Photoisomerization of Bicyclopropylidene and 1,2-Dimethylenecyclobutane in Rare-Gas Matrices: Towards the IR-Spectroscopic Identification of Tetramethyleneethane (2,3-Dimethylenebutane-1,4-diyl)

Günther Maier*[a] and Stefan Senger[a]

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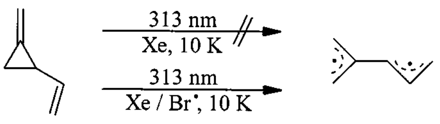
Bicyclopropylidene (**3**) and 1,2-dimethylenecyclobutane (**7**) have been irradiated in rare-gas matrices. If 1,2-dimethylenecyclobutane (**7**) is exposed to the light of a KrF excimer laser (λ = 248 nm), an isomeric species is produced, showing an absorption at 793.1 cm^{-1} (argon matrix) or 791.2 cm^{-1} (xenon matrix) in the IR spectrum. The back reaction can be induced with light of λ = 254 nm. This photochemical interconversion, together with the comparison between the experimental and calculated band positions, supports the assignment of the IR absorption near 790 cm^{-1} to tetramethyleneethane (**5**).

Recently, we succeeded in generating 4-methylene-2-pentene-1,5-diyl (**2**) in a xenon matrix and were able to characterize this species IR-spectroscopically.[1] This success was made possible by the application of a new method for generating highly reactive species in rare-gas matrices that we have developed: **2** was formed in situ by irradiation of 1-methylene-2-vinylcyclopropane (**1**) in a xenon matrix additionally doped with bromine atoms. Our method evolved on the basis of experiences we gained in connection with the IR-spectroscopic detection of trimethylenemethane.[2]

Whereas **1** is photostable if irradiated at λ = 313 nm in a xenon matrix, photolysis of **1** at the same wavelength in a bromine-doped xenon matrix leads to the formation of the diradical **2**.



1 **2**

4-Methylene-2-pentene-1,5-diyl (**2**) is also designated as a 1,2′-bis(allyl) diradical since it can formally be obtained by the combination of two allyl radicals under hydrogen abstraction. Accordingly, tetramethyleneethane (**5**) is a 2,2′-bis(allyl) diradical. Furthermore, **5** represents one of the simplest non-Kekulé hydrocarbons.[3,4]

Even though more than 25 years have elapsed since Dowd[5] succeeded in characterizing tetramethyleneethane (**5**) by means of ESR spectroscopy, as yet this species has not been detected IR-spectroscopically. Encouraged by the successful identification of the 1,2′-bis(allyl) diradical **2**, we decided to direct our attention towards the 2,2′-bis(allyl) diradical **5** in the hope that application of our new method would prove fruitful. As promising precursors for the matrix experiments bicyclopropylidene (**3**) and 1,2-dimethylenecyclobutane (**7**) were selected.

Matrix Experiments

Bicyclopropylidene (3)

In a xenon matrix at 10 K, bicyclopropylidene (**3**) was exposed to light of wavelength λ = 313 nm. Even after 20 h, no change in the matrix IR spectrum could be detected. Thus, **3** proved to be photostable under these conditions. However, the result was completely different when the xenon matrix was additionally doped with bromine (ratio $3/Br_2/Xe$ = 1.5:1.5:1000). After just 1 h, the intensities of the IR absorptions of bicyclopropylidene (**3**) had decreased by 5.5%, and after 15 h, the degree of conversion was approximately 47%. 1,2-Dimethylenecyclobutane (**7**) was formed almost exclusively, with just a small amount of methylenespiropentane (**6**) additionally being detected [Scheme 1, path (a)].

It is most likely that the initial product in the conversion of bicyclopropylidene (**3**) to 1,2-dimethylenecyclobutane (**7**) is the singlet diradical **S-4**. 2-Cyclopropylidenepropane-1,3-diyl (**4**) is a member of the series of trimethylenemethane diradicals and therefore should have a triplet ground state, as is the case for trimethylenemethane[6] itself and many of its derivatives.[7] In this context, we assumed that in the course of the irradiation of **3**, **T-4** could also be formed from **S-4** by ISC.

