

4,4-Dimethylbicyclo[3.1.0]hexa-1(6),2-diene— A Highly Strained 1,3-Bridged Cyclopropene

Reinhard Albers, Wolfram Sander,* Carl-Henrik Ottosson, and Dieter Cremer*

Dedicated to Professor Rolf Gleiter on the occasion of his 60th birthday

Abstract: The photochemical rearrangement of 4,4-dimethylcyclohexa-2,5-dienylidene (**3**) to 4,4-dimethylbicyclo[3.1.0]hexa-1(6),2-diene (**5**) was investigated by means of the matrix isolation technique. Carbene **3** was generated in argon matrices at 10 K by photolysis of the corresponding diazo compound ($\lambda > 550$ nm) and was characterized by IR and UV/Vis spectroscopy and its characteristic thermal reaction with triplet oxygen. Long-wavelength irradiation

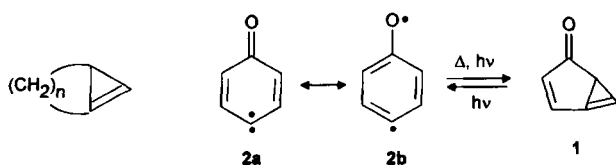
($\lambda > 515$ nm) induced an irreversible rearrangement of carbene **3** to the highly strained cyclopropene **5**. This is in contrast to the previously investigated 1*H*-bicyclo[3.1.0]hexa-3,5-dien-2-one (**1**), which is thermally labile even at 10 K and

rearranges back to 4-oxo-2,5-cyclohexadienylidene. The experimental findings were confirmed by ab initio calculations at the MP2/6-31 G(d) level. MP2 and experimental IR frequencies are in good agreement. The strain energies of **5** and **1** are 75 and 78 kcal mol⁻¹, more than 20 kcal mol⁻¹ larger than that of cyclopropene. The somewhat greater stability of **5** than **1** is a consequence of better π delocalization in the diene unit of the bicyclic system.

Keywords: ab initio calculations · carbenes · cyclopropenes · matrix isolation · rearrangements

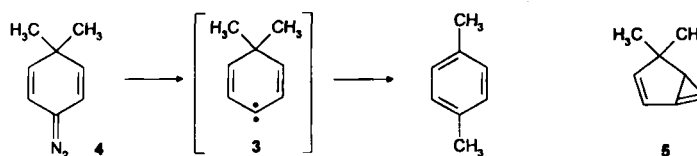
Introduction

1,3-Bridged cyclopropenes are highly labile if the number *n* of carbon atoms in the bridge is smaller than 6.^{11–41} Thus 1*H*-bicyclo[3.1.0]hexa-3,5-dien-2-one (**1**)¹³ and several of its derivatives have been shown to thermally rearrange to 4-oxocyclohexa-2,5-dienylidenes **2** even at temperatures as low as 10 K. This clearly demonstrates that carbene **2** is thermodynamically more stable



than cyclopropene **1**. This experimental finding was confirmed recently by extensive ab initio calculations by Olivella et al.¹⁵ At the CASPT2 + ZPE level of theory, triplet **2** is predicted to be 19.1 kcal mol⁻¹ below **1**. The question arises whether triplet cyclohexadienylidenes are generally more stable than the corresponding bicyclo[3.1.0]hexadienes. We therefore investigated

the chemistry of 4,4-dimethylcyclohexa-2,5-dienylidene **3** by the matrix isolation technique. Addition reactions and rearrangements in the gas phase of **3** were reported by Jones et al.^{16, 71}



These authors demonstrated by ESR spectroscopy that the ground state of **3** is triplet; however, addition reactions to olefins were mainly stereospecific, which implies that the singlet carbene is trapped in solution.¹⁶ Pyrolysis in the gas phase at 380 °C resulted in the formation of a mixture of *p*-xylene and toluene as the major products.⁷¹ The formation of free radicals and the intermolecular transfer of the methyl group was demonstrated by crossover experiments. No hint of the formation of the bicyclic intermediate **5** was obtained from these experiments.

