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Bicyclo[3.2.2]non-1-ene: Matrix Isolation and Spectroscopic Characterization of a Moderately Strained Bridgehead Olefin

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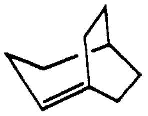
Bicyclo[3.2.2]non-1-ene was generated in low-temperature matrices and in fluid solutions by photodecomposition of bicyclo[2.2.2]oct-1-yldiazomethane and its photorearrangement product, 3-(bicyclo[2.2.2]oct-1-yl)diazirine. It was characterized by IR and UV absorption and by ^1H and ^{13}C NMR spectroscopy. Further evidence for the proposed structure was provided by self-trapping and by the spectral effects of deuteration on the olefinic carbon. Observed IR spectra and isotopic shifts agree well with the results of semiempirical (MNDO) and *ab initio* (SCF/6-31G*) calculations.

Introduction

Continued interest in the properties and reactivity of compounds with highly strained double bonds[2,3] led us to undertake a more detailed spectroscopic characterization of bicyclo[3.2.2]non-1-ene (1) than has been available so far. Although this bridgehead olefin is only moderately strained, up to now only the vinyl proton region of the ^1H NMR spectrum of its mixture with the isomer, bicyclo[3.2.2]non-1(7)-ene, has been reported,[4] and it was not known which signal belongs to which isomer.



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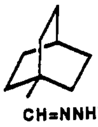

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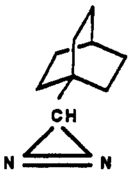
3-*d₁*



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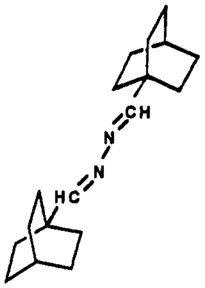

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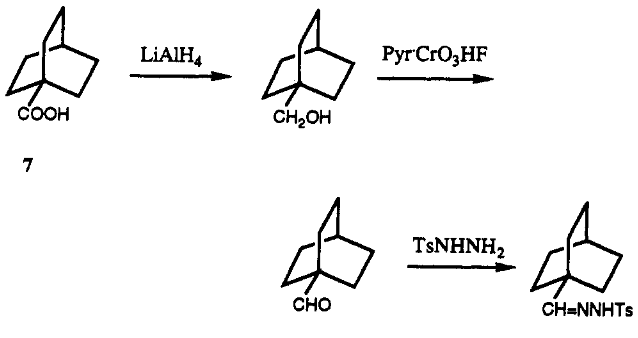
In this paper we report a more complete NMR characterization and vibrational (infrared) and electronic spectra of 1 and 1-*d₁*, generated photochemically from bicyclo[2.2.2]oct-1-yldiazomethane (2) and stabilized in a low-temperature solution or matrix. The precursor 2 is accessible by pyrolysis of the lithium salt of bicyclo[2.2.2]octane-1-carboxaldehyde tosylhydrazone (3). We find that 2 interconverts photochemically with bicyclo[2.2.2]oct-1-yldiazirine (4). Both the conversion of diazo compounds to diazirines[5] by visible irradiation and the reverse of this process, induced by UV (~300 nm) irradiation of diazirines[6] have been known for a long time. In the case of 2 and 4, both processes are accompanied by the formation of a third species that is photostable under these conditions and is identified as 1.

The photochemical generation of olefins from both diazo compounds and diazirines is well precedented[2,3] and may involve carbene intermediates. In the present case, we find some indications that trace amounts of bicyclo[2.2.2]oct-1-ylcarbene (5) are formed, since the azine 6 is detected as one of the produts of matrix warm-up.

Results

Precursor Synthesis. The known tosylhydrazone[7] 3 was prepared in 57% overall yield based on the starting bicyclo[2.2.2]octane-1-carboxylic acid[8] (7). The acid 7 was reduced with lithium aluminum hydride, the product was oxidized with pyridinium fluorochromate,[9] and the resulting crude aldehyde was treated with toluenesulfonyl hydrazide to yield 3. The deuterated hydrazone 3-*d₁* was prepared in a similar way, using lithium aluminum deuteride in the reduction step.



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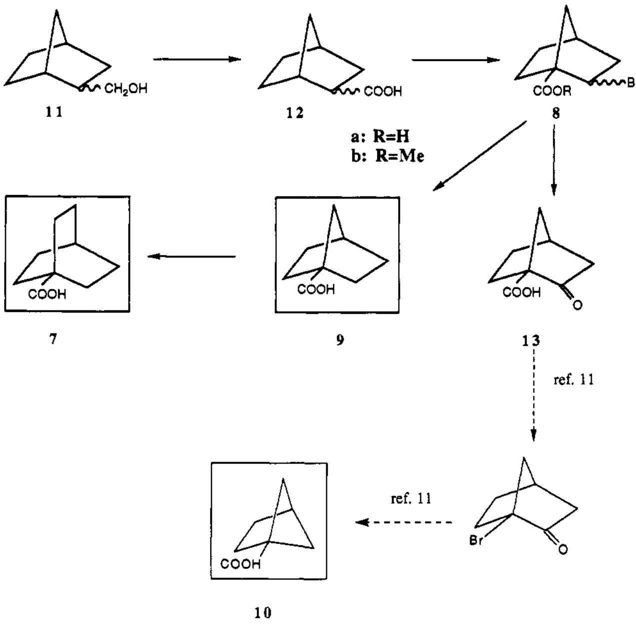
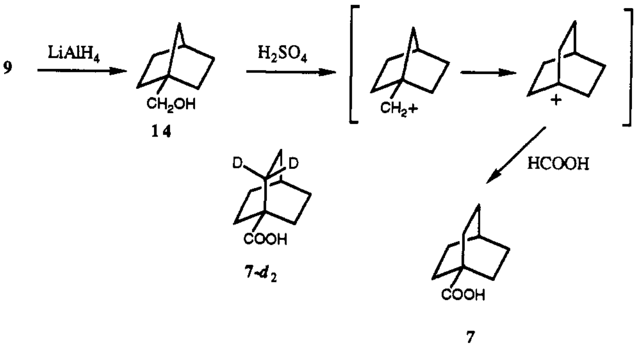
Scheme I



