Ring Opening of 1-Methylcyclopropene and Cyclopropene: Matrix Infrared Spectroscopic Identification of 2-Butene-1,3-diyl and Propene-1,3-diyl

Günther Maier,* Christian Lautz, and Stefan Senger[a]

Abstract: Triplet 2-butene-1,3-diyl (**T-11**) was generated on irradiation of 1-methylcyclopropene (**10**) in a bromine-doped xenon matrix and was characterized by means of IR spectroscopy for the first time. Experimental results suggest that triplet propene-1,3-diyl (**T-3**) is formed from cyclopropene (**1**) under similar conditions. In accordance with theoretical calculations, the experimental data indicate that the reactions **1** → **3** and **10** → **11** are the lowest energy ground-state pathways for the ring opening of **1** and **10**, respectively.

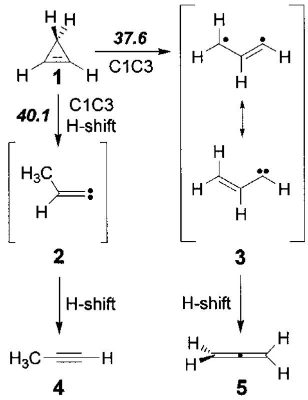
Keywords: cyclopropenes • IR spectroscopy • matrix isolation • photochemistry • ring opening

Introduction

The matrix isolation technique[1] is ideally suited for the generation and spectroscopic characterization of highly reactive molecules. We especially use this technique to study reactive intermediates that play a pivotal role in chemical reactions. By doing this, we hope to gain a better understanding of the underlying reaction mechanisms.

In the last few years, we have investigated several ring-opening reactions of cyclic hydrocarbons.[2–7] Only recently, we reported on our attempts to detect the IR spectrum of the diradical tetramethyleneethane (2,3-dimethylenebutane-1,4-diyl), the primary ring-opening product of 1,2-dimethylenecyclobutane.[7] Irradiations in halogen-doped xenon matrices—a new method for the generation of reactive species which has been developed by us[2–8]—proved to be particularly useful for the formation of intermediates with triplet ground states. For example, we were able to use IR spectroscopy to characterize the diradicals trimethylenemethane[2] and 4-methylene-2-pentene-1,5-diyl[5] (an intermediate in the 2-vinylmethylenecyclopropane/3-methylenecyclopentene rearrangement), which we generated on irradiation of methylenecyclopropane and 2-vinylmethylenecyclopropane, respectively, in bromine-doped xenon matrices.

The experimental study of the ring opening of cyclopropene (**1**) represents a special challenge. Neither of the two conceivable primary products of a C1−C3 bond cleavage, methylvinylidene (**2**) and propene-1,3-diyl (**3**) (Scheme 1), have been detected spectroscopically.[9] In the course of our studies of the photochemically induced ring opening of cyclopropane in halogen-doped xenon matrices, we have already examined the behaviour of cyclopropene (**1**) under similar conditions.[3] Irradiation of **1** in argon matrices, undoped xenon, and bromine-doped xenon matrices showed that the matrix material has a significant influence on the observed product distribution and the photolysis rate. However, it was not possible in our previous experiments to gain any spectroscopic information about a reactive intermediate



Scheme 1. Thermal isomerization of cyclopropene (**1**) to propyne (**4**) and allene (**5**). [The numbers in bold italic typeface are the barriers (kcal mol^{-1}) for the ring opening of **1**; these were calculated with B3-LYP/6–31G(d).]

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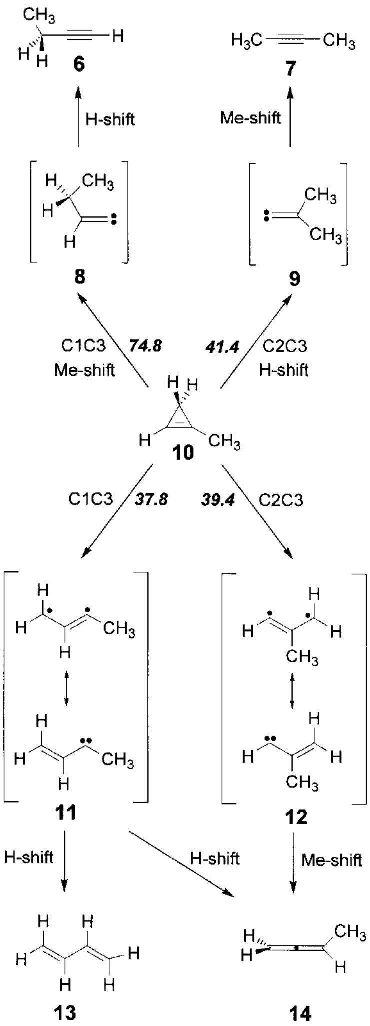
Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author. It contains a) the calculated structures of **1**, **2**, **8**, **9**, **10**, **T-12t**, and **T-12c**, and the transition structures of the ring-opening reactions **1** → **2**, **1** → **3**, **10** → **8**, **10** → **9**, **10** → **11** and **10** → **12**, b) the calculated IR spectra of **2**, **8**, **9**, **T-12c** and **T-12t** and c) the calculated energies of the structures mentioned under a) and those depicted in Figure 3.

in the isomerization of **1** to propyne (**4**) and allene (**5**) (cf. Scheme 1).

