYP/6-31G\*), which demand an IR band in this position for the *s-cis*- but not for the *s-trans*-conformer.

The result was completely different when the xenon matrix was doped with bromine: In a matrix prepared by cocondensation of 2-vinylmethylenecyclopropane/xenon (3:1000) and bromine/xenon (4:1000) gas mixtures, **6** was not photostable on irradiation with the same wavelength ( $\lambda = 313$  nm). After 15 h, we reached an amount of conversion of approximately 40%. The necessary bromine atoms were generated *in situ* by photolysis of the bromine molecules.<sup>1</sup> As the main product of the reaction 3-methylenecyclopentene (**7**) was observed, several of the new IR absorptions could not be assigned. Of special interest was an intense band at  $752.6\text{ cm}^{-1}$ . The most likely candidate for this absorption was diradical **4**. By comparison, the most intense absorption of trimethylenemethane (**2**) is located at  $755.5\text{ cm}^{-1}$ .<sup>1</sup>

In a further experiment, we first irradiated the 2-vinylmethylenecyclopropane/Br<sub>2</sub>/xenon matrix for 1 h with  $\lambda = 254$  nm, because this wavelength is much more effective in generating the bromine atoms.<sup>1</sup> Subsequently, the maximum intensity of the band at  $752.6\text{ cm}^{-1}$  was reached, when the matrix had been irradiated with  $\lambda = 313$  nm for approximately 5 h. If the wavelength  $\lambda = 297$  nm was used instead of 313 nm the maximum intensity could once more be slightly increased.

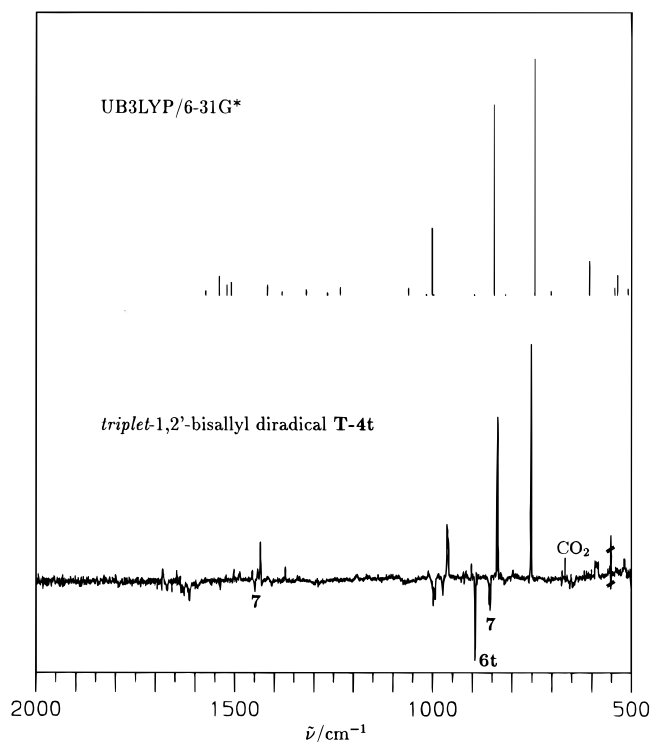
When the wavelength was changed back to  $\lambda = 254$  nm, the intensity of the absorption at  $752.6\text{ cm}^{-1}$  started to decrease rapidly. Using the difference spectrum (Figure 1), it was possible to locate additional bands which displayed the same behavior on irradiation. As the discussion in the next section will show, these bands can indeed be assigned to the diradical **T-4t**.

The difference spectrum also reveals the structure of the photoproducts of **T-4t**. The most intense product band at  $893.4\text{ cm}^{-1}$  originates from the *s-trans*-conformer of 2-vinylmethylenecyclopropane (**6t**), while the absorptions at  $855.3/858.7\text{ cm}^{-1}$  are caused by the formation of 3-methylenecyclopentene (**7**). The IR spectrum of matrix-isolated **7** has been obtained by flash pyrolysis of a 2-vinylmethylenecyclopropane (**6**)/xenon gas mixture and condensation of the product on a spectroscopic

(7) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; John Wiley & Sons: New York, 1982; pp 1–72.

(8) Dowd, P. *J. Am. Chem. Soc.* **1970**, *92*, 1066–1068.

(9) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587–4594.