Scheme II



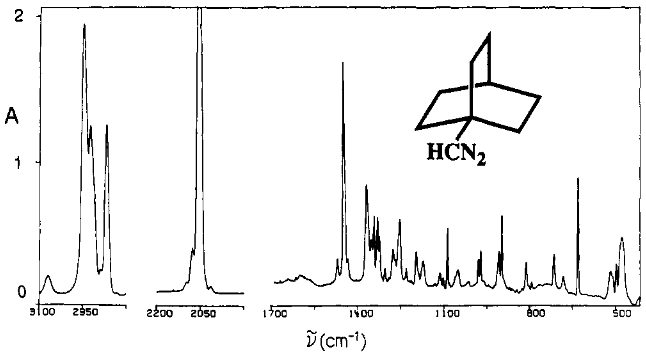


Figure 1. The IR spectrum of bicyclo[2.2.2]oct-1-yldiazomethane (**2**) in Ar matrix at 12 K.

Bicyclo[2.2.2]octane-1-carboxylic acid[8] (**7**) was obtained according to a new synthetic scheme in which 2-bromobicyclo[2.2.1]heptane-1-carboxylic acid[10] (**8a**) serves as a common precursor for three bicyclic acids useful as starting materials for the synthesis of bridgehead olefins (Scheme I): bicyclo[2.2.1]heptane-1-carboxylic acid (**9**), bicyclo[2.2.2]octane-1-carboxylic acid (**7**), and bicyclo[2.1.1]hexane-1-carboxylic acid (**10**). The bromo acid **8a** was obtained by permanganate oxidation of the commercially available mixture of *endo*-, *exo*-bicyclo[2.2.1]heptane-2-methanols (**11**) and bromination[10] of the resulting mixture of acids **12**. Recrystallization of the crude product yielded pure *exo*-2-bromobicyclo[2.2.1]heptane-1-carboxylic acid[10] (**8a**). The filtrate containing some of the *exo*-acid **8a** and presumably also other isomeric bromobicyclo[2.2.1]heptanecarboxylic acids was hydrolyzed and oxidized yielding the keto acid **13**.[11] This is known to offer access to bicyclo[2.1.1]hexane-1-carboxylic acid (**10**) in an efficient two-step transformation.[11] The bromo acid **8a** was converted into methyl 2-bromobicyclo[2.2.1]heptane-1-carboxylate (**8b**), which was reduced with trimethyltin hydride under catalytic conditions[12] and hydrolyzed to yield bicyclo[2.2.1]heptane-1-carboxylic acid[13] (**9**). Finally, Haaf carboxylation[14] was used in the conversion of **9** to **7** (Scheme II), based on several literature reports[15] of facile rearrangement of the bicyclo[2.2.1]heptane-1-methyl cation to the bicyclo[2.2.2]oct-1-yl cation. Thus, acid **9** was reduced with $LiAlH_4$, and the resulting crude bicyclo[2.2.1]heptane-1-methanol[13] (**14**) was stirred with formic acid in the presence of sulfuric acid to yield **7**. Reduction of the acid **9** with lithium aluminum deuteride similarly led to 2,2-dideuteriobicyclo[2.2.2]octane-1-carboxylic acid (**7-*d*$_2$**).

The hydrazones **3** and **3-*d*$_1$** were converted to their lithium salts by reaction with butyllithium in THF followed by vacuum drying.[16]

Matrix Isolation. Bicyclo[2.2.2]oct-1-yldiazomethane (**2**) was generated *in situ* by flash vacuum pyrolysis of the lithium salt of the tosylhydrazone **3** at 100 °C in a low pressure (1–2 torr) stream of argon. The gas mixture was condensed onto a CsI window held at 28 K. The resulting matrix was kept at 12 K. The diazo compound **2** was characterized by its UV and IR absorption spectra. The UV spectrum consisted of a very strong absorption below 250 nm. Diazo compounds are known to have a very weak and broad absorption in the visible region, but our samples were so dilute that this was barely observable (λ_{max} = 471 nm). In the infrared spectrum, a characteristic C=N=N stretching vibration at 2054 cm^{-1} as well as a bending vibration at 640 cm^{-1} were observed (Figure 1).

UV light at 248 or 254 nm destroys **2** very fast, but it interferes with a selective observation of the primary photoproducts. Therefore, the definitive experiments were conducted with either 488- or 514-nm Ar ion laser lines. The intense visible light converted **2** very slowly into a mixture of products. A 95% conversion of a matrix sample containing ~1 mg of **2** was achieved over a period of 8–10 h with ~5 W of laser light. The UV absorption of the products consists of a broad structured band between 250 and 360 nm (Figure 2, λ_{max} = 309 nm). After nearly complete (~98%) bleaching of the starting material, further irradiation was carried out at 308 or 351 nm. The photoconversion was very facile as manifested by a fast simultaneous decrease of the structured UV absorption (Figure 2) and of a subset of IR peaks, accompanied by an increase in the IR intensities of the starting diazo compound **2**. The primary photoproduct that reverts to