Results and Discussion

Diazo-4,4-dimethylcyclohexa-2,5-diene (**4**) was synthesized by the procedure of Jones et al.¹⁶ by warming the sodium salt of 4,4-dimethylcyclohexadienone tosylhydrazone to 95 °C and trapping **4** at –78 °C. The diazo compound **4** was slowly deposited with a large excess of argon on top of a cold window at

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30 K. The IR spectrum of **4** exhibits a very strong absorption at 2054 cm^{-1} , assigned to $\nu(\text{N}=\text{N})$ of the diazo group. Deuteration at C(3) and C(5) resulted in a small red shift of 7 cm^{-1} . Other characteristic absorptions are the asymmetric and symmetric C=C stretching vibrations at 1647 cm^{-1} ($[\text{D}_2]\mathbf{4}$: -19 cm^{-1}) and 1594 cm^{-1} ($[\text{D}_2]\mathbf{4}$: -12 cm^{-1}), respectively. In the UV/Vis spectrum **4** exhibits an intense absorption with $\lambda_{\text{max}} = 285\text{ nm}$ and a very weak absorption with $\lambda_{\text{max}} = 580\text{ nm}$.

Irradiation into the long-wavelength absorption of matrix-isolated **4** (argon, 10 K, $\lambda > 550\text{ nm}$) led exclusively to a new compound with an intense IR absorption at 733 cm^{-1} (Table 1)

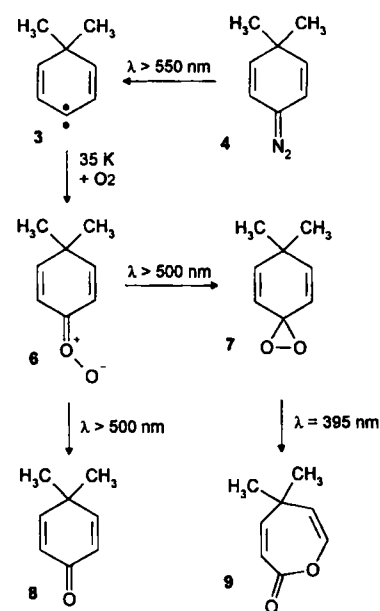
Table 1. IR Spectroscopic data of carbene **3** isolated in an argon matrix at 10 K.

$\tilde{\nu}$ (cm^{-1})	I_{rel} [a]	d_i [b]	polarization [c]
3043	1	1.23	Z
3032	1	—	—
2991	3	—	—
2973	3	1.16	Z
2943	4	—	—
2919	4	—	—
2901	3	—	—
2863	4	—	—
1510	8	0.88	X;Y
1471	12	—	—
1454	3	—	—
1439	3	—	—
1401	4	—	—
1367	10	0.90	X;Y
1353	11	0.85	X;Y
1227	4	0.95	X;Y
1149	5	0.95	X;Y
1108	11	—	—
952	12	0.83	X;Y
905	5	—	—
733	100	1.15	Z
698	2	—	—
668	1	—	—
614	3	—	—
563	2	—	—

[a] Relative intensities. [b] Dichroic ratios I_z/I_y . [c] Polarization direction determined after irradiation with Z-polarized light.

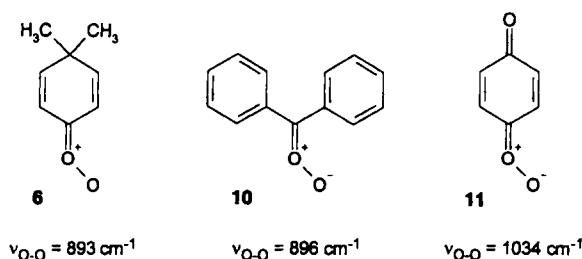
and a structured UV absorption in the range 270–307 nm. The new compound was assigned to carbene **3** on the basis of an oxygen trapping experiment. Flash vacuum pyrolysis of **4** at 650°C with subsequent trapping of the products in argon at 10 K resulted in the formation of toluene as the major product. Other products were methane (1304 cm^{-1}), methyl radicals (617 cm^{-1}),^[8,9] and an unknown product with IR absorptions at 1282, 1351, and 1355 cm^{-1} . Xylene was not formed under these reaction conditions, which confirms the conclusion of Jones et al.^[6,7] that xylene is the product of intermolecular reactions.