**Figure 1.** Comparison of the experimental (bottom) and calculated (UB3LYP/6-31G\*, bars at top) IR spectrum of the *s-trans*-conformer of the *triplet*-1,2'-bisallyl diradical **T-4t**. The experimental spectrum (bromine-doped xenon matrix, 10 K) is a difference spectrum (irradiation with  $\lambda = 254$  nm, when matrix-isolated **6** has initially been exposed to  $\lambda = 313$  nm). The bands with positive values diminish, while those with negative values are enhanced upon 254 nm irradiation.

window at 10 K. Taking into account the calculated absolute intensities of the observed bands of 3-methylenecyclopentene (**7**) and 2-vinylmethylenecyclopropane (**6t**), the resulting product ratio **7/6t** was 1.0:1.3.<sup>10</sup> Further absorptions at 975.4, 994.6, 999.0, and  $1614.2\text{ cm}^{-1}$  could not be assigned.

### IR Spectrum of *triplet*-4-Methylene-2-pentene-1,5-diyI

Calculations (CAS(6,6)/6-31G\*) of Davidson et al.<sup>11</sup> led to the conclusion that the 1,2'-bisallyl diradical **4** should have a triplet ground state, just as it is the case for trimethylenemethane (**2**). In addition, they computed that the planar *s-trans*-conformer **T-4t** is about 5.1 kcal mol<sup>-1</sup> lower in energy than the corresponding *s-cis* conformer **T-4c**. The calculated energy gap between **T-4t** and the minima on the singlet energy surface **S-4t** and **S-4c**, which lie about 19 kcal mol<sup>-1</sup> higher in energy than **6t**, is about 8.6 kcal mol<sup>-1</sup>.

As can be seen in Figure 1, the correlation between the calculated IR spectrum of **T-4t** (UB3LYP/6-31G\*) and the experimentally determined IR spectrum is excellent. Therefore, the formation of **T-4** from **6** can be regarded as securely established.

All absorptions in the experimental IR spectrum located below  $1000\text{ cm}^{-1}$  have been assigned. They are listed together with the calculated band positions in Table 1. As a comparison

(10) A comparison between the calculated (B3LYP/6-31G\*) and the experimental IR spectrum of **6t** suggests that the most intense absorption in the experimental spectrum of **6t** originates from the overlap of three vibrations. The sum of the calculated absolute intensities is  $95.5\text{ km mol}^{-1}$ , while the calculated intensity of the most intense absorption of **7** is only  $37.4\text{ km mol}^{-1}$ . The ratio **7/6t** of the peak areas which have been determined from the difference spectrum is 1.00:3.29 which leads to an product ratio of 1.0:1.3.

(11) Davidson, E. R.; Gajewski, J. J.; Shook, C. A.; Cohen, T. *J. Am. Chem. Soc.* **1995**, *117*, 8495–8501.

**Table 1.** Comparison between the Calculated and Experimental<sup>a</sup> (Xenon Matrix, 10 K) Band Positions of the *s-trans*-Conformer of the triplet-1,2'-Bisallyl Diradical **T-4t** (*C<sub>s</sub>* Symmetry)