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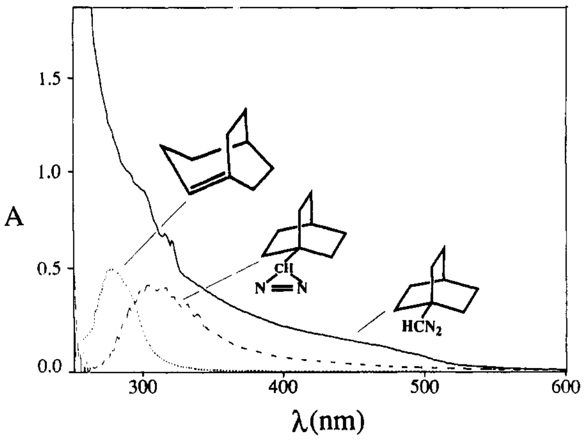

Figure 2. UV-vis spectra of bicyclo[2.2.2]oct-1-yldiazomethane (2, solid line), bicyclo[3.2.2]non-1-ene (1, dotted line), and bicyclo[2.2.2]oct-1-yldiazirine (4, dashed line) isolated in Ar matrix at 12 K. The last two spectra were obtained by subtracting spectra of 2 (also serving as a baseline) and the other component present in a photochemical mixture under conditions that minimized the concentration of the latter.

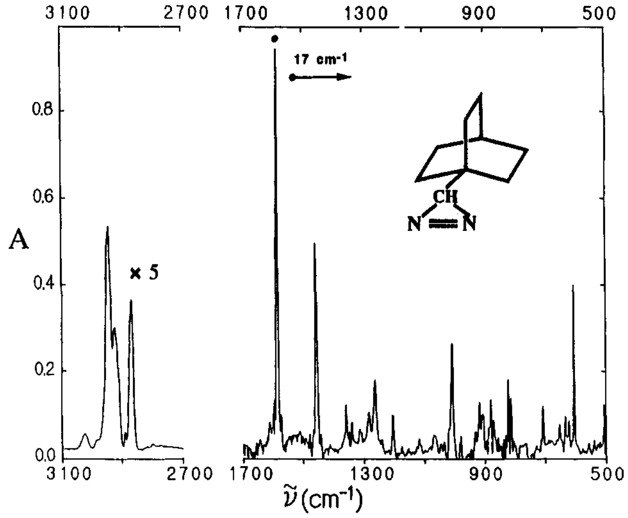

Figure 3. The IR spectrum of bicyclo[2.2.2]oct-1-yldiazirine (4) in Ar matrix at 12 K..

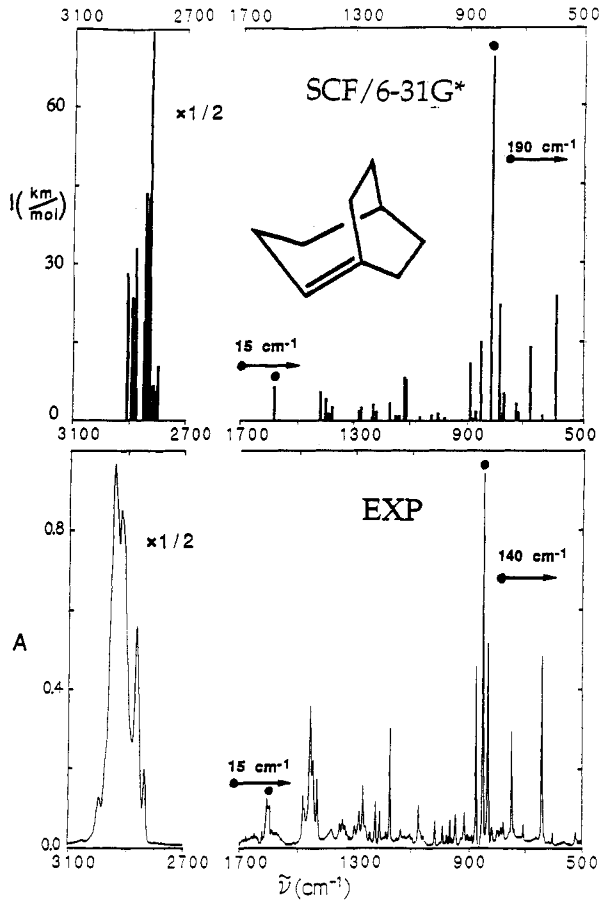

Figure 4. The IR spectrum of bicyclo[3.2.2]non-1-ene (1) in Ar matrix at 12 K (bottom), and calculated spectrum (top). All frequencies in the latter were multiplied by a scaling factor of 0.9. In both spectra arrows indicate isotopic frequency shifts in the monodeuteriated compound for the C═C double bond stretch and for the C-H out-of-plane bending.

2 upon UV irradiation is characterized by a structured UV band between 260 and 360 nm and an intense IR peak at 1585.5 cm^{-1} (N═N stretch) and is assigned the diazirine structure 4. Its IR spectrum, obtained by computer subtraction, is shown in Figure 3.

Alternate irradiation of the sample at 514 and 308 nm eventually destroyed all the UV and IR peaks corresponding to 2 and 4. The resulting IR spectrum was assigned to 1, characterized by an intense IR peak at 853 cm^{-1} (CH bend), a weak one at 1608 cm^{-1} (C═C stretch), and a broad UV absorption maximum at 276 nm. Prolonged irradiation at 248 nm slowly destroyed 1 as evidenced by the concurrent disappearance of all the IR and UV peaks attributed to it. This permitted us to obtain its spectra independently by computer subtraction (Figure 4).

The interconversion of 2 and 4 was clearly demonstrated by an experiment in which the measurements and irradiation were carried out in the FTIR instrument without moving the sample. Increase in the intensities of the peaks due to 2 was observed when a matrix containing a mixture of 2 and 4 was irradiated at 308 nm. When the wavelength of irradiation was changed to 514 nm, the intensities of the peaks due to 4 increased. At both wavelengths of irradiation, a gradual increase in the peaks of 1 was observed.