In the geometry calculated for the triplet state of **4** by the UB3LYP/6-31G* method, all carbon atoms lie in the same plane such that the molecule possesses C_{2v} symmetry. Exactly as for trimethylenemethane,[2] by far the most intense absorption of **T-4** is that due to the ωCH_2 vibration of the olefinic methylene groups. In the IR spectrum of **T-4** calculated by the UB3LYP/6-31G* method, this vibration is located at 718.2 cm^{-1}. Correction of the calculated value by a factor of 1.011, determined in the case of trimethylene-

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[a] Institut für Organische Chemie der Justus-Liebig-Universität,
Heinrich-Buff-Ring 58, D-35392 Giessen, Germany
Fax: (internat.) + 49(0)641/99-34309

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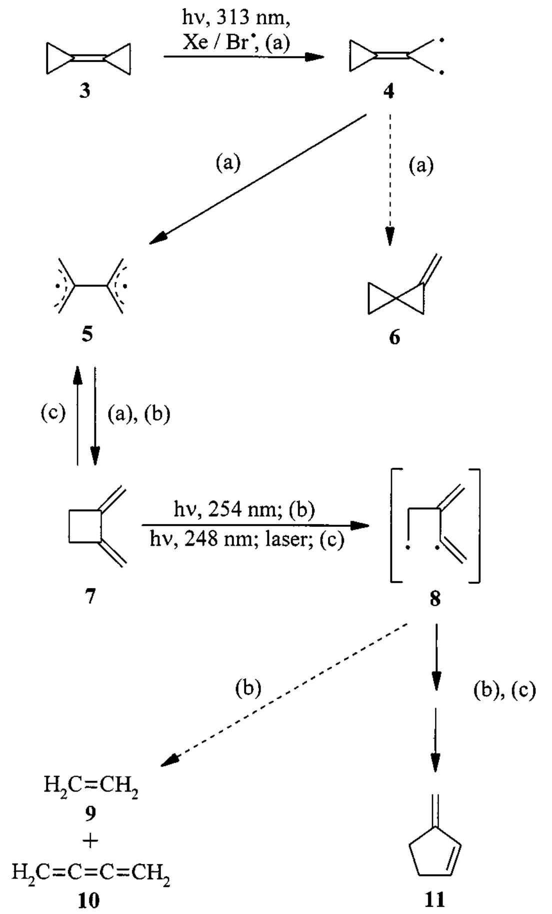

Scheme 1. Survey of the reaction pathways of bicyclopropylidene (**3**) and 1,2-dimethylenecyclobutane (**7**) on irradiation in rare-gas matrices; irradiation conditions: (a) at λ = 313 nm in a bromine-doped xenon matrix, (b) at λ = 254 nm in an argon or xenon matrix, (c) with a KrF excimer laser (λ = 248 nm) in an argon or xenon matrix

methane, results in a band near 726 cm^{-1}. However, in our matrix experiments no product absorptions were detected in this spectral region. Likewise, there was no experimental indication that tetramethyleneethane (**5**) had been formed.

The band positions of methylenespiropentane (**6**)[8] in a xenon matrix have been observed by flash pyrolysis of a bicyclopropylidene (**3**)/xenon gas mixture and condensation of the products on a spectroscopic window at 10 K. In the course of a subsequent irradiation at λ = 254 nm, 1,2-dimethylenecyclobutane (**7**) and 3-methylenecyclopentene (**11**) were formed as photoproducts.