Ab initio studies of Yoshimine et al.[12] suggest that **2** is not a stable intermediate on the C_3H_4 potential-energy surface. The hydrogen migration coupled with linearization of the carbon skeleton, which leads to the formation of **4**, requires essentially no energy. The situation is different for dimethylvinylidene (**9**), the analogue of **2** in the the ring-opening reaction of 1-methylcyclopropene (**10**; Scheme 2). In the isomerization of **9** to 2-butyne (**7**) the migration of a methyl group is required, for which a theoretical barrier (B3-LYP/6–31G(d)) of approximately 11.1 kcal mol^{-1} was predicted.[13] Therefore, **9** should be a stable intermediate on the C_4H_6 potential-energy surface, and spectroscopic characterization of **9** should, in principle, be possible. Since we could not find any matrix isolation studies of 1-methylcyclopropene (**10**) in the literature, we decided to study the behaviour of matrix-isolated **10** experimentally. Additionally, we repeated our previous experiments with **1** in order to make a direct comparison with the experimental data obtained for **10**. In both cases we focussed on the IR-spectroscopic detection of the primary ring-opening products of the cyclopropenes.



Scheme 2. Ring-opening reactions of 1-methylcyclopropene (**10**). [The numbers in bold italic typeface are the barriers (kcal mol^{-1}) for the primary reaction step, calculated with B3-LYP/6–31G(d)].

Abstract in German: *Triplett-2-Buten-1,3-diyl (**T-11**) konnte in einer mit Brom dotierten Xenon-Matrix durch die Belichtung von 1-Methylcyclopropen (**10**) erzeugt und zum ersten Mal infrarotspektroskopisch nachgewiesen werden. Die experimentellen Ergebnisse lassen weiterhin vermuten, daß unter den gleichen Bedingungen Triplett-Propen-1,3-diyl (**T-3**) aus Cyclopropen (**1**) entsteht. In Übereinstimmung mit theoretischen Berechnungen lassen die experimentellen Ergebnisse den Schluß zu, daß die Reaktionen **1**→**3** und **10**→**11** die energetisch günstigsten Reaktionspfade der Ringöffnung von **1** bzw. **10** darstellen.*

Since the experimental results are more convincing in the case of **10** than they are for the parent cyclopropene (**1**), we begin the discussion with the methylated derivative **10**.

Results

Matrix experiments

*1-Methylcyclopropene (**10**)*: Substrate **10** was exposed to light of different wavelengths in undoped as well as bromine-doped argon and xenon matrices at 10 K. On irradiation at 313 nm, **10** was photostable except in a bromine-doped xenon matrix (ratio **10**/Br_2/Xe = 7:2.5:1000), in which it isomerized to a mixture of 1,3-butadiene (**13**) and methylallene (**14**) (Scheme 2).

On irradiation at 254 nm (or at 248 nm with a KrF excimer laser), **10** was again photostable in doped or undoped argon matrices. However, in undoped or bromine-doped xenon matrices, isomerization of **10** to compounds **13** and **14** was again observed. In addition to the absorptions belonging to **13** and **14**, we also located some product bands in the bromine-doped xenon matrix that we could not readily assign. On subsequent irradiation at 313 or 366 nm, the intensities of six of these unassigned absorptions decreased rapidly. These absorptions were positioned at 767.1 (s), 874.6 (m), 1354.4 (vw), 1402.8 (w), 1421.5 (m) and 1454.6 (m) cm^{-1}. As the discussion in the next section will show, these bands can be assigned to **T-11**. The difference spectrum of the secondary photolysis at 366 nm is depicted in Figure 1. The products of the secondary photolyis are exclusively hydrocarbons with the elemental composition C_4H_6, namely **10**, **13** and **14**. There was a large variation in the relative intensities of the product absorptions in our experimental IR spectra, so that it was not possible to determine a reliable product ratio **10**:**13**:**14**.