The proposed IR band assignments are supported by isotopic labeling experiments. Irradiation of 2 labeled with a single deuterium yielded the monodeuterio derivatives of 1 and 4. The deuterium-induced shift in the C═C stretching frequency of 1 (Figure 4) is $\Delta = -15$ cm^{-1} (C═CH, 1608 cm^{-1}; C═CD, 1593 cm^{-1}) and the shift in the ═C—H out-of-plane bend is -140 cm^{-1} (═C—H, 853 cm^{-1}; ═C—D, 713 cm^{-1}). For the N═N stretch in 4 (Figure 3) the shift is -17 cm^{-1} (1585.5 cm^{-1} for unlabeled and 1568.5 cm^{-1} for deuteriated material). The assignment of the strong band at 1586 cm^{-1} in the IR spectrum of 4 to N═N stretching is also consistent with literature reports for diazirines.[17] The broad-structured band between 260 and 360 nm in the UV spectrum of 4 agrees very well with that reported for diazirine.[18,19] The IR spectrum of 1 agrees well with an *ab initio* prediction, scaled by the standard factor of 0.9 (Figure 4, Table I).

We conclude that one of the two major products formed from 2 by visible photolysis, the one that is destroyed by

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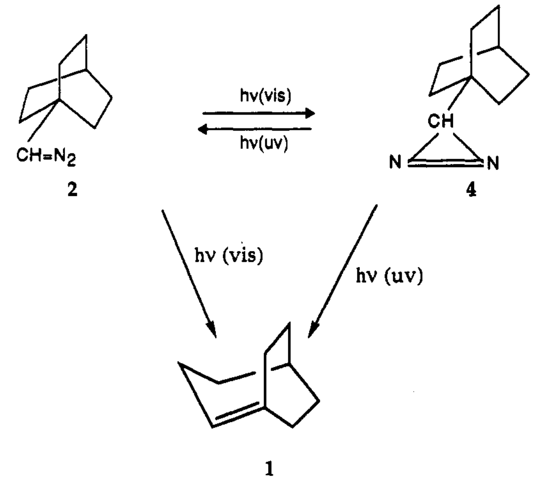
Table I. IR Vibrations of Bicyclo[3.2.2]non-1-ene (1)

exp			calcd[b]			calcd[b]		
$\tilde{\nu}$, cm^{-1}	I^a		$\tilde{\nu}$, cm^{-1}	I^a		$\tilde{\nu}$, cm^{-1}	I^a	
489	0.1		150	0.1		1364	0.9	
523	0.3		280	0.1		1388	2.7	
603	0.4		329	0.1		1394	0.3	
643	5.8		349	0.1		1444	1.5	
748	2.7		398	0.8		1458	2.5	
835	6.5		433	1.3		1464	0.7	
853	10.4	C–H oop	508	1.0		1475	0.3	
877	4.8		535	0.7		1497	0.2	
919	0.9		571	1.1		1507	2.1	
949	1.0		707	17.1		1517	1.6	
969	0.7		761	1.0		1520	0.3	
994	0.8		811	10.2		1623	0.3	
1021	0.8		859	1.4		1627	2.1	
1077	1.5		870	2.6		1643	1.2	
1175	3.1		921	4.0		1647	0.7	
1210	1.0		926	1.3		1654	3.2	
1227	1.5		941	15.9		1677	4.1	
1271	1.7		976[c]	53.2	C–H oop	1866[d]	4.8	C═C stretch
1284	0.9		1019	10.9		3178	25.9	
1300	0.6		1040	1.5		3190	17.5	
1342	0.4		1056	0.6		3198	19.5	
1433	1.3		1063	8.0		3213	137.3	
1447	1.0		1096	0.4		3216	20.3	
1457	7.5		1120	0.3		3218	81.1	
1483	1.6		1167	0.7		3225	75.7	
1608	3.0	C═C stretch	1194	1.3		3233	82.6	
2838	4.0		1220	1.0		3236	7.9	
2866	26.2		1266	0.8		3238	40.4	
2918	87.5		1321	5.8		3267	18.3	
2945	100.5		1328	6.1		3271	64.3	
2995	2.0		1350	0.9		3286	48.2	
						3306	56.1	

[a] Relative integrated intensity. [b] SCF/6–31 G*, unscaled. [c] 1-d_1, 765 cm^{-1}. [d] 1-d_1, 1849 cm^{-1}.

308- or 351-nm light, is the diazirine 4, and that the other is the bridgehead olefin 1.



Supporting evidence for the presence of structures 1, 2, and 5 in the matrix was provided by two different warm-up trapping experiments: (i) self-trapping of the photoproducts and (ii) trapping in a matrix containing 10% furan in Ar. In both cases, mixtures of products were formed and were analyzed on a capillary column by GC-MS. The self-trapping produced dimers, one of which was a major product (m/z = 244, ordinary, and 246, deuterated), traces of a stable isomer (m/z at 122 or 123), and products with m/z at 272 (or 274), corresponding to the adducts of the olefin 1 or carbene 5 to the diazo precursor 2, or possibly to the diazirine 4.

The relative abundance of the m/z 122 species increased when the matrices were warmed up and analyzed only after prolonged matrix irradiation at 248 nm, and it is likely that this is a photorearrangement product from 1.

