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A Matrix Isolation Study of 2-Isopropylidenecyclopentane-1,3-diyl (Berson-Type Diradical)

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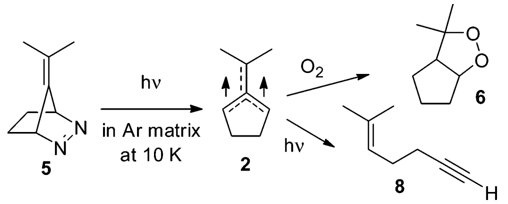
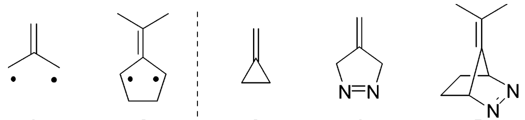


The photodenitrogenation of diazene **5** in an argon matrix at 10 K permitted the first observation of an IR spectrum of 2-isopropylidenecyclopentane-1,3-diyl **2** (a Berson-type diradical). A comparison of the IR spectrum with a vibrational simulation at the B3LYP/6-31G(d) level of theory revealed that the diradical **2** has a planar structure. The oxygen-trapping reaction of **2** produced regioselectively fused peroxide **6** in an oxygen-doped argon matrix at 10 K. Irradiation of the diradical **2** afforded enyne **8** in an argon matrix at 10 K.

Trimethylenemethane (TMM) derivatives have been widely discussed in the fields of theoretical[1] and synthetic chemistry.[2] Dowd's pioneering work on the parent TMM (**1**) showed that the triplet state is the ground-state spin-multiplicity.[3] The longer lived 2-alkylidenecyclopentane-1,3-diyl (Berson-type TMM)[4] **2** provided additional opportunities to study the chemistry of TMM species. For examples, a spin-state dependent change in the intermolecular reactivity was revealed[5] and the possibility of its use as a ferromagnetic material[6] was proposed. To date, the detection of the diradicals has generally achieved by ultraviolet−visible (UV−vis) spectroscopic analyses[7] and EPR measurements.[8] However, an analysis of the three-dimensional structure was quite difficult to perform using the spectroscopic methods. Combined studies of matrix-isolation IR spectroscopy and vibrational calculations are ideally suited for determining the structures of labile reaction intermediates.[9] Maier and coworkers reported the detection of the parent TMM (**1**) by IR spectroscopy during the photoisomerization of methylenecyclopropane (**3**) in a halogen-doped xenon matrix at 10 K.[10] However, it was not possible to detect the diradical **1** using a more conventional method, e.g. the photodenitrogenation of 4-methylenedihydropyrazole (**4**), because of the lability of **1** (i.e. fast formation of **3**) under the reaction conditions employed. In the present study, we wish to report on the first study using a combination of theoretical calculations and matrix-isolation IR spectroscopy of the Berson-type diradical **2** ($\lambda = 299$, 308, 322, 405, and 428 nm)[7a] generated during the photodenitrogenation of diazene **5** ($\lambda_{\max} = 343$ nm, $\epsilon = 120$ M^{-1}cm^{-1}).[7a] The photochemical reactivity of **2** was also examined in an argon matrix at 10 K.



1 **2** **3** **4** **5**

The diazene **5** was prepared according to the reported method.[11] Good agreement was found between the IR spectrum of **5** (Figure 1b) in an argon matrix at 10 K and the simulated spectrum calculated at the B3LYP/6-31G(d)[12] level of theory using the Gaussian 98 suite of programs[13] (Figure 1a).[14]