Oxygen trapping of carbene 3: The thermal reaction in oxygen-doped matrices to give carbonyl *O*-oxides is highly characteristic of triplet carbenes.^[10] Annealing of a 2% O_2 -doped argon matrix containing carbene **3** at 45 K rapidly resulted in a yellow coloring of the matrix caused by the strong visible absorption ($\lambda_{\text{max}} = 444\text{ nm}$) of 4,4-dimethyl-2,5-cyclohexadienone *O*-oxide **6** (Scheme 1). In the IR, the most intense absorption of **6** at 893 cm^{-1} is assigned to the O–O stretch, which exhibits a red shift of 37.5 cm^{-1} if $^{18}\text{O}_2$ is used for the oxygenation of **3**. In benzophenone *O*-oxide **10** the O–O stretching vibration is observed at 896 cm^{-1} ,^[11] very close to that of **6**, while in *p*-benzoquinone oxide **11** it is blue-shifted to 1034 cm^{-1} .^[12,13] This is in



Scheme 1. Formation of carbene **3** and thermal reaction with oxygen.

line with the observation that π acceptors stabilize the O–O bond in carbonyl oxides and thus lead to a blue shift of the O–O stretching vibration.^[13]



The carbonyl oxide is highly photolabile, and irradiation with $\lambda > 500\text{ nm}$ for several minutes results in the formation of 6,6-dimethyl-1,2-dioxaspiro[2.5]octa-4,7-diene (**7**) and 4,4-dimethyl-2,5-cyclohexadienone (**8**) (Fig. 1). Ketone **8** is formed as minor by-product only, with increasing yield at higher O_2 concentrations in the matrix ($> 1\%$). Dioxirane **7** was identified by its subsequent photochemistry and ketone **8** by comparison with authentic matrix-isolated material. In contrast to **6**, irradiation of **11** resulted exclusively in rearrangement to the corresponding

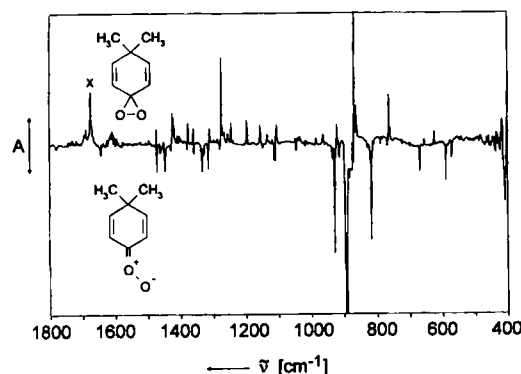


Fig. 1. IR difference spectrum showing the photolysis of matrix-isolated **6** (Ar/1% O_2 , 10 K). Bottom: bands disappearing, top: bands appearing on irradiation ($\lambda > 500\text{ nm}$). X: band assigned to water.

dioxirane, while *p*-benzoquinone was not formed.^{11,21} This suggests that the O–O bond in **6** is less strong than that in **11**.

Irradiation of **7** with $\lambda = 395$ nm resulted in the formation of a carbonyl compound with the most intense IR absorption at 1744 cm^{-1} , red-shifted by 37 cm^{-1} on ^{18}O labeling. Based on the observed IR spectrum and ^{18}O isotopic shifts, the new compound is tentatively assigned the structure of 5,5-dimethyl-5H-oxepin-2-one (**9**). Thus, the photochemistry of carbonyl oxide **6** is completely analogous to that of **11** and other similar carbonyl O-oxides.¹¹⁰

Photochemistry of carbene 3: Long-wavelength irradiation of carbene **3** ($\lambda > 515$ nm) in argon at 10 K resulted in the slow but complete disappearance of all IR absorptions assigned to **3** (Fig. 2). A new medium-intensity absorption appeared at