One of the adducts with the m/z 272 (or 274) parent ion was identified to be the azine 6 which was independently observed when a mixture of hydrazine and bicyclo[2.2.2]octane-1-carboxaldehyde was injected into the GC mass spectrometer at 150 °C. Under matrix isolation conditions, 6 could originate from an addition of 2 to 5. Furan trapping carried out with deuteriated starting diazo compound obtained from **3-*d*₁** again yielded the secondary stable isomer, a furan adduct (m/z 191), the azine 6, and traces of dimers. The fragmentation pattern of the furan adduct (base ion m/z 109, next intense ion at m/z 82) suggests that its structure is not derived from the olefin 1 but from the carbene 5.

In order to find out more about the role of carbene 5 in the reaction, an experiment was conducted with 2 in a $^{15}N_2$/Ar (1:1) matrix. After the initial irradiation at 514 nm, a small peak due to the ^{15}N labeled C═N═N stretch (1993 cm^{-1} in ordinary and 1991 cm^{-1} in monodeuteriated compounds) was observed. Matrix annealing at 35 K did not affect the intensity of this peak substantially. Further irradiation at 308, 351, or 514 nm caused only a very small increase in the intensity of the ^{15}N labeled C═N═N stretching band. This indicates that the carbene 5 is formed only as a minor product. We were not able to detect any vibrations that could be safely assigned to it.

Cold Fluid Solution. Prompted by the relative stability of 1 reported earlier,[4] solution NMR, IR, and UV experiments were carried out, in order to obtain additional evidence for the assignment of the second product as 1.

The bicyclo[2.2.2]oct-1-yldiazomethane (2) was prepared by flash vacuum pyrolysis at 100 °C and trapped into degassed $CFCl_3$. Subsequently, the sample was cooled to about −110 °C in an ethanol–liquid nitrogen slurry and irradiated simultaneously with laser light at 514 and 308 nm. The resulting mixture was sufficiently stable at −90 °C to measure spectra. Initial attempts suggested that unless the diazo compound 2 and the diazirine 4 are first destroyed to a large extent, 1 does not survive very long. Most probably it reacts with one or both of 2 and 4 even at −90 °C. In the absence of large amounts of 2 and 4, the stability of 1 was adequate for spectral measurements.

^{1}H NMR in $CFCl_3$ at −90 °C showed two peaks in the low-field region, corresponding to the three-membered ring proton of the diazirine 4 (δ 6.5 ppm) and to the vinyl proton of the olefin 1: a doublet of doublets at δ 5.52 ppm, with coupling constants of 10.5 and 4.5 Hz. This is in excellent agreement with one of the two vinyl proton signals reported[4] for a mixture containing 1 (δ 5.44, J_{HH} = 10.5 and 4.8 Hz). From the coupled and decoupled ^{13}C NMR spectra, one can immediately assign C1 (s) at 144.7 and C2 (d) at 129.1 ppm (J_{CH} = 157 Hz). Thus, under these conditions, a bridgehead olefin is clearly observed. The NMR peaks disappear after warming to −70 °C for 30 min.

IR measurements performed under similar conditions (−100 °C) in $CFCl_3$ solution at different intervals of simultaneous irradiation at 514 and 308 nm revealed the appearance of a strong peak at 1586 cm^{-1} and a weak peak at 1608 cm^{-1}. As the photolysis proceeded, the peak at 1586 cm^{-1} disappeared and the peak at 1608 cm^{-1} grew. In a similar fashion, in the UV absorption spectrum a band due to the diazirine and a band at λ_{max} = 276 nm appeared upon irradiation but the former then gradually disappeared so that only the latter was observed at the end of the photolysis. Thus, the results of the low-temperature solution NMR, IR, and UV experiments correlate very well with the matrix experiments and show that the same species are being observed by all three types of spectroscopy. The correlation with the previously known[4] ^{1}H NMR spectrum supports the assignment of structure 1 to the second photoproduct.

Discussion

Structural Identification. We believe that the results presented above leave no doubt about the identity of the carrier of the observed spectra and consider the structure 1 secured. The exact geometry is not known. The three particularly interesting structural characteristics are the double bond torsion angle θ, the bridgehead pyramidalization angle ω, and the methine pyramidalization angle ω'. The values obtained in our calculations are (in degrees using the definitions of ref 3; SCF/6-31G* followed by MNDO in parentheses): 33.4(37), 10.8(10), 9.5(6).

Spectral Properties. The ^{13}C NMR chemical shifts of the doubly bonded carbons are quite unexceptional. The δ values of 144.7 for the bridgehead carbon and 129.1 for the methine carbon can be compared with the values of 135.7 and 139.7 for the two inequivalent carbons in *trans*-cycloheptene.[20] The J_{CH} coupling constant for the vinyl proton, 157 Hz, is very similar to the 158 Hz value in *trans*-cycloheptene.[20] The inequivalence of the two allylic hydrogens, with dihedral angles relative to the vinylic hydrogen close to 0° (J_{HH} = 10.5 Hz) and close to 120° (J_{HH} = 4.5 Hz), clearly shows that the double bond is not twisted to orthogonality (to C_s symmetry) and that 1 is chiral. Unfortunately, the limited thermal stability of our solutions did not permit us to observe the coalescence of the allylic proton signals into a triplet, from which the barrier to racemization and thus the strength of the twisted π bond could have been determined. The magnitudes of the coupling constants are nearly identical to those reported for the analogous hydrogens in *trans*-cycloheptene,[21] 10.2 and 5.7 Hz, suggesting very similar conformations in 1 and in the monocyclic species.