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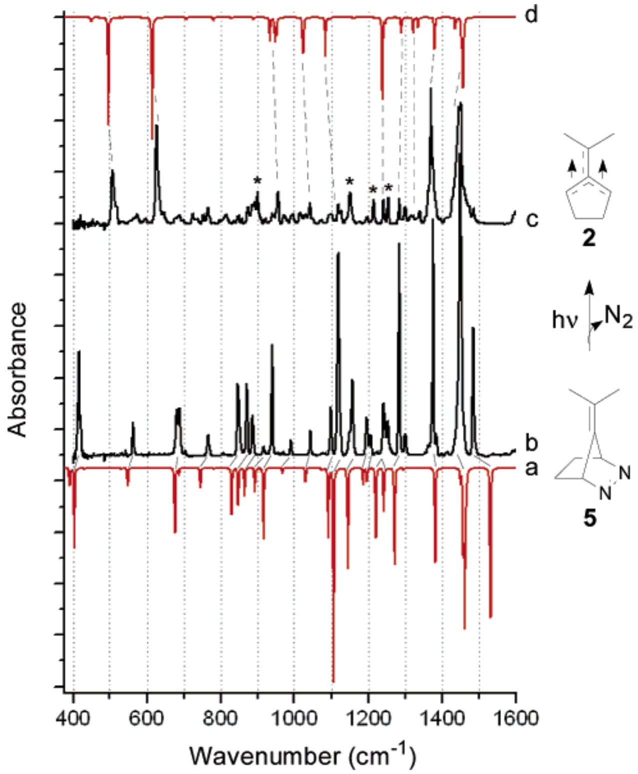

FIGURE 1. Photolysis ($\lambda = 320-380$ nm) of diazene **5** in an argon matrix at 10 K. (a) Calculated IR spectrum for diazene **5** optimized at the B3LYP/6-31G(d) level of theory, scaled by 0.9614. (b) IR spectrum for diazene **5**. (c) IR spectrum obtained after 6 h of irradiation. Bands due to **8** (*), see Figure 3. (d) Calculated IR spectrum for the triplet state of diradical **2** optimized at the UB3LYP/6-31G(d), scaled by 0.9614. The dihedral angle around the exo double-bond was calculated to be 2.7°. The calculated IR spectra were recorded using the Molview 3.0 program (ref 14).

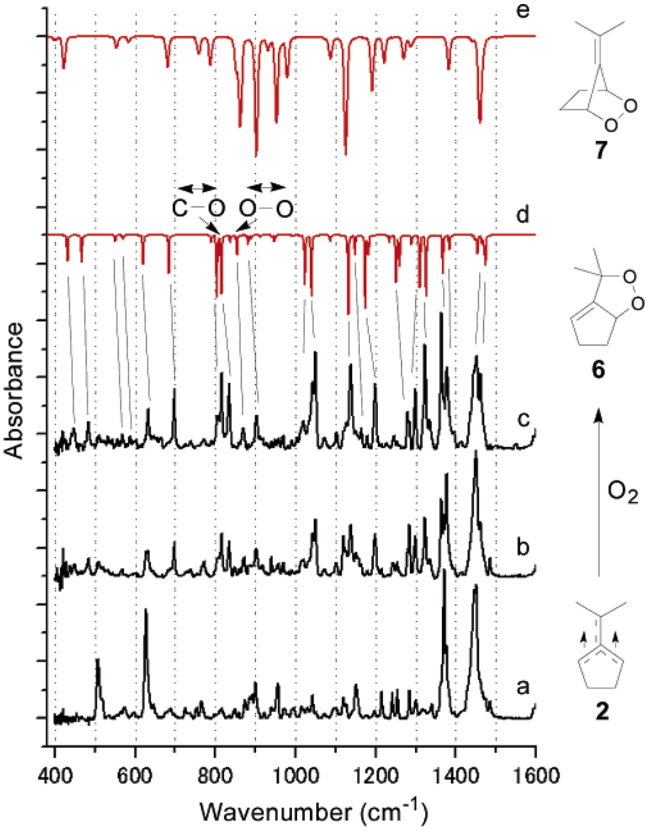

FIGURE 2. Photolysis ($\lambda = 320-380$ nm) of diazene **5** in an oxygen-doped argon matrix at 10 K. (a) IR spectrum for diradical **2** in an argon matrix at 10 K. (b) IR spectrum obtained after 7 h of irradiation of diazene **5** in a 1% oxygen doped argon matrix at 10 K. (c) IR spectrum obtained after 6 h of irradiation of diazene **5** in a 5% oxygen doped argon matrix at 10 K. (d) Calculated IR spectrum for fused peroxide **6** optimized at the B3LYP/6-31G(d) level of theory, scaled by 0.9614. (e) Calculated IR spectrum for endoperoxide **7** optimized at the B3LYP/6-31G(d) level of theory, scaled by 0.9614.