1,2-Dimethylenecyclobutane (7)

Unlike bicyclopropylidene (**3**), 1,2-dimethylenecyclobutane (**7**) proved to be photostable on irradiation at λ = 313 nm in a bromine-doped xenon matrix. If light of the wavelength of λ = 254 nm was used instead, a photoreaction was observed in the undoped xenon matrix as well as in an argon matrix, because **7** is able to absorb light of this wavelength *directly* [Scheme 1, path (b)]. The maximum in the UV spectrum of a solution of **7** in isooctane is reported to be at λ = 246 nm.[9]

As the product of irradiation at λ = 254 nm, 3-methylenecyclopentene (**11**) was formed almost exclusively. In addition, only weak absorptions due to ethylene (**9**) and butatriene (**10**) could be observed in the IR spectrum. Allene, which is found as a photoproduct of **7** upon irradiation at λ = 254 nm in the gas phase,[10] could not be observed in the matrix. Likewise, no absorptions indicating the intermediacy of tetramethyleneethane (**5**) could be detected.

The formation of 3-methylenecyclopentene (**11**), ethylene (**9**), as well as butatriene (**10**) can be rationalized in terms of the formation of diradical **8** upon cleavage of the C2−C3 bond in 1,2-dimethylenecyclobutane (**7**) in the initial reaction step. Through the formation of a five-membered ring and a subsequent hydrogen shift, the diradical **8** can react further to give **11**, whereas a second C−C bond cleavage leads to **9** and **10**.

1,2-Dimethylenecyclobutane (**7**) was also exposed to the light of a KrF excimer laser (λ = 248 nm) in both argon and xenon matrices [Scheme 1, path (c)]. Again, 3-methylenecyclopentene (**11**) was found as the main product of the photolysis. In contrast to the irradiation at λ = 254 nm, no absorptions due to ethylene (**9**) or butatriene (**10**) could be detected in the IR spectrum after the laser photolysis of **7**.

Besides the absorptions due to **11**, several weak bands were seen in the difference spectrum (xenon matrix: 791.2, 1191.2, 1670.6, 1761.7 cm^{-1}, cf. Figure 1). Of special interest is the absorption found at 791.2 cm^{-1} in a xenon matrix and at 793.1 cm^{-1} in an argon matrix. This absorption would appear to be a very promising candidate for assignment to the elusive tetramethyleneethane (**5**) as it is positioned in the same region of the IR spectrum as the most intense vibration of the structurally related allyl radical. In an argon matrix, the most intense absorption of the allyl radical is seen at 802 cm^{-1}.[11]

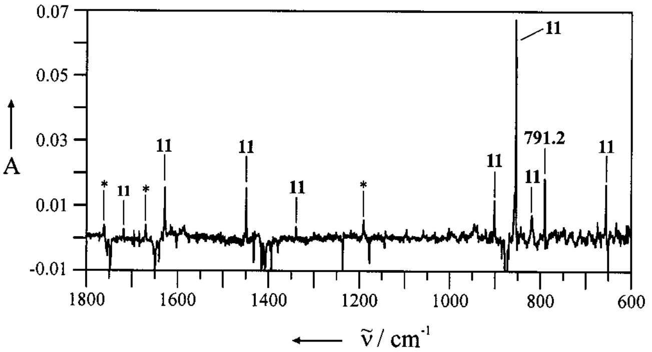

Figure 1. IR difference spectrum of the laser irradiation (λ = 248 nm) of 1,2-dimethylenecyclobutane (**7**) in a xenon matrix [Scheme 1, path (c)]; the bands marked * could not be assigned; the bands with positive values were enhanced upon irradiation

Following the laser photolysis at λ = 248 nm, the argon and xenon matrices were exposed to the light of a low-pressure mercury lamp equipped with a vycor filter (λ = 254 nm). As a result, the intensity of the IR band at 791.2 cm^{-1} (xenon matrix) or 793.1 cm^{-1} (argon matrix) decreased rapidly. As the sole product, 1,2-dimethylenecyclobutane (**7**) could be detected by means of the difference spectrum (see Figure 2). If the matrices were then further irradiated with the KrF excimer laser (λ = 248 nm), the intensity of the absorption at 791.2 cm^{-1} (xenon matrix) or 793.1 cm^{-1} (argon matrix) increased once more.