Vibrational spectra provide a sensitive probe of the distortion to which the double bond in 1 is subjected. The C=C stretching frequency of 1608 cm^{-1} lies about 70 cm^{-1} below the value of 1675 cm^{-1} characteristic of undistorted trialkylethylenes, and thus is a little higher than expected from the general rule,[3] which predicts a shift to lower frequencies of about 100 cm^{-1} for *trans*-cycloheptenes and of about 200 cm^{-1} for *trans*-cyclohexenes. It appears that the less rigid structure of 1 relative to cage structures such as protoadamant-3-ene[3] (C=C stretch at 1587 cm^{-1}) permits the double bond to be somewhat less strained.

The UV absorption band of 1, peaking at 276 nm, lies at somewhat longer wavelengths than reported[21] for *trans*-cycloheptene, ~240 nm (cf. protoadamant-3-ene,[3] ~250 nm) and at noticeably shorter wavelengths than that of the polycyclic *trans*-cyclohexene, adamantene (~310 nm).[3]

Reactivity. With regard to its chemical reactivity, bicyclo[3.2.2]non-1-ene (1) again appears to be a typical member of the *trans*-cycloheptene family. Like parent *trans*-cycloheptene itself,[20,21] it is reasonably stable in fluid solution at dry ice temperatures and is amenable to NMR measurements. It does not dimerize nearly as readily as the members of the *trans*-cyclohexene family, for instance, adamantene.[22]

The same pattern of behavior is observed in Diels–Alder reactivity. While 1 apparently does not give a 2 + 4 adduct to furan at low temperatures, bicyclo[2.2.1]hept-1-ene does,[23] and adamantene adds to 2,4-dimethylfuran with extraordinary ease.[24] These reactivity differences reflect the calculated olefinic strain energies.[25] The value for 1 is quite moderate, 19.5 kcal/mol, whereas those for bicyclo[2.2.1]hept-1-ene (34.9 kcal/mol) and adamantene (39.5 kcal/mol) are high. Still, membership in the *trans*-cycloheptene family endows 1 with considerable reactivity relative to the next higher set of homologues, the *trans*-cyclooctenes. This is reflected in its ready low-temperature reaction with the diazomethane 2 (or, less likely, diazirine 4) and in the formation of complex mixtures upon warming up to room temperature. Now that a fairly thorough spectral characterization of 1 has been accomplished, a more detailed study of its reactions appears warranted.

Experimental Section

Matrix Isolation. The argon deposition rate was 1 torr/min. The CsI window was mounted on an Air Products Displex closed-cycle helium cryostat at 29 K. For photochemical work and spectroscopic measurements, samples were cooled to 12 K. Irradiations were conducted using a tunable argon-ion laser operating either at 488 or 514 nm, and an excimer laser providing

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light at 308 nm (XeCl) or at 351 nm (XeF). GC-MS spectra were obtained on a Hewlett-Packard HP-5000 instrument. Infrared absorption spectra were measured on a Nicolet 60-SXR FTIR instrument with 1 cm^{-1} resolution. UV spectra were measured on a Varian 2300 spectrometer. After the warm-up, the products were trapped in liquid N_2-cooled trap under vacuum.

Solution NMR, UV, and IR Spectroscopy. NMR spectra were measured on a GE 500-MHz instrument at −90 °C. For NMR spectroscopy, a solution of **2** in $CFCl_3$ (1.5% $CDCl_3$) in a degassed, sealed quartz tube was irradiated simultaneously at 514 nm (5 W, defocused) and 308 nm (0.5 W). After 3 h of irradiation, the contents were transferred into a 5-mm NMR tube which had been connected to the quartz tube as a side arm. The reaction mixtures were always kept at −100 °C or below. The NMR tube was sealed and disconnected from the quartz tube for further measurements. For IR and UV measurements in $CFCl_3$ at −100 °C, a homemade cell was used. It consisted of an O-ring sandwiched between two CsI windows and mounted in the cryostat window holder. A degassed solution of **2** in $CFCl_3$ was introduced into the cell through a syringe. The cryostat was evacuated to $\sim 10^{-5}$ torr and cooled to −100 °C. Temperature fluctuations throughout the experiment were not larger than 5°. Irradiation was conducted in the same manner as in the NMR experiments, and IR and UV spectra were recorded periodically.

Synthesis. Boiling points are uncorrected. Melting points were determined on a Boetius PHMK05 apparatus with microscope attachment (4 °C/min). NMR spectra were run on a Nicolet NT-360 in $CDCl_3$ unless specified otherwise. Mass spectra were taken on a GC-MS HP 5995 instrument. High resolution and chemical ionization mass spectra were measured on a VG ZAB-2E spectrometer. Elemental analysis was performed by Atlantic Microlabs, Norcross, GA.