Irradiation of **5** at $\lambda = 320-380$ nm (150 W Xe-lamp) produced a high yield of the triplet state of 2-isopropylidenecyclopentane-1,3-diyl (**2**) after 6 h at 10 K (Figure 1c). A DFT calculation for the triplet state of **2** at the UB3LYP/6-31G(d) level of theory leads to a good reproduction of the experimental spectrum (Figure 1d). For example, the strong peaks at 507 and 626 cm^{-1} are in good agreement with the calculated IR bands of 515 and 639 cm^{-1} (Figure 1c,d). Thus, the Berson-type TMM **2** was successfully observed in the conventional matrix-isolation conditions, unlike the parent TMM **1**, and possesses an almost planar structure. The dihedral angle around the exo double bond was calculated to be 2.7°.

The irradiation ($\lambda = 320-380$ nm) of diazene **5** in an oxygen-doped argon matrix (5% oxygen in argon, **5**/O_2 = ca. 3/1) at 10 K produced a new compound at the expense of TMM **2** (Figure 2c). The obtained IR bands are consistent with those calculated for the fused peroxide **6** at the B3LYP/6-31G(d) level of theory (Figure 2d), the oxygen-trapping product of **2**. For example, the vibrational mode for C−O bond stretching ($\lambda_{calcd} = 814$ cm^{-1}) was observed at 834 cm^{-1} and that for O−O bond stretching (λ_{calcd} 832 cm^{-1}) was detected at 870 cm^{-1}. Endoperoxide **7** was not detected in the matrix-isolation experiments (Figure 2e). If the endoperoxide **7** were formed in the reaction, the chemical yield would likely be very low. It was reported that the fused peroxide **6** was produced selectively in the photodenitrogenation of diazene **5** under high-pressure oxygen atmosphere.[15] In a 1% oxygen-doped argon matrix (**5**/O_2 = ca. 1/0.7), both the diradical **2** and the peroxide **6** were observed (Figure 2b). The selective formation of the fused peroxide **6** can be reasonably explained by the relative stability of peroxides **6** and **7**. DFT calculations at the B3LYP/6-31G(d) level of theory showed that the fused isomer is more stable by 6.1 kcal/mol (including a zero-point energy correction). Even at a low concentration of O_2 (0.5% doped, O_2/**5** = ca. 0.3/1), we could observe TMM **2** and peroxide **6** after irradiation of azoalkane **5** at 10 K. After warming the sample to 40 K, we could not see any detectable conversion from **2** to **6**, as judged by the relative

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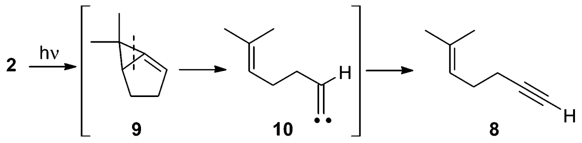
SCHEME 1. Photochemical Reaction of Berson-Type Diradical 2



intensity of the two products. From this experiment, we could not determine the mechanism for the formation of the peroxide, i.e., photochemical or thermal reaction. Finally, we tried to see the thermal conversion from **2** to **6** by the deposition of excess amounts of O_2 during warming the sample of TMM **2** to 38 K under dark conditions. Although the observed spectrum was broadened, the thermal conversion of **2** to **6** was actually observed (see Figure S1 in the Supporting Information). This experiment proved the thermal conversion from **2** to **6**, but does not exclude the possibility of the photochemical production of **6** in the denitrogenation of azoalkane **5** in oxygen-doped argon matrix at 10 K.