*Cyclopropene (**1**)*: In undoped argon and xenon matrices, **1** was photostable on irradiation at 313 nm. On the other hand, isomerization occurred when **1** was exposed to light of the same wavelength in a xenon matrix additionally doped with bromine (ratio **1**/Br_2/Xe = 1:1:1000). We identified allene (**5**) as the sole product; propyne (**4**) could not be detected.

Irradiation of **1** at 254 nm in undoped argon and xenon matrices induced a photorearrangement which led to **4** and **5**. The observed reaction rate showed a strong dependence on the matrix material. Whereas in a xenon matrix approximately 50 % of substrate **1** had reacted after an exposure time of

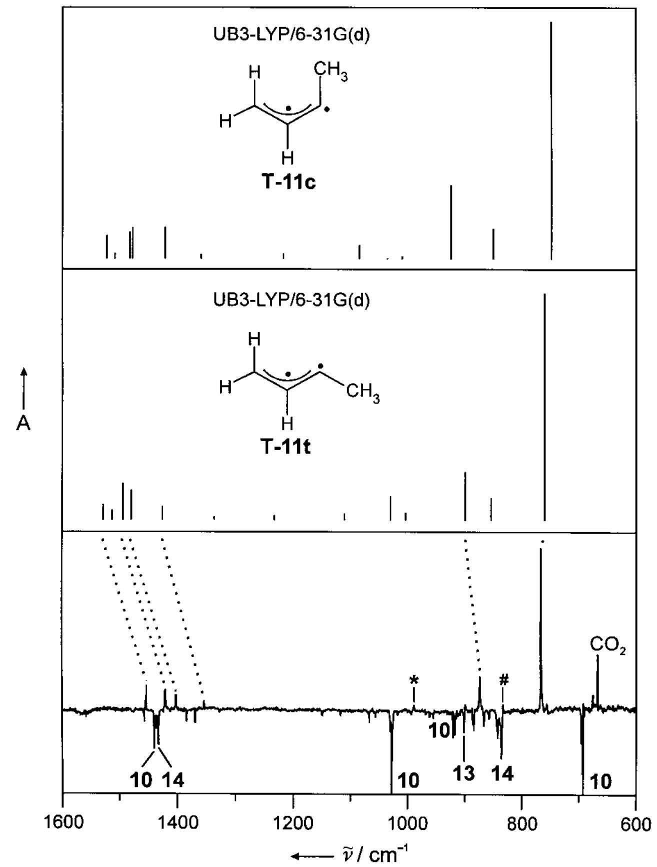


Figure 1. Comparison of the experimental (bottom) and calculated (UB3-LYP/6–31G(d)) IR spectra of the *cis* (**T-11c**, top) and *trans* isomer (**T-11t**, middle) of triplet 2-butene-1,3-diyl (**T-11**). The experimental spectrum (bromine-doped xenon matrix, 10 K) is a difference spectrum [irradiation at 366 nm, when matrix-isolated **10** has initially been exposed to the light of a KrF excimer laser ($\lambda = 248$ nm)]. The bands with positive values are diminished, while those with negative values are enhanced upon 366 nm irradiation (# = 833.8 cm^{-1}, * = 994.2 cm^{-1}, see text).

24 h, only 10 % of **1** rearranged within the same period of time in an argon matrix.

A dramatic change in the product ratio was observed if the xenon matrix was additionally doped with bromine. On irradiation of **1** in a bromine-doped xenon matrix at 254 nm, the main product was **5** (Figure 2b). Propyne (**4**), which was an additional product in the undoped xenon matrix, was only formed in minor amounts. Apart from this significant change in the product ratio, we observed a further effect of the presence of bromine in the xenon matrix. In the IR spectrum, which we detected after irradiating **1** in a bromine-doped xenon matrix (ratio **1**/Br_2/Xe = 6:2:1000) at 254 nm, we observed a small absorption at 786.6 cm^{-1}, which we could not readily assign. As the discussion in the next section will show, this band can be tentatively assigned to **T-3**. This absorption was absent in the experiments in undoped xenon matrices (Figure 2a). A secondary photolysis at 366 nm led to a rapid decrease of the intensity of the new absorption. Because the absorption at 786.6 cm^{-1} had only a very low intensity, we were not able to identify the products of the secondary photolysis. The use of a KrF excimer laser ($\lambda = 248$ nm) instead of a low-pressure mercury lamp ($\lambda = 254$ nm) did not lead to an increase in the intensity of this absorption.