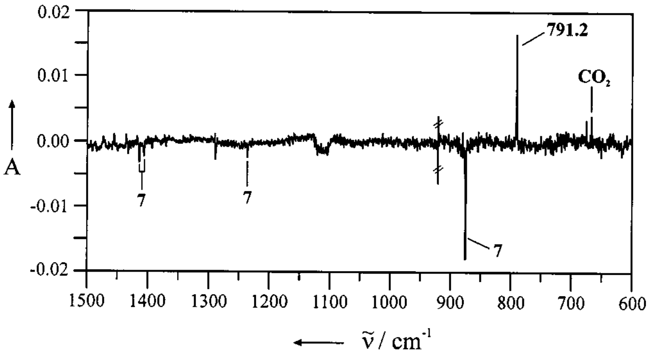

Figure 2. IR difference spectrum of the photochemically induced back reaction at λ = 254 nm (40 min) after previous irradiation of 1,2-dimethylenecyclobutane (**7**) with a KrF excimer laser (λ = 248 nm); the bands with positive values diminished, while those with negative values were enhanced upon irradiation

Thus, the species responsible for the absorption near 790 cm^{-1} can be generated from 1,2-dimethylenecyclobutane (**7**) by laser photolysis at λ = 248 nm and can subsequently be transformed back into **7** by exposing the matrix to light of wavelength λ = 254 nm. This behavior strongly supports the assignment of the 790 cm^{-1} absorption to tetramethyleneethane (**5**).

It seems rather surprising that tetramethyleneethane (**5**) could only be detected in the IR spectrum when 1,2-dimethylenecyclobutane (**7**) was irradiated with the excimer laser (λ = 248 nm), whereas photolysis with the low-pressure mercury lamp (λ = 254 nm) did not lead to the formation of this species. Apparently, the high photon density of the laser is essential to bring about this photoreaction.

As mentioned above, methylenespiropentane (**6**) yields 1,2-dimethylenecyclobutane (**7**) upon irradiation at λ = 254 nm in a xenon matrix. Therefore, **6** does not represent a valid candidate for an independent approach to **5** since its irradiation will invariably give rise to **7** as an intermediate.

IR Spectrum

The theoretical IR spectrum of tetramethyleneethane (**5**) has not previously been reported in the literature. Consequently, we performed ab initio calculations with the Gaussian 94 package of programs[12] using the CAS(6,6) and UB3LYP methods in combination with the basis set 6-31G* . Since the RB3LYP wavefunction for **S-5** was not stable, we had to perform the calculations for the singlet state of tetramethyleneethane (**5**) with UB3LYP and the keyword "guess=mix". With both theoretical approaches [CAS(6,6) and UB3LYP], *singlet*-tetramethyleneethane (**S-5**) was predicted to be the ground state ($\Delta E_{ST} = E_T - E_S = +1.3$ and $+0.9$ kcal mol^{-1}, respectively) and the localized minima obtained for **S-5** and **T-5** were of D_2 symmetry. The dihedral angles between the allylic subunits were calculated as 44.8° (CAS) and 44.9° (UB3LYP) in **S-5**. For **T-5**, we calculated slightly larger dihedral angles of 50.3° (CAS) and 47.7° (UB3LYP).

Table 1. Calculated IR absorptions and relative intensities of singlet and triplet tetramethyleneethane **S-5** and **T-5**