In 1982, Berson and co-workers reported that the irradiation ($\lambda = 300$ nm) of diradical **2** in an ether−methylcyclopentane glass at 77 K produced enyne **8** (Scheme 1).[16] They proposed a hypothetical mechanism involving the photochemical ring closure of the diradical **2** to the bicyclo[3.1.0]hex-1-ene **9** followed by a cycloreversion to give **10**, which, via a hydrogen shift produces **8**. To obtain additional information concerning the formation of the putative intermediates **9** and **10**, the photochemical reaction of the Berson-type diradical **2**, prepared by photolysis of **5** (6 h irradiation in an argon matrix at 10 K), was examined in an argon matrix at 10 K (Figure 3). After irradiation ($\lambda = 320{-}380$ nm) for 10 h at 10 K, the complete disappearance of **2** and new IR bands were observed (Figure 3a,b). A DFT calculation revealed that the new IR bands corresponded to enyne **8** (Figure 3b,c). For example: (1) The vibrational mode of the acetylenic C−H stretching ($\lambda_{calcd} = 3361$ cm^{-1}, Figure 3c) was detected at 3226 cm^{-1} (Figure 3b). (2) The vibrational mode of the C−C triple bond stretching ($\lambda_{calcd} = 2153$ cm^{-1}, Figure 3c) was detected at 2129 cm^{-1} (Figure 3b). (3) The bending modes ($\lambda_{calcd} = 588$ and 574 cm^{-1}, Figure 3c) of acetylenic C−H were observed at 633 and 624 cm^{-1} (Figure 3b). IR bands corresponding to **9** and **10** were not observed under the matrix-isolation conditions employed. As indicated in Figure 3a, the enyne **8** (*) was already formed, to some degree, during the denitrogenation of diazene **5**; see also Figure 1c. The formation of **8** in the photodenitrogenation of **5** is quite reasonable, since the diradical **2** also absorbs light in the 320−380 nm region,[7a] which was used for the photodecomposition of diazene **5**. The activation energy for the hydrogen shift in **10** was calculated to be only 0.5 kcal/mol at the B3LYP/6-31G(d) level of theory. Thus, the fact that the carbene **10** was not detected is not surprising even under the matrix-isolation conditions employed here. The cycloreversion step from **9** to **10** is a well-known photochemical reaction of methylenecyclopropanes.[17] However, the methylenecyclopropanes **9** would not absorb light at wavelengths over 300 nm. Thus, the fast photochemical cycloreversion of **9** is not the reason **9** was not observed in the photochemical decomposition of **2**. Since a similar structure, **11**, is known to be thermally stable at temperatures below −30 °C,[18] the fast thermal cycloreversion from **9** to **10** does not explain why **9** was not observed in the matrix-isolation conditions employed here. One possible explanation is that the cycloreversion of **9** occurs from the excited state of **9** before relaxation to the ground state.[16]

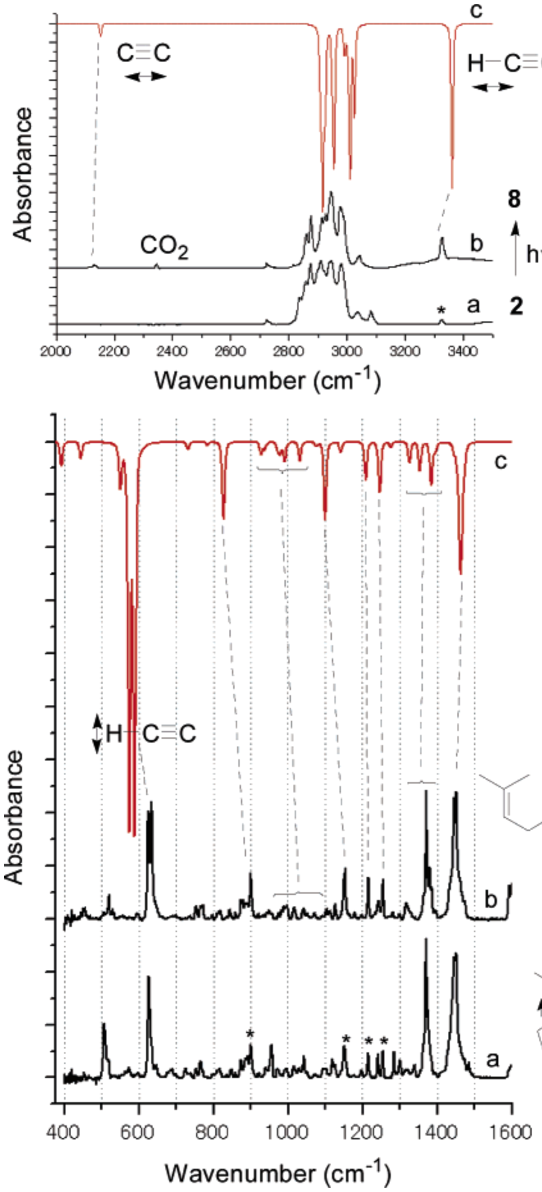
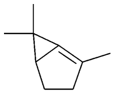