| experiment                   |                  | calculated                   |       |                              |       | symmetry |
|------------------------------|------------------|------------------------------|-------|------------------------------|-------|----------|
|                              |                  | UB3LYP/6-31G*                |       | UMP2/6-31G*                  |       |          |
| $\tilde{\nu}/\text{cm}^{-1}$ | int <sup>b</sup> | $\tilde{\nu}/\text{cm}^{-1}$ | int   | $\tilde{\nu}/\text{cm}^{-1}$ | int   |          |
|                              |                  | 109.9                        | <0.01 | 103.7                        | <0.01 | A''      |
|                              |                  | 162.6                        | 0.01  | 159.6                        | 0.01  | A''      |
|                              |                  | 209.7                        | <0.01 | 217.3                        | <0.01 | A'       |
|                              |                  | 384.3                        | <0.01 | 395.6                        | <0.01 | A'       |
|                              |                  | 448.0                        | 0.05  | 458.0                        | 0.04  | A'       |
|                              |                  | 467.3                        | 0.02  | 484.1                        | 0.03  | A''      |
|                              |                  | 508.9                        | 0.03  | 527.1                        | 0.05  | A''      |
| 518.3                        | 0.09             | 535.4                        | 0.08  | 536.4                        | 0.03  | A''      |
|                              |                  | 542.2                        | 0.03  | 555.6                        | 0.02  | A'       |
| 589.2 <sup>c</sup>           | 0.23             | 605.9                        | 0.14  | 647.6                        | 0.10  | A''      |
|                              |                  | 702.0                        | 0.02  | 694.1                        | 0.21  | A''      |
| 752.6                        | 1.00             | 742.9                        | 1.00  | 724.0                        | 1.00  | A''      |
|                              |                  | 816.9                        | <0.01 | 797.9                        | 0.07  | A''      |
| 837.0                        | 0.82             | 845.6                        | 0.80  | 908.5                        | 0.64  | A''      |
|                              |                  | 894.8                        | <0.01 | 923.9                        | <0.01 | A'       |
|                              |                  | 997.1                        | <0.01 | 1019.4                       | <0.01 | A'       |
| 960.9/<br>963.8              | 0.41             | 1001.3                       | 0.28  | 1054.2                       | 0.34  | A''      |
|                              |                  | 1016.3                       | <0.01 | 1046.4                       | <0.01 | A'       |
|                              |                  | 1060.8                       | 0.03  | 1087.3                       | 0.04  | A'       |
|                              |                  | 1232.9                       | 0.03  | 1204.9                       | 0.02  | A'       |
|                              |                  | 1265.1                       | 0.01  | 1293.1                       | 0.01  | A'       |
|                              |                  | 1319.0                       | 0.02  | 1363.8                       | 0.02  | A'       |
|                              |                  | 1380.5                       | 0.01  | 1405.7                       | 0.02  | A'       |
|                              |                  | 1417.8                       | 0.04  | 1458.4                       | 0.06  | A'       |
|                              |                  | 1509.4                       | 0.05  | 1519.6                       | 0.04  | A'       |
|                              |                  | 1519.6                       | 0.04  | 1545.4                       | 0.07  | A'       |
|                              |                  | 1539.2                       | 0.08  | 1573.0                       | 0.08  | A'       |
|                              |                  | 1573.3                       | 0.02  | 1609.4                       | 0.02  | A'       |
|                              |                  | 3156.8                       | 0.01  | 3217.8                       | 0.05  | A'       |
|                              |                  | 3166.7                       | 0.29  | 3228.4                       | 0.13  | A'       |
|                              |                  | 3168.8                       | 0.07  | 3234.6                       | 0.07  | A'       |
|                              |                  | 3174.6                       | 0.22  | 3238.4                       | 0.08  | A'       |
|                              |                  | 3186.2                       | 0.11  | 3248.8                       | 0.11  | A'       |
|                              |                  | 3256.1                       | 0.21  | 3329.2                       | 0.11  | A'       |
|                              |                  | 3266.5                       | 0.14  | 3338.3                       | 0.07  | A'       |
|                              |                  | 3275.4                       | 0.15  | 3349.0                       | 0.07  | A'       |

<sup>a</sup> The following bands could not be assigned and therefore are not included in this table: 1373.1 (0.07), 1435.8 (0.18), 1442.5 (0.08), 1456.0 (0.03), 1488.3 (0.03), 1502.8 (0.06), 1681.7 (0.07) cm<sup>-1</sup>. <sup>b</sup> Int = intensity, relative to the strongest band. <sup>c</sup> This is a group of bands: 584.8, 589.2, 592.1 cm<sup>-1</sup>.

shows, there is much better correspondence between the experiment and the results obtained with UB3LYP than for the ones computed with UMP2.

In the spectral region between 1000 and 2000 cm<sup>-1</sup>, several small absorptions (see footnote *a* in Table 1) can be found in the difference spectrum. They are not listed in Table 1 because they could not be assigned to a definite vibration. It is most likely that the most intense absorption in this region (1435.8 cm<sup>-1</sup>) is an overtone of the band at 752.6 cm<sup>-1</sup>, while the band at 1681.7 cm<sup>-1</sup> may be interpreted as combination tone of the bands at 752.6 and 960.9(963.8) cm<sup>-1</sup>. As a result of the low optical transmittance of the doped xenon matrices, we were not able to locate absorptions of **T-4t** above 2000 cm<sup>-1</sup> in the IR spectra.

There have been no absorptions which can, by comparison with the calculated spectrum of **T-4t**, be assigned to the *s-cis*-conformer **T-4c**.