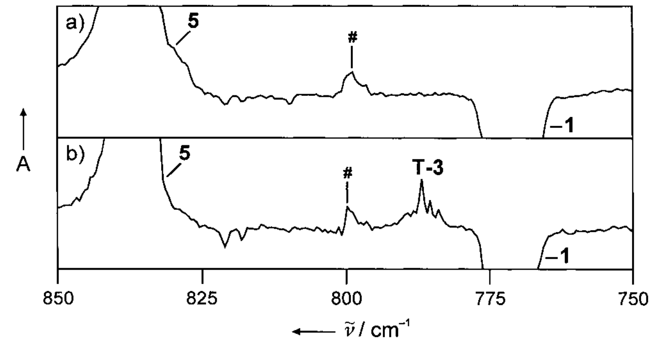


Figure 2. IR difference spectra (750–850 cm^{-1}) of the 254 nm photolysis of cyclopropene (**1**) in a) an undoped xenon matrix and b) a bromine-doped xenon matrix. The bands with positive values are enhanced, while those with negative values are diminished upon irradiation. The absorption marked with # is due to the formation of the allyl radical.

IR spectra

If not otherwise noted, we performed geometry optimizations and frequency calculations with the hybrid DFT method B3-LYP and the basis set 6–31G(d). Our previous studies have shown that this combination yields accurate theoretical IR spectra (for examples see below).[5, 7] All calculated B3-LYP/6–31G(d) relative energies were corrected by the zero-point vibrational energies at the same level of theory.

*Spectra originating from irradiation of 1-methylcyclopropene (**10**)*: In Scheme 2, the four conceivable primary products of the ring opening of **10** and the corresponding final reaction products are shown. On the basis of results of extensive theoretical[12, 13] and experimental[14–16] studies, we propose that the alkynes are generated via vinylidene intermediates.

In our matrix experiments, we detected 1,3-butadiene (**13**) and methylallene (**14**) as reaction products of **10**. As can be seen in Scheme 2, the only intermediate which can account for the simultaneous formation of **13** *and* **14** is 2-butene-1,3-diyl (**11**). A hydrogen migration from the methyl group to the adjacent carbon atom in **11** leads to **13**, whereas **14** is the product of the analogous hydrogen shift from the methyne group to the carbenic center. Therefore, it is very reasonable to assume that the unassigned experimental absorptions are due to the presence of **11** in the matrix.

Hutton, Manion, Roth and Wasserman[10] have shown by ESR spectroscopy that propene-1,3-diyl (**3**) has a triplet ground state. Yoshimine et al.[17] calculated (MRCI*(DZP)) that the lowest singlet state of **3** ($^1A'$) should be approximately 14 kcal mol^{-1} higher in energy than the ground state ($^3A''$). 2-Butene-1,3-diyl (**11**) should therefore also have a triplet ground state. Substituted triplet vinylmethylenes, which close to form the corresponding cyclopropenes under normal conditions, have been studied by Arnold et al.[18].

In Figure 1 and Table 1, the experimental band positions are compared with the calculated IR spectra of triplet *trans*-2-butene-1,3-diyl (**T-11t**) and triplet *cis*-2-butene-1,3-diyl (**T-11c**). By far the most intense absorptions of **T-11t** and **T-11c** in the calculated IR spectra are due to wagging vibrations of the methylene groups (ω-CH_2) at 760.2 cm^{-1}

Table 1. Comparison between the experimental (xenon matrix,10 K) band positions and relative intensities (int) of triplet 2-butene-1,3-diyl (**T-11**) and the calculated IR spectra (UB3-LYP/6–31G(d), 450–3500 cm^{-1}) of the *cis* and *trans* isomers **T-11c** and **T-11t**.

Experiment		UB3-LYP/6–31G(d) **T-11t**		**T-11c**	
$\tilde{\nu}$ [cm^{-1}]	int	$\tilde{\nu}$ [cm^{-1}]	int	$\tilde{\nu}$ [cm^{-1}]	int
		474.3	0.01	539.2	0.07
		549.9	0.06	574.3	0.05
767.1	1.00	760.2	1.00	747.7	1.00
		853.8	0.10	850.0	0.13
874.6	0.22	899.2	0.21	924.2	0.31
		1003.6	0.03	1009.4	0.01
		1030.1	0.11	1035.3	0.01
		1110.4	0.03	1084.3	0.06
		1232.5	0.02	1217.0	0.02
		1336.6	0.02	1359.2	0.02
1354.4	0.05	1425.6	0.06	1421.5	0.13
1402.8	0.09	1480.1	0.13	1477.8	0.13
1421.5	0.13	1494.6	0.16	1482.5	0.11
		1512.7	0.04	1508.3	0.02
1454.6	0.15	1528.4	0.07	1522.4	0.10
		2982.9	0.73	2991.5	0.44
		3036.9	0.54	3054.2	0.52
		3047.2	0.68	3068.2	0.37
		3060.2	0.46	3120.4	0.30
		3176.7	0.20	3170.9	0.17
		3269.2	0.31	3261.4	0.35