FIGURE 3. Photolysis ($\lambda = 320{-}380$ nm) of diradical **2** in an argon matrix at 10 K. (a) IR spectrum of diradical **2** in an argon matrix at 10 K. Top: in the 2000−3500 cm^{-1} region. Bottom: in the 400−1600 cm^{-1} region. (b) IR spectrum obtained after 10 h of irradiation of diradical **2** in an argon matrix at 10 K. (c) Calculated IR spectrum for enyne **8** optimized at the B3LYP/6-31G(d) level of theory, scaled by 0.9614.



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In summary, a Berson-type diradical **2** was observed for the first time in conventional matrix-isolation experiments (in an

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argon matrix at 10 K) during the photodenitrogenation of diazene **5**. Combined computational calculations and matrix-isolation experiments revealed that the triplet diradical **2** possesses a planar structure. The planar triplet diradical was regioselectively trapped by molecular oxygen to give the fused peroxide **6** under the matrix-isolation conditions employed. In the photochemical conversion of **2** to **8**, the putative intermediates **9** and **10** were not observed under our matrix-isolation conditions used.

Experimental Section

Matrix IR experiments were performed by means of standard techniques[19] using a closed-cycle helium cryostat. A CsI window was attached to the copper holder at the bottom of the cold head. Two opposing ports of a vacuum shroud surrounding the cold head were fit with KBr with a quartz plate for UV irradiation and a deposition plate for admitting the sample and matrix gas. Irradiation was carried out with a 150 W xenon lamp. IR spectra (1 cm^{-1} resolution) were recorded with a FTIR spectrometer.

7-Isopropylidene-2,3-diazabicyclo[2.2.1]hept-2-ene (5): IR (Ar, 10 K) ν 3033 (m), 3023 (m), 2987 (s), 2951 (s), 2919 (s), 2879 (m), 2866 (m), 2736 (w), 1743 (w), 1485 (m), 1449 (s), 1376 (s), 1301 (w), 1284 (s), 1253 (w), 1241 (w), 1207 (w), 1196 (w), 1157 (m), 1118 (s), 1099 (w), 1043 (w), 990 (w), 940 (m), 916 (w), 886 (w), 871 (m), 846 (m), 767 (w), 688 (m), 562 (m), 416 (m) cm^{-1}.

2-Isopropylidenecyclopentane-1,3-diyl (2): IR (Ar, 10 K) ν 3080 (m), 2979 (s), 2943 (s), 2908 (s), 2898 (s), 2873 (s), 2858 (m), 1451 (s), 1370 (s), 1301 (w), 1284 (w), 1243 (w), 1042 (w), 956 (w), 626 (m), 507 (s) cm^{-1}.

3,3-Dimethyl-3,5,6,6a-tetrahydrocyclopenta[1,2]dioxole (6): IR (Ar, 10 K) ν 2984 (s), 2942 (s), 2940 (s), 2867 (s), 1460 (m), 1452 (m), 1377 (m), 1363 (s), 1322 (m), 1298 (m), 1279 (w), 1198 (m), 1138 (m), 1050 (m), 1043 (m), 902 (w), 870 (w), 834 (m), 815 (m), 698 (m), 633 (m), 484 (w), 445 (w) cm^{-1}.

6-Methylhept-5-en-1-yne (8): IR (Ar, 10 K) ν 3326 (m), 3043 (m), 2988 (s), 2975 (s), 2875 (s), 2129 (w), 1704 (m), 1451 (s), 1445 (s), 1371 (s), 1254 (m), 1215 (m), 1153 (m), 900 (m), 633 (m), 624 (m) cm^{-1}.

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Supporting Information Available: Computational details and Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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