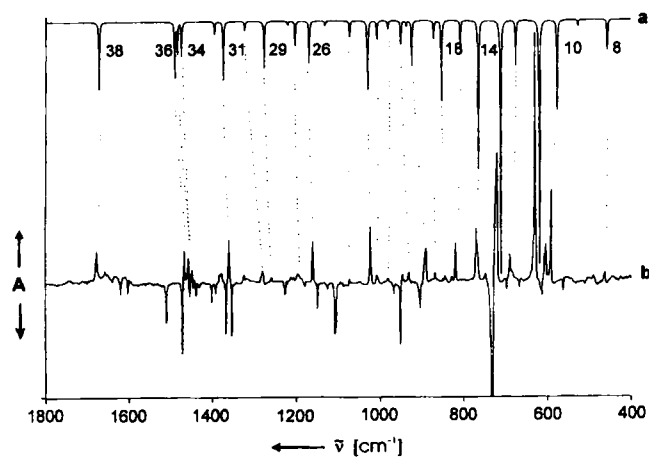
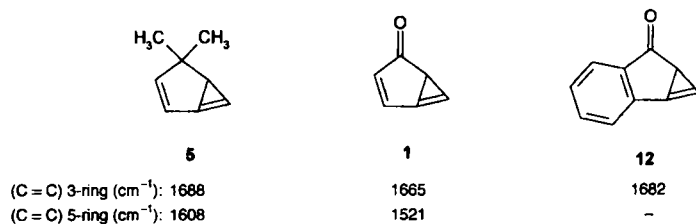


Fig. 2. IR difference spectrum showing the photolysis of matrix-isolated **3**. a) Ab initio calculated IR spectrum of **5** at MP2/6-31G(d). b) Bottom: bands disappearing, top: bands appearing on irradiation ($\lambda > 515$ nm).

1688 cm^{-1} , which is shifted to 1656 cm^{-1} on deuterium labeling of the 2- and 6-positions. Since a carbonyl vibration can be excluded, this absorption is assigned to a C=C stretching vibration in a strained cyclopropene. Similar band positions and deuterium shifts were described for other strained cyclopropenes such as **1**³¹ or **12**⁴¹ (Scheme 2). The newly formed compound is therefore assigned the structure of 4,4-dimethylbicyclo[3.1.0]hexa-1(6),2-diene **5** (Table 2).



Scheme 2. C=C stretching vibration in strained cyclopropenes **5**, **1**, and **12**.

The cyclopentene C=C stretching mode in **5** is observed as a weak absorption at 1608 cm^{-1} , very close to the C=C stretching mode in cyclopentene (1612 cm^{-1}), but compared with **1** blue-shifted by 87 cm^{-1} . Further confirmation of the assignment of **5** comes from the comparison of experimental and ab initio calculated IR spectra. At the MP2/6-31G(d) level of theory

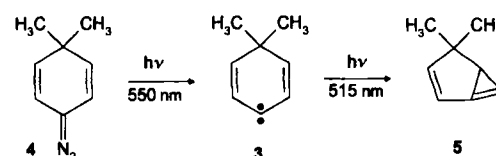
Table 2. IR Spectroscopic data observed for 4,4-dimethylbicyclo[3.1.0]hexadiene (**5**) isolated in an argon matrix at 10 K and calculated at MP2/6-31G(d).