Bicyclo[2.2.2]octane-1-carboxaldehyde Tosylhydrazone[7] (3). A solution of bicyclo[2.2.2]octane-1-carboxylic acid (**7**, 3.08 g, 20 mmol) in ether (20 mL) was added dropwise to a stirred suspension of lithium aluminum hydride (0.90 g) in dry ether (20 mL). The mixture was refluxed for 2 h and then was quenched by careful addition of ether (30 mL) saturated with water, followed by water (3.5 mL), 15% sodium hydroxide (3.5 mL), and water (11 mL). The ethereal solution was decanted, inorganic salts were washed twice with ether, and combined organic fractions were dried (Na_2SO_4). The solvent was evaporated, the resulting crude alcohol was dissolved in methylene chloride (10 mL), and the solution was added at once to a stirred suspension of pyridinium fluorochromate[9] (6.0 g) in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature until the starting alcohol was no longer observable by GC. Ether (20 mL) was added to the resulting dark reaction mixture, which was then passed through a short silica gel column, which was eluted with ether. The colorless eluent was carefully evaporated, and the residual crude aldehyde was dissolved in methanol (15 mL) and added to *p*-toluenesulfonyl hydrazide (3.0 g, 16 mmol) dissolved in methanol (10 mL) containing 4 drops of acetic acid. The mixture was refluxed for 1 h, and then water (10 mL) and pentane (5 mL) were added. The mixture was kept in a freezer overnight. Crystallized material was filtered off and recrystallized from aqueous ethanol to give 3.50 g (57% yield based on **8**) of the product: mp 148–149 °C (lit.[7] mp 142–143 °C); ^{1}H NMR (benzene-d_6) δ 1.33 (s, 13H), 1.86 (s, 3H), 6.70 (s, 1H), 6.50 (d, J = 8.1 Hz, 2H), 8.05 (d, J = 8.1 Hz, 2H) 8.24 (br s, 1H); ^{13}C NMR (benzene-d_6) δ 21.12, 24.77, 25.65, 28.94, 34.79, 128.47, 129.52, 136.76, 143.52, 158.63; EIMS, *m/z* (rel inten) 306(2), 151(58), 93(100), 91(37), 80(38), 79(62); HRMS, *m/z* (calcd for $C_{16}H_{22}N_2O_2S$: 306.1402) 306.1395, (calcd for $C_9H_{15}N_2$: 151.1235) 151.1236. Anal. Calcd for $C_{16}H_{22}N_2O_2S$: C, 62.72; H, 7.24; N, 9.14; S, 10.46. Found: C, 62.82; H, 7.26; N, 9.09; S, 10.38.

Bicyclo[2.2.2]octane-1-carboxaldehyde-*d* Tosylhydrazone (3-*d*$_1$). The compound was prepared the same way as described above for **3**: HRMS, *m/z* (calcd for $C_{16}H_{21}DN_2O_2S$: 307.1465) 307.1460.

Lithium Salt of Tosylhydrazone of 3. A solution of tosylhydrazone **3** (2 mmol) in dry THF (15 mL) was cooled down in a dry ice–acetone bath, and butyllithium in hexanes (2.5 M, 0.80 mL) was slowly added. The reaction mixture was kept at −78 °C for 30 min and then at room temperature for 30 min, and the solvent was removed under vacuum. The residual white powder was further dried under high vacuum at 30–40 °C giving pure, dry lithium salt of the tosylhydrazone of **3**.

Bicyclo[2.2.2]octane-1-carboxylic Acid[8] (7). Bicyclo[2.2.1]heptane-1-carboxylic acid (**9**, 8.40 g, 60 mmol) was dissolved in anhydrous ether (90 mL) and added dropwise to a solution of lithium aluminum hydride (LAH, 2.80 g, 73 mmol) dissolved in dry ether (100 mL). After 2.5 h of additional stirring and reflux, excess LAH was carefully decomposed by addition of ether saturated with water (100 mL) and then water (11 mL), 15% aqueous sodium hydroxide (11 mL), and finally water (32 mL). The gray suspension of the inorganic salts was filtered through Celite and washed with ether, and the filtrate was dried (Na_2SO_4). The solvent was evaporated to leave 7.7 g of the crude carbinol **14**. The alcohol **14** was dissolved in 90% formic acid (13 mL) and added dropwise to a well-stirred mixture of fuming sulfuric acid (15–17% of SO_3, 20 mL), 96% sulfuric acid (35 mL), and 90% formic acid (1 mL), at such a rate that the temperature was maintained at 15–20 °C. After the addition was completed, the reaction mixture was stirred at 20 °C for 2 h and then poured into ice (250 g). The resulting mixture was extracted with methylene chloride, the extract was washed twice with 5% sodium hydroxide, the aqueous phase was acidified with hydrochloric acid, and the crude product was extracted with methylene chloride. The extract was dried (Na_2SO_4), solvent was evaporated, and a white, crystalline residue was sublimed (105 °C/0.25 mmHg) giving 8.00 g of acid **7** which melted at 131–137 °C. Recrystallization from heptane gave 7.52 g of pure acid (81% yield based on **9**): mp 139.5–140 °C (lit.[8] mp 140.8–141.3 °C); ^{1}H NMR δ 1.55–1.65 (m, 7H), 1.72–1.79 (m, 6H), 11–12 (br s, 1H); EIMS, *m/z* (rel inten) 154(47), 125(55), 109(66), 81(32), 79(37), 67(100).

Bicyclo[2.2.2]octane-1-carboxylic-2,2-*d*$_2$ Acid (7-*d*$_2$). The deuterated acid was prepared in 80% overall yield according to the above procedure, by using lithium aluminum deuteride instead of lithium aluminum hydride: mp 140–41 °C; ^{1}H NMR δ 1.54–1.65 (m, 7H), 1.72–1.77 (m, 4H), 11–12 (br s, 1H); ^{13}C NMR δ 23.73, 25.08, 25.31, 27.15 (p, J = 20 Hz), 27.84, 38.01, 184.95; EIMS, *m/z* (rel inten) 156(38), 127(48), 125(26), 111(100), 81(28), 69(49), 68(60), 67(34); HRMS, *m/z* (calcd for $C_9H_{12}D_2O_2$: 156.1119) 156.1123. Anal. Calcd for $C_9H_{12}D_2O_2$: C, 69.19; H + D, 9.03. Found: C, 69.26, H, 9.07.