### Structure of triplet-4-Methylene-2-pentene-1,5-diyl

All atoms of the *s-trans*-conformer **T-4t** are placed in the same plane so that the molecule possesses *C<sub>s</sub>* symmetry.<sup>11</sup> In Table 2, the C—C bond distances and the dihedral angles which are needed to describe the structure of the carbon skeletons of **T-4t** and **T-4c** are grouped together. In addition, Table 2

**Table 2.** Comparison of the Calculated (UB3LYP/6-31G\*) Energies  $E_{\text{rel}}$ , C—C Bond Lengths  $d$ , and Some Dihedral Angles  $\Theta$  of the Conformers of the triplet-1,2'-Bisallyl Diradical **T-4** and the Transition State of the Conformational Isomerization<sup>a</sup>

|                                       | <i>s-trans</i> -conformer<br>( <b>T-4t</b> ) | transition<br>state | <i>s-cis</i> -conformer<br>( <b>T-4c</b> ) |
|---------------------------------------|--|---------------------|--|
| symmetry                              | C <sub>s</sub>                               | C <sub>1</sub>      | C <sub>1</sub>                             |
| $E_{\text{rel}}/\text{kcal mol}^{-1}$ | 0.0  | 11.8                | 4.1  |
| $\Theta(4231)/\text{deg}$             | 180.0  | 179.9               | 179.8                                      |
| $\Theta(6532)/\text{deg}$             | 180.0  | 94.3                | 12.3                                       |
| $\Theta(5324)/\text{deg}$             | 0.0  | -3.5                | 19.4                                       |
| $d(12)/\text{\AA}$                    | 1.407  | 1.415               | 1.407                                      |
| $d(42)/\text{\AA}$                    | 1.409  | 1.413               | 1.407                                      |
| $d(32)/\text{\AA}$                    | 1.443  | 1.425               | 1.448                                      |
| $d(53)/\text{\AA}$                    | 1.409  | 1.478               | 1.415                                      |
| $d(65)/\text{\AA}$                    | 1.369  | 1.336               | 1.370                                      |

<sup>a</sup> The numbers of the atoms refer to Scheme 1.

contains the geometry parameters for the transition state of the conformational isomerization.

With UB3LYP/6-31G\*, we calculated the relative energy of the *s-cis*-conformer **T-4c** as 4.1 kcal mol<sup>-1</sup>, about 1 kcal mol<sup>-1</sup> less than the energy obtained by Davidson et al.<sup>11</sup> The calculated activation energy for the transition of **T-4c** into the more stable conformer **T-4t** is 7.7 kcal mol<sup>-1</sup> (Table 2).