and 747.7 cm^{-1}, respectively. The theoretical band positions of the ω-CH$_2$ vibrations correspond very well with the position of the most intense absorption in the experimental difference spectrum (767.1 cm^{-1}, cf. Figure 1). That B3-LYP/6–31G(d) yields such good results for ω-CH$_2$ vibrations is known from several other examples [e.g., 4-methylene-2-pentene-1,5-diyl: 752.6 cm^{-1} (xenon matrix),[5] 742.9 cm^{-1} (calcd); trimethylenemethane: 755.5 cm^{-1} (xenon matrix),[2] 747.3 cm^{-1} (calcd); allyl radical: 797.0 cm^{-1} (xenon matrix),[6, 19] 797.0 cm^{-1} (calcd)]. In view of this, the slightly better match between the calculated and experimental band position for the most intense vibration of **T-11t** may be taken as an indication for the presence of the *trans* isomer of triplet 2-butene-1,3-diyl (**T-11**) in the matrix. A similar conclusion may be drawn from the assignment of the experimental absorption at 874.6 cm^{-1}. Whereas the corresponding vibration in the theoretical IR spectrum of **T-11t** is shifted by 25 cm^{-1} to higher wavenumbers, the deviation from the experimental value would be 50 cm^{-1} for **T-11c**.

No experimental absorption could be assigned to the vibration located in the calculated IR spectra of **T-11t** and **T-11c** at 853.8 cm^{-1} and 850.0 cm^{-1}, respectively. The small band at 833.8 cm^{-1}, which is marked with # in the experimental difference spectrum (Figure 1), is an artefact. It is most likely that the absorption of **T-11** in this spectral region cannot be detected due to the intense absorption of **14** at 836.0/842.8 cm^{-1}. The small absorption at 994.2 cm^{-1} in the experimental difference spectrum (marked with * in Figure 1) has not been assigned to **T-11**, because on photolysis at 366 nm its intensity decreases much more slowly than the intensities of the six absorptions that have been attributed to the presence of **T-11**.

Based on the good correspondence between the theoretical and experimental IR spectrum and the fact that all products of the secondary photolysis at 366 nm have the elemental composition C$_4$H$_6$ (see above), we assign the observed IR absorptions (Table 1) to triplet 2-butene-1,3-diyl (**T-11**). The above comparison slightly favours the assignment to the *trans* isomer **T-11t**. The experimental band positions did not correspond to the calculated IR spectra of the other three primary ring-opening products of 1-methylcyclopropene (**10**) (cf. Scheme 2; for the calculated IR spectra of **8**, **9**, **T-12c** and **T-12t** see the Supporting Information). In particular, there was no IR-spectroscopic indication that dimethylvinylidene (**9**) was formed in our matrix experiments.

The calculated structures of **T-11c** and **T-11t** together with the transition structure **15(TS)** for the *cis*–*trans* isomerization are shown in Figure 3a. As can be seen from the calculated C–C bond lengths, **T-11** is not a localized carbene with single and double C–C bonds, but can best be described as a delocalized carbene with an allylic π structure. Previous experimental[10] and theoretical studies[17] came to the same conclusion for **T-3**.

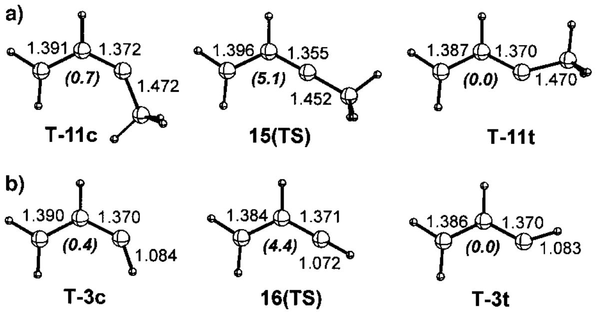


Figure 3. Calculated structures (UB3-LYP/6–31G(d)) of the *cis* and *trans* isomers and the transition states of the *cis*–*trans* isomerization of a) triplet 2-butene-1,3-diyl (**T-11**) and b) triplet propene-1,3-diyl (**T-3**). Relevant bond lengths are given in Å, relative energies in kcal mol^{-1} (numbers in parentheses). All structures have C_s symmetry.

The two isomers **T-11c** and **T-11t** are nearly isoenergetic. Our calculations predict that the *trans* isomer **T-11t** is only favoured by 0.7 kcal mol^{-1}. The calculated barrier (B3-LYP/6–31G(d)) for the isomerization **T-11c**→**T-11t** is 4.4 kcal mol^{-1}.