UB3LYP/6-31G*				CAS(6,6)/6-31G*		
S-5		**T-5**		**S-5**	**T-5**	
$\tilde{\nu}$ [cm^{-1}]	int.	$\tilde{\nu}$ [cm^{-1}]	int.	$\tilde{\nu}$ [cm^{-1}]	$\tilde{\nu}$ [cm^{-1}]	symmetry
271.4	< 0.01	264.8	< 0.01	281.8	271.2	B_2
304.4	0.02	293.7	0.02	314.5	298.1	B_1
462.7	0.02	461.4	0.02	492.4	490.1	B_3
552.4	0.01	555.4	0.02	572.5	576.6	B_2
553.8	0.04	553.9	0.04	577.5	579.4	B_1
558.2	< 0.01	561.8	< 0.01	586.7	589.4	B_3
562.8	0.07	567.5	0.06	584.7	588.6	B_1
684.2	0.03	672.5	0.01	694.1	681.9	B_2
760.9	0.01	764.8	0.01	689.9	693.3	B_3
795.8	1.00	797.7	1.00	722.9	722.2	B_1
803.4	0.10	806.2	0.13	728.1	727.1	B_2
993.8	< 0.01	992.4	< 0.01	1045.9	1040.3	B_1
995.8	< 0.01	994.4	< 0.01	1055.7	1048.8	B_2
1045.4	0.01	1047.5	0.01	1094.6	1096.8	B_3
1285.2	0.03	1275.3	0.04	1262.9	1237.4	B_2
1300.5	0.02	1301.3	0.02	1371.6	1371.7	B_3
1362.6	< 0.01	1353.9	< 0.01	1372.0	1346.9	B_1
1509.9	0.09	1506.8	0.09	1620.8	1616.3	B_2
1509.9	0.01	1506.5	0.01	1614.8	1611.4	B_1
1544.2	0.08	1544.6	0.08	1658.4	1658.1	B_3
3170.0	0.02	3169.0	0.02	3336.4	3335.1	B_1
3171.5	0.07	3170.3	0.07	3338.3	3337.2	B_2
3176.7	0.16	3175.8	0.17	3345.9	3344.3	B_3
3265.7	0.01	3264.9	0.02	3433.8	3432.2	B_1
3267.6	0.26	3266.8	0.27	3437.2	3435.4	B_3
3268.6	0.03	3267.6	0.03	3437.7	3435.2	B_2

In the calculated IR spectra of **S-5** and **T-5**, the wagging vibration of the methylene groups (ωCH_2) gives by far the most intense band. The calculated IR spectral bands are listed in Table 1. The results obtained with CAS(6,6) and UB3LYP lead to the prediction that in the IR spectra of both **S-5** and **T-5**, the most intense absorption lies in close proximity to the corresponding vibration of the allyl radical. Since the calculated band positions for the singlet and triplet states of tetramethyleneethane (**5**) differ by less than 2 cm^{-1}, it is not possible to determine the multiplicity of this species through comparison of the calculated and experimental frequencies.

If the band position of the ωCH_2 vibration of the allyl radical is computed using the UB3LYP/6-31G* approach, the result (797.0 cm^{-1}) is in extremely satisfying accordance with the experimental value (802 cm^{--1}).[11] This corresponds very well with the findings we made in studying the 1,2′-bis(allyl) diradical **2**. In the case of **2**, the deviation of the theoretical value from the experimentally determined band position of the ωCH_2 vibration was only about 10 cm^{-1}. In order to assess the suitability of the UB3LYP method for open-shell singlet molecules such as **S-5**, we compared the calculated and experimental IR spectra of *singlet*-1,2,4,5-tetramethylenebenzene [2,3,5,6-tetrakis-(methylene)-1,4-cyclohexanediyl]. Berson et al.[13] reported the most prominent features in the matrix IR spectrum (argon matrix) of *singlet*-1,2,4,5-tetramethylenebenzene to appear at 807.6 and 849.3 cm^{-1}. Roth, Maier et al.[14] assigned two absorptions at 810 and 854 cm^{-1} (argon matrix) to 1,2,4,5-tetramethylenebenzene. At the UB3LYP/6-31G* level of theory, the two most intense vibrations of *singlet*-1,2,4,5-tetramethylenebenzene (D_{2h} symmetry) are located at 804.2 and 859.6 cm^{-1}, in excellent agreement with the experimental data. With UB3LYP/6-31G*, the singlet state of 1,2,4,5-tetramethylenebenzene is calculated to be 4.1 kcal mol^{-1} more stable than the triplet, a result also in accordance with experiment.[13] Therefore, application of the UB3LYP method may be expected to offer a very reliable prediction of the position of the ωCH_2 vibration of not only **T-5** but also **S-5**.