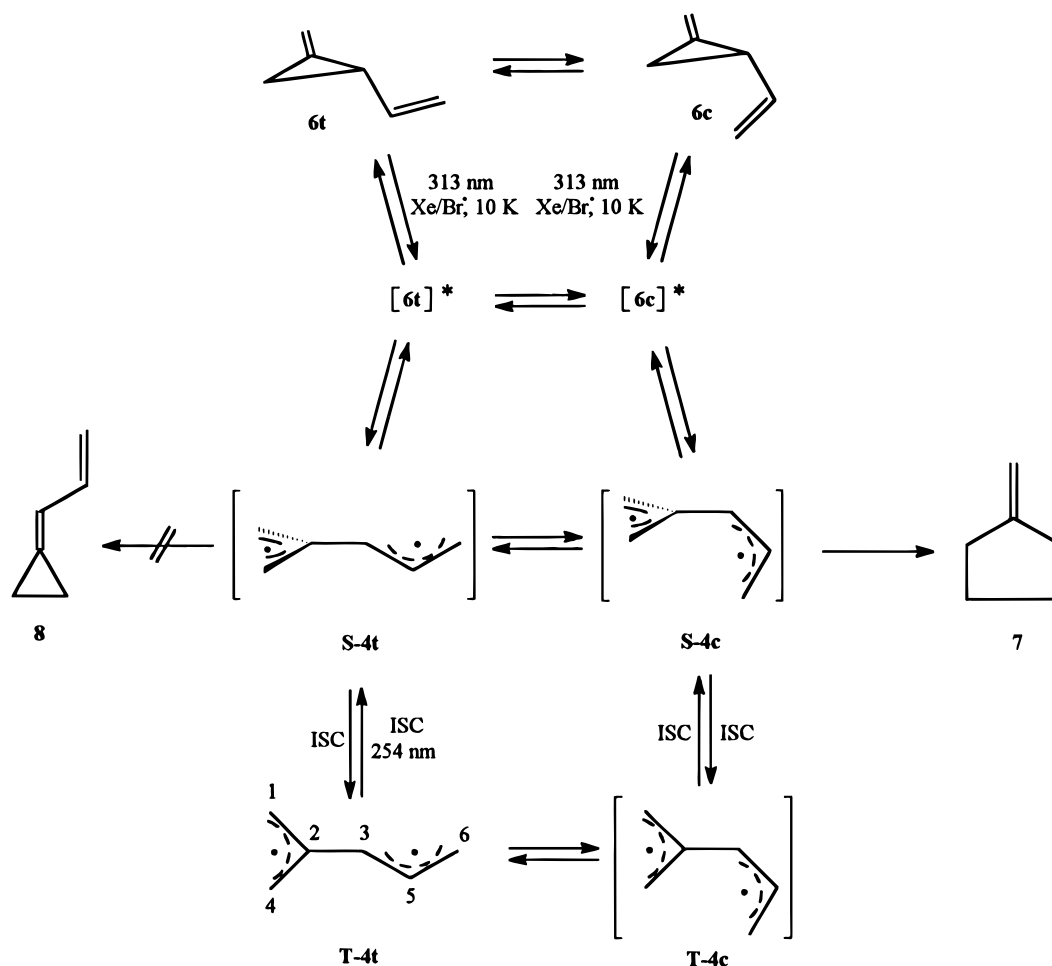
At the transition state of the **T-4c** ⇌ **T-4t** rearrangement, the vinyl group is located nearly orthogonal to the trimethylenemethane part of the carbon skeleton. Thus, the transition state can serve as a model for a vinyl-substituted trimethylenemethane diradical in which there is no interaction between the two  $\pi$  systems. Consequently, by going from the transition state to **T-4c** or **T-4t**, the main force for a change in geometry is the increasing interaction between the vinyl group and the  $\pi$  system of the trimethylenemethane part of the molecule. Most extreme is the alteration of the C5—C3 bond, which is shortened by 0.06–0.07 Å.

### Discussion

The photobehavior of **6** is heavily dependent on the reaction conditions. Photolysis in an argon matrix at 10 K with  $\lambda = 185$  nm leads mainly to acetylene and 1,3-butadiene. Under standard conditions ( $\lambda = 254$  nm, argon matrix), **6** is photo-stable.

The situation is completely changed if 2-vinylmethylenecyclopropane (**6**) is irradiated with  $\lambda = 313$  nm in a xenon matrix. In this experiment, the *s-cis*-conformer of **6** is converted to the *s-trans*-conformer **6t** but no additional absorptions can be detected in the IR spectrum. Under these conditions, the C2—C3 bond in **6** is not broken and no diradical **T-4t** is formed (Scheme 1).

If the xenon matrix is doped with bromine atoms, which can be generated *in situ* by photolysis of Br<sub>2</sub>, the irradiation of **6** with the same wavelength ( $\lambda = 313$  nm) gives rise to 3-methylenecyclopentene (**7**), which is normally formed on pyrolysis of **6**. That means, in spite of the fact that the observed reaction is initiated by irradiation, the reaction product is *not* formed by a photoreaction. The wavelength that is employed is initially absorbed by the bromine atoms embedded in the xenon matrix in a photochemical process. Only then is the stored energy transferred to the organic educt molecule **6**. Although we do not yet know exactly how the energy transfer proceeds, it seems most reasonable to assume that the bond breakage occurs in the vibrationally excited **6\***. Therefore it is not a surprise that, as for the thermal isomerization of **6**, the main reaction product is 3-methylenecyclopentene (**7**). As already discussed, the thermal isomerization from **6** to **7** can be formulated as a concerted process or a reaction proceeding via the 1,2'-bisallyl diradical.

**Scheme 1.** Reaction Scheme of the Isomerization of 2-Vinylmethylencyclopropane (**6**) to 3-Methylenecyclopentene (**7**) on Irradiation of **6** in a Bromine-Doped Xenon Matrix

For our studies, the utilization of xenon as a matrix material implies a further advantage. In chemical reactions which are carried out in the presence of xenon, an enhanced intersystem crossing (ISC) rate<sup>12,13</sup> has been observed. This effect is caused by the external heavy-atom effect of xenon.