No. [a]	Argon, 10 K				MP2/6-31 G(d)			Assignment [f]
	$\tilde{\nu}$ [cm^{-1}]	I_{rel} [b]	$\tilde{\nu}/\tilde{\nu}$ [c]	d_r [d]	$\tilde{\nu}$ [e]	I_{rel} [b]	$\tilde{\nu}/\tilde{\nu}$ [c]	
1					133	0		
2	–	–	–	–	214	0		
3	–	–	–	–	247	0		
4	–	–	–	–	277	1		
5	–	–	–	–	305	12		
6	–	–	–	–	320	4		
7	–	–	–	–	340	4		
8	462	11	0.966		456	11	0.972	
9	529	6	0.966		527	2	0.941	
10	592	40	0.929	0.61	577	35	0.934	
11	630	100	0.944	0.78	619	96	0.936	
12	690	51	0.903	0.84	675	17	0.904	
13	722	97	0.907	0.67	711	100	0.919	
14	771	24		1.17	764	58		
15	796	8			807	10		
16	820	17		1.09	852	31		
17					871	7		
18	918	14			923	17		
19	932	8		1.18	936	2		
20	947	5		1.24	949	9		
21	981	5			980	3		
22	1008	5		0.86	1006	7		
23	1024	24		1.12	1028	27		
24	1074	5			1071	6		
25	1129	6	0.981		1130	1	0.987	
26	1161	17	0.998		1168	16	0.997	
27	1216	10	0.977		1201	9	0.991	
28	–	–	–	–	1219	1	0.991	
29	1280	8	0.970	0.89	1275	18	0.973	
30	1324	6	0.986	0.94	1321	3	0.994	
31	1361	24	1.0	0.91	1372	23	1.0	
32	1377	8	1.002		1393	5	1.0	
33	–	–	–	–	1468	0	1.0	
34	1457	16	0.995	1.13	1472	13	1.0	
35	1467	21	0.999	1.41	1482	12	0.998	
36	1473	16	1.000		1488	22	1.0	
37	–	–	–	–	1508	0	0.989	C=C asym str.
38	1688	17	0.973	1.09	1671	26	0.974	C=C asym str.
39	2870	4	1.0		2933	61	1.0	CH str.
40	2904	14	1.0		2936	64	1.0	CH str.
41	2968	21	1.0		3000	89	1.0	CH str.
42	–	–	–	–	3018	38	1.0	CH str.
43	–	–	–	–	3020	65	1.0	CH str.
44	–	–	–	–	3026	67	1.0	CH str.
45	3036	2	1.0		3029	65	1.0	CH str.
46	–	–	–	–	3060	10	1.0	CH str.
47	3107	7	0.742		3115	32	0.741	CH str.
48	–	–	–	–	3123	12	0.749	CH str.

[a] Number of calculated vibrations. The assignment is based on band positions and relative intensities and is only tentative. [b] Relative intensities based on the most intense band (100). [c] Ratio of D/H isotopic frequencies. [d] Dichroic ratios. [e] Calculated frequencies (in cm^{-1}) are scaled by 0.95. [f] Approximate description.

calculated band positions, intensities, as well as deuterium shifts (3,5-dideuterated bicyclic species [D_2]**5**) are in good agreement with the experimental values (Table 2, Fig. 2).

The reaction sequence **4** \rightarrow **3** \rightarrow **5** could also be followed by UV/Vis spectroscopy (Fig. 3). Diazo compound **4** is characterized by a very intense absorption at 285 nm and a weak absorption with a maximum at 580 nm. 550 nm irradiation of **4** resulted in the formation of carbene **3** with a structured absorption at 288 nm. Subsequent irradiation with $\lambda = 515$ nm led to bicyclic



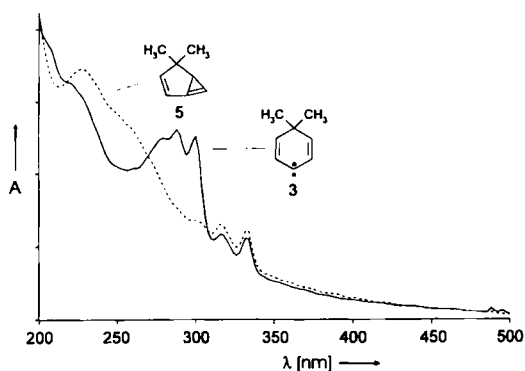
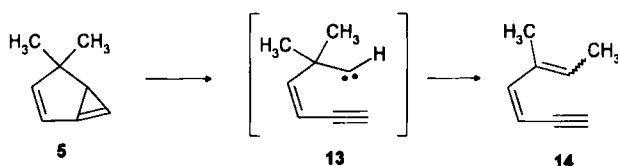