***exo*-2-Bromobicyclo[2.2.1]hexane-1-carboxylic Acid[10] (8a).** Potassium permanganate (200 g) was slowly added over a period of 4 h to a well-stirred mixture of *exo,endo*-norbornane-2-methanols (**11**, 63 g, 0.50 mol) and sodium carbonate (20 g) in water (1500 mL) at a temperature of 5–8 °C. The reaction mixture was stirred at room temperature overnight. Manganese dioxide was filtered off, and the aqueous solution was extracted with methylene chloride and acidified with hydrochloric acid. The liberated acids were extracted with methylene chloride and dried (Na_2SO_4), and the solvent was evaporated leaving 35.5 g (51% yield)[26] of an oily mixture of *endo*- and *exo*-norbornane-2-carboxylic acids (**12**). A mixture of the acids **12** (54 g, 0.38 mol), bromine (22 mL, 0.43 mol), and red phosphorus (0.3 g) was stirred at 70–80 °C for 10 h. Bromine (12 mL, 0.23 mol) was added and the stirring was continued overnight. Heptane (100 mL) was added, and the precipitated products were recrystallized from toluene giving 29.0 g (35% yield based on acids **12**) of white crystals: mp 148 – 151 °C (lit.[10] mp 150–151 °C).

Methyl *exo*-2-Bromobicyclo[2.2.1]heptane-1-carboxylate[27] (8b). *exo*-2-Bromobicyclo[2.2.1]heptane-1-carboxylic acid (**8a**, 28.5 g, 0.13 mol, mp 149–151 °C) and thionyl chloride (30 mL) were refluxed for 2 h. Excess thionyl chloride was evaporated and the white crystalline residue was dissolved in dry methanol (30 mL) and refluxed for 1 h. The solvent was evaporated and the residual oil was distilled on Kugelrohr (85 °C/0.3 mmHg; lit.[27] bp 108–110 °C/4.8 mmHg) to yield 29.2 g of colorless oil (96.5% yield): ^{1}H NMR (benzene-d_6) δ 0.71 (br s, 1H), 1.12–1.32 (m, 2H), 1.45–1.49 (m, 1H), 1.58–1.72 (m, 2H), 1.77 (br s, 1H), 1.97–2.17 (m, 2H), 3.45 (s, 3H), 3.94–3.98 (m, 1H); ^{13}C NMR (benzene-d_6) 29.16, 32.34, 36.78, 37.39, 43.97, 51.28, 54.21, 59.33, 172.59; EIMS, *m/z* (rel inten) 203(1), 201(1), 153(48), 121(9), 93(42), 91(21), 87(100), 59(22).

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(26) Jones oxidation of the alcohols yielded 47% of the mixture of the acids.

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Bicyclo[2.2.1]heptane-1-carboxylic Acid[13] (9). A solution of sodium borohydride (6.0 g, 0.158 mol) in ethanol (150 mL) was carefully added to a solution of the bromo ester **8b** (29.2 g, 0.125 mol) and trimethyltin chloride (2.5 g, 0.0125 mol) in anhydrous, deoxygenated ethanol (500 mL). The mixture was magnetically stirred at a temperature below 15 °C, and irradiated with a medium pressure mercury lamp until no more gas was evolved (3 h). Acetone (15 mL) was added to the resulting milky reaction mixture, and after 15 min 25% sodium hydroxide (120 mL) was added and stirred overnight. The reaction mixture was evaporated to dryness and the white solid residue was dissolved in warm water (400 mL). The resulting solution was extracted with choroform, acidified with hydrochloric acid, and the product was extracted with chloroform (4X50 mL). Combined organic extracts were dried (Na_2SO_4), the solvent was evaporated and the crystalline residue was sublimed (90 °C/0.25 mm Hg) yielding 16.8 g (96% yield) of a white crystalline product: mp 111–112 °C (lit.[13] mp 113.8–115.5 °C); ^{1}H NMR δ 1.30–1.38 (m, 2H), 1.52–1.59 (m, 2H), 1.60 (br s, 2H), 1.65–1.75 (m, 2H) 1.88–1.97 (m, 2H), 2.31–2.35 (m, 1H), 11.0–12.0 (br s, 1H); ^{13}C NMR δ 29.98, 32.96, 37.83, 42.37, 52.08, 183.30.

2-Ketobicyclo[2.2.1]heptane-1-carboxylic Acid[28] (13). The mother liquor obtained from crystallization of the crude bromo acid **8a** was extracted with aqueous sodium bicarbonate and the extract was heated for 2 h. The solution was cooled to 5 °C and carefully acidified with concentrated hydrochloric acid to pH 2–3. The aqueous solution was extracted with hexanes, saturated with solid sodium chloride, and the product was extracted with ether (4×). Combined extracts were dried (Na_2SO_4), and the solvent was evaporated, yielding 25.9 g of crude oily 2-hydroxynorbornane-1-carboxylic acid (43% yield based on the mixture of the acids **12**). The crude product was dissolved in diethyl ether (100 mL) and Jones reagent prepared from sodium dichromate (31.5 g), sulfuric acid (23.8 mL), and water (160 mL), was slowly added at a temperature below 15 °C and stirred overnight. The organic phase was separated, and the aqueous solution was saturated with NaCl and extracted with ether. Combined organic extracts were extracted with sodium bicarbonate, and the resulting aqueous solution was acidified with hydrochloric acid to pH 2–3. The solvent was evaporated, leaving 12.4 g of crude product. The keto acid solution was saturated with NaCl, extracted with ether (4×), dried (Na_2SO_4), and then sublimed (105 °C/0.2 mmHg) and recrystallized from hexanes to yield 8.0 g (13% overall yield based on starting acids **12**) of white crystals: mp 126–128 °C (lit.[27] mp 128.0–128.5 °C); ^{1}H NMR δ 1.48–1.57 (m, 1H), 1.74–1.83 (m, 1H), 1.90–2.16 (m, 5H), 2.24–2.33 (m, 1H), 2.67 (br s, 1H), 11.34 (br s, 1H); ^{13}C NMR δ 27.56, 27.85, 34.24, 40.98, 44.96, 62.71, 175.13, 211.74.

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