*Spectra originating from irradiation of cyclopropene (**1**)*: The unassigned absorption at 786.6 cm^{-1} in the difference spectrum of the photolysis of **1** at 254 nm (Figure 2b) is located very close to the absorption of triplet 2-butene-1,3-diyl (**T-11**) in this spectral region at 767.1 cm^{-1}. Therefore, it seems reasonable to assume that the absorption at 786.6 cm^{-1} can be assigned to triplet propene-1,3-diyl (**T-3**), formed on photolysis of **1** in a bromine-doped xenon matrix. The calculated IR absorptions and relative intensities of the *trans* and *cis* isomers of **T-3** are grouped together in Table 2. As can be seen, there is excellent agreement between the experimental absorption at 786.6 cm^{-1} and the calculated band position for the ω-CH$_2$ vibration in **T-3t** at 783.2 cm^{-1}. We take this as a strong indication that **T-3** did actually form in our matrix experiments.

The correspondence between the experimental band position at 786.6 cm^{-1} and the theoretical result for the ωCH$_2$

Table 2. Calculated band positions and relative intensities (int) (UB3-LYP/6–31G(d)) of the *cis* and *trans* isomers (**T-3c** and **T-3t**, respectively) of triplet propene-1,3-diyl (**T-3**).

T-3t		**T-3c**	
$\tilde{\nu}$ [cm^{-1}]	int	$\tilde{\nu}$ [cm^{-1}]	int
421.4	0.08	399.9	0.05
531.5	0.71	515.0	0.46
557.4	0.04	641.5	0.08
783.2	1.00	773.8	1.00
844.7	0.39	866.7	0.39
904.7	0.16	954.5	0.46
1022.1	0.01	1034.3	0.08
1224.9	0.04	1221.0	0.02
1254.3	0.07	1247.4	0.02
1431.1	0.04	1427.1	0.01
1528.2	0.03	1520.4	0.02
3055.5	0.33	3123.2	0.22
3177.6	0.15	3170.1	0.16
3259.4	0.06	3244.0	0.06
3271.5	0.24	3263.2	0.27

vibration of the *cis* isomer **T-3c** (773.8 cm^{-1}) is not as good as it is for the *trans* isomer **T-3t** (783.2 cm^{-1}). 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, this may be taken as an indication in favour of the assignment of the IR absorption at 786.6 cm^{-1} to the *trans* isomer of **T-3**.

In the IR spectra of our experiments with bromine-doped xenon matrices, high optical scattering occurred in the spectral regions below 600 cm^{-1} and above 3000 cm^{-1}. Therefore, we have not been able to locate and assign experimental absorptions in this spectral regions.

The calculated structures of **T-3t**, **T-3c**, and the transition structure **16(TS)** for the *cis–trans* isomerization can be seen in Figure 3b. Our calculations predict that the *trans* isomer **T-3t** is favoured by 0.4 kcal mol^{-1}. This is in good agreement with the results of Yoshimine et al.[17], whose calculations predicted that the two isomers of **T-3** should be isoenergetic. They had calculated a barrier of 5.7 kcal mol^{-1} for the *cis–trans* isomerization of the triplet molecules, in reasonable agreement with the B3-LYP/6–31G(d) barrier of 4.0 kcal mol^{-1}.

Discussion

As we have shown by comparison of our experimental and calculated IR-spectroscopic data, the reactive intermediates, 2-butene-1,3-diyl (**11**) and propene-1,3-diyl (**3**) can be generated from matrix-isolated 1-methylcyclopropene (**10**) and cyclopropene (**1**), respectively. In our matrix experiments **11** and **3** could only be detected when the corresponding cyclopropenes, **10** or **1**, were irradiated in bromine-doped xenon matrices. Neither diradical could be detected in our experiments in undoped xenon and argon matrices or in bromine-doped argon matrices. Therefore, these results are another example (cf. refs. [2–8]) that clearly demonstrates the powerful potential of irradiations in bromine-doped xenon matrices as a technique for the formation of reactive intermediates.