Our calculations lead to the conclusion that the most intense vibration of tetramethyleneethane (**5**) should be located near 800 cm^{-1}. This is a further strong argument in favor of our assignment of the absorption found in the experimental IR spectrum near 790 cm^{-1} to species **5**.

Results and Conclusions

On irradiation of matrix-isolated 1,2-dimethylenecyclobutane (**7**) with a KrF excimer laser (λ = 248 nm), an absorption near 790 cm^{-1} (argon matrix: 793.1 cm^{-1}, xenon matrix: 791.2 cm^{-1}) has been observed in the IR spectrum. Subsequent exposure of the matrix to the light of a low-pressure mercury lamp (λ = 254 nm) led to a decrease in the intensity of this IR band. By means of the IR difference spectrum, **7** was identified as the sole product of the photochemically induced back reaction. This experimental result leads to the conclusion that the species responsible for the absorption near 790 cm^{-1} has the elemental composition C_6H_8.

The band position calculated (UB3LYP/6-31G*) for the most intense vibration of tetramethyleneethane (**5**) is in in very good agreement with the experimentally determined band position of the C_6H_8 species. Although we are well aware that it is not possible to unequivocally characterize a chemical species on the basis of only one IR-active vibration, we assign the IR absorption at 793.1 cm^{-1} in an argon matrix or at 791.2 cm^{-1} in a xenon matrix to the ωCH_2 vibration of tetramethyleneethane (**5**).

Experimental Section

General: The cryostat used for matrix isolation was a Displex CSA 202 closed-cycle refrigeration system from Air Products. The temperature measurement and control were performed with a digital temperature indicator/controller 3700-APD-E from Air Products [gold (0.07% iron)/chromel thermo element]. The matrix window consisted of CsI and spectra were obtained with a Bruker IFS 85 FT-IR spectrometer. The light sources used were a low-pressure spiral mercury lamp with a vycor filter and an LPX 105 MC excimer laser from Lambda Physics. − Bicyclopropylidene (**3**) was prepared according to the procedure of de Meijere et al.[15] 1,2-Dimethylenecyclobutane (**7**) was prepared from 1,2-bis(hydroxymethyl)cyclobutane.[9] − Compounds **3** and **7** were condensed onto the matrix window at 10 K as gas mixtures with xenon or argon (ratio 3:1000). The most intense absorption of **3** in a xenon matrix was located at 952.5 cm^{-1}. In the case of **7**, the main band was seen at 875.6 cm^{-1}. The bromine-doped matrices were prepared by co-condensation of the **3**/xenon gas mixture with a bromine/xenon gas mixture (ratio 3:1000) in a 1:1 ratio.

Calculations: The calculations were performed with the Gaussian 94 package of programs.[12] The 6-31G* basis set was used throughout. For the DFT calculations of **S-5**, UB3LYP was used in combination with the keyword "guess=mix". For these calculations, the stability of the wavefunction was tested with the "stable" keyword. The energies E and zero-point energies ZPE (au) calculated for **5** and 1,2,4,5-tetramethylenebenzene were as follows. CAS(6,6)/6-31G*: **S-5** (D_2 symmetry, dihedral angle: 44.8°, $E = -231.8135643$, $ZPE = 0.119171$), **T-5** (D_2 symmetry, dihedral angle: 50.3°, $E = -231.81139$, $ZPE = 0.119011$). UB3LYP/6-31G*: **S-5** (D_2 symmetry, dihedral angle: 44.9°, $E = -233.3258507$, $ZPE = 0.114328$), **T-5** (D_2 symmetry, dihedral angle: 47.7°, $E = -233.324513$, $ZPE = 0.114349$), *singlet*-1,2,4,5-tetramethylenebenzene (D_{2h} symmetry, $E = -386.9648356$, $ZPE = 0.161541$), *triplet*-1,2,4,5-tetramethylenebenzene (D_{2h} symmetry, $E = -386.9580914$, $ZPE = 0.161294$).

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