Which consequences has this effect on the isomerization under investigation? If diradical **4** is really an intermediate in the rearrangement of **6** to **7**, then the presence of xenon as a matrix material should enhance the ISC rate so that more of the diradicals **S-4** can reach the triplet ground state before the ring closure to 3-methylenecyclopentene (**7**) occurs. As our matrix experiments have shown, it is indeed possible to detect the 1,2'-bisallyl diradical **T-4t** by means of IR spectroscopy.

Gisin and Wirz<sup>14</sup> used the semiempirical method PPP-SCF-SCI to calculate the absorption maxima of **T-4t**. They obtained two maxima at 223 and 259 nm. In accordance with these calculations, the IR absorptions of the diradical **T-4t** decrease if the matrix is irradiated with  $\lambda = 254$  nm. As products, we detected the *s-trans*-conformer of the starting compound **6t** and also 3-methylenecyclopentene (**7**).

On irradiation of **T-4t** with  $\lambda = 254$  nm, obviously an ISC back to the singlet potential energy surface is induced. According to the calculated relative energies,<sup>11</sup> the conformers **S-4t** and **S-4c** have nearly the same energy; therefore, both should be formed. The calculated activation energy<sup>11</sup> (CAS(6,6)/6-

31G\*) for the reaction of **S-4t** to **6t** ( $E_a = 6.5$  kcal mol<sup>-1</sup>) is about 1.7 kcal mol<sup>-1</sup> smaller than the barrier to **7**; thus, the formation of **6t** should be favored a little. Within the accuracy of the calculated activation energies and absolute band intensities, the described expectations are in total agreement with the experimentally determined product ratio **7/6t** of 1.0:1.3. As to be expected from the high activation energy for the reaction **S-4t**  $\rightarrow$  **8** ( $E_a \approx 12.2$  kcal mol<sup>-1</sup>),<sup>11</sup> no allylidene-cyclopropane (**8**) was formed.

On the basis of these considerations, we come to the conclusion that the thermal isomerization of 2-vinylmethylencyclopropane (**6**) to 3-methylenecyclopentene (**7**) proceeds via the diradical **4** as an intermediate.

## Conclusions

By the irradiation of 2-vinylmethylencyclopropane (**6**) in a bromine-doped xenon matrix, we were able to generate the 1,2'-bisallyl radical **4** and to characterize it by means of IR spectroscopy for the first time. In this procedure the reactive species are not produced by *direct* photolysis but via a vibrationally excited state ( $6t^*$  or  $6c^*$ ) of the substrate, so that we can draw conclusions concerning the mechanism of the thermal isomerization of **6** to 3-methylenecyclopentene (**7**). All of our experimental results indicate that the isomerization proceeds via the diradical **S-4** as an intermediate.

## Experimental Section

The cryostat for matrix isolation was a duplex closed-cycle refrigeration system CSA 202 from Air Products. The temperature measurement and control were with a digital temperature indicator/

(12) Kelley, D. F.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 1820–1824.

(13) Anderson, M. A.; Grissom, C. B. *J. Am. Chem. Soc.* **1996**, *118*, 9552–9556.

(14) Gisin, M.; Wirz, J. *Helv. Chim. Acta* **1983**, *66*, 1556–1568.

controller 3700-APD-E from Air Products, gold (0.07% iron)/chromel thermo element. The matrix window was CsI and the spectrometer was a FTIR spectrometer IFS 85 from Bruker. The light sources used were a mercury high-pressure lamp with monochromator and a mercury low-pressure spiral lamp with a vycor filter.

2-Vinylmethylenecyclopropane (**6**) was prepared according to the procedure of Arora and Binger<sup>15</sup> starting from 1,3-butadiene. Compound **6** was condensed to the matrix window at 10 K as a gas mixture (ratio 3:1000) with xenon. The most intense absorption of **6** in a xenon matrix is located at 888.6/893.9 cm<sup>-1</sup>.

The bromine-doped matrices were prepared by cocondensation of the **6**/xenon gas mixture with a bromine/xenon gas mixture (ratio 4:1000) in the ratio of 1:1.

The IR spectra of **6** in the undoped and bromine-doped xenon matrices were identical, so that we could exclude the presence of 2-vinylmethylenecyclopropane (**6**)/bromine adducts in significant amounts.

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(15) Arora, S.; Binger, P. *Synthesis* **1974**, 801–803.

**Ab Initio Calculations.** All calculations were performed with the Gaussian 94 package of programs.<sup>16</sup>

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(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, Revision B.1; Gaussian, Inc.: Pittsburgh, PA, 1995.