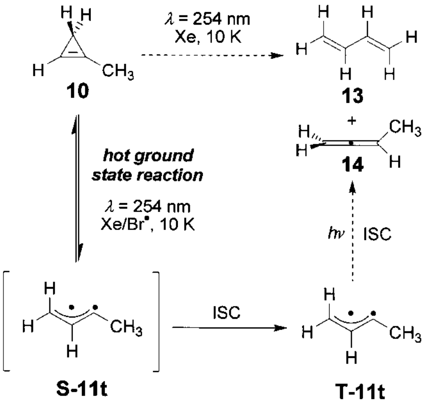
A characteristic feature of irradiations in halogen-doped xenon matrices is the possibility to induce chemical reactions on irradiation with wavelengths which the organic precursor does *not* absorb. The energy of the irradiation is first absorbed by the halogen atoms, which are embedded in the xenon matrix, and subsequently transferred to the organic molecules. It has to be emphasized that both the halogen atoms as well as the organic molecules are matrix isolated. As a consequence, the energy transfer cannot proceed by direct interaction between the molecules and the halogen atoms, rather, the solid xenon acts as the medium for the transfer of the absorbed energy. Thus, the reactions that can be observed are not the result of *direct* photolysis; they are only photochemically induced. For example, in an undoped xenon matrix, 2-vinylmethylenecyclopropane is photostable if exposed to light of 313 nm, but it isomerizes to 3-methylenecyclopentene if exposed to the same wavelength in a bromine-doped xenon matrix.[5] Cyclopropene (**1**) and 1-methylcyclopropene (**10**) show similar behaviour. Whereas both are photostable on irradiation at 313 nm in undoped xenon matrices, isomerizations occur if **1** and **10** are irradiated with the same wavelength in bromine-doped xenon matrices. That **T-3** or **T-11** could not be detected under these conditions can be explained by the fact that both species undergo secondary photoreactions when irradiated at 313 nm.

In the matrix experiments with 254 nm light, the distinction between *direct* photolysis and *indirect* photochemically induced reactions is not as clear-cut as for the irradiations at 313 nm. Since both **10** and **1** are not photostable in an undoped xenon matrix on irradiation at 254 nm, it is more difficult to differentiate between the two alternatives in the bromine-doped xenon matrices when this wavelength is used. For **1**, a distinction between the two types of reactions is possible because different reaction products are formed. The *direct* photolysis of **1** ($\lambda = 254$ nm, undoped xenon matrix, 10 K) yields propyne (**4**) and allene (**5**) as the photoproducts, whereas the *indirect* photochemically induced reaction ($\lambda = 254$ nm, bromine-doped xenon matrix, 10 K) leads preferentially to the formation of allene (**5**). Since only a minor amount of **4** is formed in the bromine-doped xenon matrix, we conclude that *direct* photolysis does not contribute significantly to the product formation, and that the dominating process under these experimental conditions is the photochemically induced reaction. This conclusion implies that propene-1,3-diyl (**3**) is the initial product of the photochemically induced ring opening of **1**. For **10**, it is not possible to differentiate between the two processes on the basis of the reaction products, because 1,3-butadiene (**13**) and methylallene (**14**) are formed both in the undoped as well as in the bromine-doped xenon matrix on irradiation of **10** at 254 nm. Nevertheless, we conclude that, in analogy to the formation of **3** from **1**, 2-butene-1,3-diyl (**11**) is also generated primarily from **10** in the *indirect* photochemically induced reaction.

Although we do not know exactly how the radiation energy is transferred from the bromine atoms—which initially absorb the light in the bromine-doped xenon matrix—to the matrix-isolated organic substrate molecules, our previous experimental studies[5, 6] indicate that the product formation in the observed photochemically induced reactions occur from vibrationally excited substrate molecules. This conclusion is mainly based on the fact that the observed reaction products are identical with those of the corresponding thermal reactions.

At first glance, our present results seem to be in direct contradiction to these earlier results. The main product of the pyrolysis of **1** is propyne (**4**)[20, 21], whereas allene (**5**) is formed nearly exclusively on irradiation ($\lambda = 254$ nm or 313 nm) of **1** in the bromine-doped xenon matrix. The situation is similar for **10**. 2-Butyne (**7**) is the main product of the pyrolysis of **10**[20, 22], but 1,3-butadiene (**13**) and methylallene (**14**) are formed on irradiation ($\lambda = 254$ nm or 313 nm) of **10** in bromine-doped xenon matrices, where no alkyne could be detected. Does this necessarily imply that the ring cleavage of **1** and **10** in the halogen-doped xenon matrices does not start from vibrationally excited substrate molecules? Not at all, since the contradiction is resolved if the rate-determining first reaction step, the ring cleavage, instead of the overall reaction barrier that governs the pyrolysis of **1** and **10**[12, 20–22] is considered. Schemes 1 and 2 show (the numbers in bold italic typeface in these schemes) the calculated barriers (B3-LYP/6–31G(d)) for the different ring-opening reactions of **1** and **10**, respectively. The calculated barriers indicate that for a hot ground-state reaction the pathways $\mathbf{1} \rightarrow \mathbf{3}$ and $\mathbf{10} \rightarrow \mathbf{11}$ should be energetically preferred. This is in total accordance with our experimental results. This is also in good agreement with the results of Bergman and co-workers,[23] who found that racemization of 1,3-diethylcyclopropene on pyrolysis in the gas phase occurs considerably faster than its conversion to the ring-opening products does. The authors explain this racemization through the intermediacy of a "vinylcarbene" analogous to **3** and **11**.

In Scheme 3, our postulated mechanism for the reaction in the bromine-doped xenon matrix is shown for **10**. In the first step, substrate **10** reacts in a hot ground-state reaction to form **S-11t**. Subsequently, **S-11t** is stabilized by intersystem crossing (ISC) to the triplet species **T-11t**. It is well known that chemical reactions that are carried out in the presence of xenon have an enhanced intersystem-crossing rate.[24, 25] This effect is caused by the external heavy-atom effect of xenon. In the third step, light is absorbed by **T-11t** and products **13** and **14** are eventually formed. Our experimental results do not allow us to be more specific on the mechanism of the transformation of **T-11t** to the final products **13** and **14**.



Scheme 3. Survey of the proposed mechanism for the isomerization of 1-methylcyclopropene (**10**) on irradiation in a bromine-doped xenon matrix.

Conclusion

The reactive intermediates propene-1,3-diyl (**3**) and 2-butene-1,3-diyl (**11**) have been identified as the primary products of the ring-opening reactions of cyclopropene (**1**) and 1-methylcyclopropene (**10**), respectively, on irradiation of these substrates at 254 nm in bromine-doped xenon matrices. Under the experimental conditions, the reactive intermediates are not produced by *direct* photolysis, but via an *indirectly* achieved vibrationally excited state of the substrate. Therefore, we can conclude that the reactions $\mathbf{1} \rightarrow \mathbf{3}$ and $\mathbf{10} \rightarrow \mathbf{11}$ (Schemes 1 and 2) are the lowest energy ground-state pathways for the ring opening of **1** and **10**, respectively.

Experimental Section

The cryostat for matrix isolation was a closed-cycle compressor unit RW2 with coldhead base unit 210 and extension module ROK from Leybold. The matrix window was CsI and the spectrometer was an FTIR spectrometer, IFS 85 from Bruker. The light sources used were a mercury high-pressure lamp, HBO 200 (Osram) with monochromator (Bausch and Lomb), a mercury low-pressure spiral lamp with a vycor filter (Gräntzel) and an excimer laser, LPX 105 MC from Lambda Physics.

1-Methylcyclopropene (**10**) was prepared according to the procedure of Fisher and Applequist,[26] from 3-chloro-2-methylpropene. Cyclopropene (**1**) was prepared according to the analogous procedure of Closs and Krantz.[27] An authentic sample of methylallene (**14**) was prepared from 1,2,3-tribromobutane.[28] Compounds **1** and **10** were condensed onto the matrix window at 10 K as gas mixtures with argon or xenon (ratio 8:1000 and 10:1000, respectively).

The bromine-doped matrices were prepared by co-condensation of **1** (or **10**)/rare gas mixtures with bromine/rare gas mixtures (ratio 6:1000) in the ratio of approximately 2:1. The IR spectra of **1** and **10** in undoped and bromine-doped xenon matrices were identical, so that we could exclude the presence of bromine adducts with **1** (cf. ref. [29]) or **10** in significant amounts.

Prominent IR absorptions (xenon matrix, 10 K)

Cyclopropene (1): 574.2, 774.8, 905.4, 1003.8, 1035.1, 1647.0, 1655.6, 2888.0/2892.3, 2962.2, 2983.4 cm^{-1}.

Propyne (4): 625.8, 1240.0, 3310.3 cm^{-1}.

Allene (5): 352.0, 834.6/837.5, 994.6, 1385.2, 1674.9, 1949.3, 1992.2 cm^{-1}.

1-Methylcyclopropene (10): 693.3, 920.9, 957.0, 1028.9, 1056.8, 1150.4, 1394.7, 1440.1, 1476.3, 1780.0, 2884.1, 2912.1, 2964.8 cm^{-1}.

***s-trans*-1,3-Butadiene (13)**: 901.5, 1018.0, 1588.3 cm^{-1}.[30]

Methylallene (14): 517.9, 549.2/552.2, 836.0/842.8, 857.7, 867.4, 1067.9, 1369.7, 1432.9, 1440.6, 1459.0, 1956.5/1962.9/1967.6, 2899.5, 2919.3, 2931.8, 2984.9 cm^{-1}.

Ab Initio Calculations: All calculations were performed with the Gaussian 94 package of programs.[31] The basis set 6–31G(d) and the DFT method B3-LYP were used throughout. For all stationary points, frequency calculations were performed and the stability of the wavefunction was tested. Relative energies were corrected with the B3-LYP/6–31G(d) zero-point vibrational energies.

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