Fig. 3. UV spectra showing the photolysis of matrix-isolated 4,4-dimethyl-2,5-cyclohexadienylidene (**3**) ($\lambda > 515$ nm, argon, 10 K). Solid line: UV spectrum of **3**; dashed line: UV spectrum of 4,4-dimethylbicyclo[3.1.0]hexadiene (**5**).

system **5** with a broad absorption at 230 nm. This is in accordance with a CIS/6-31 G(d) calculation performed on the optimal MP2/6-31 G(d) geometry of **5**. According to this calculation, absorptions at 228 and 222 nm can be expected, which is in good agreement with the experimental results. The medium-intensity absorption in the visible part of the spectrum found in **1** is absent in **5**. In contrast to **1**, which is highly labile and rapidly rearranges both thermally and photochemically to 4-oxo-2,5-cyclohexadienylidene,^[3] bicyclic compound **5** was stable under the conditions of matrix isolation and visible light



irradiation. UV irradiation ($\lambda = 305$ nm) resulted in the decomposition of **5** and formation of a new compound with IR absorptions at 3330 and 2125 cm^{-1} , characteristic of a terminal alkyne group. Other medium to intense absorptions are found at 3064 (m), 3055 (m), 2939 (m), 833 (m), 540 (s), and 439 (s) cm^{-1} . Several isomeric structures with terminal alkyne groups have to be considered, and in analogy to **1**^[3] we propose the ring-opening of **5** to give diene **14**, presumably via carbene **13**. The experimental IR spectrum is in qualitative agreement with ab initio calculated spectra of several stereoisomers of **14**. However, since these spectra are similar in the fingerprint region, the stereochemistry of **14** could not be determined.

Structure and stability of 5: Partial photolysis (30–70%) of carbene **3** by linearly polarized light results in matrices containing partially oriented molecules of **3** and **5**. The degree of orientation could be obtained by measuring the infrared dichroism. This method was shown by Michl and Thulstrup to provide information on the symmetry of matrix-isolated species;^[14] details have been described elsewhere.^[3] The dichroic ratios of various IR bands of **3** and **5** are listed in Tables 1 and 2, respectively. Because the differences in the IR intensities are very small, the errors in the dichroic ratios d_i are large, and only a qualitative interpretation of the results can be given here. For carbene **3**, two classes of

values for d_i are observed: 1.19 ± 0.1 and 0.89 ± 0.1 . This means that the transition moments of all vibrations are oriented either parallel or perpendicular to the direction of the electric field vector E of the polarized light used in the photoselection. From that we conclude that the symmetry of the carbene is C_{2v} . For cyclopropene **5**, on the other hand, a broad distribution of dichroic ratios in the range 0.61 to 1.41 is observed, indicating—as expected—the lower symmetry of the bicyclic compound.

The MP2/6-31 G(d) geometry of **5** is compared with that of **1** in Figure 4. Although the two molecules possess similar geometries, there are several differences which can be directly related to differences in stability and electronic structure. Both **5** and **1** possess nonplanar five-membered rings, which are necessary to avoid a planar or inverted arrangement of bonds at C(1). Analysis of the puckering coordinates^[15–17] reveals that the five-membered ring of **5** adopts an almost perfect envelope form (pseudorotation phase angle: 5° ; ideal envelope: 0°) with atom C(1) at the apex of the envelope, thus guaranteeing that the largest torsional angle in the 5-membered ring is at bond C(5)–C(1) (-20.7°) to relieve strain caused by annelation with the three-membered ring. The puckering amplitude is 0.198 Å, which is about 25% smaller than the corresponding amplitude of 3,3-dimethylcyclopentene (0.262 Å; phase angle 1.6° at MP2/6-31 G(d), Fig. 4). For **1**, the five-membered ring adopts a more distorted envelope form (phase angle 8.1°), which is considerably less puckered (puckering amplitude: 0.111 Å).^[3] This is also reflected by the folding angle between the five- and the three-membered ring, which is 42° ($180 - 138^\circ$) for **5** and 50° ($180 - 130^\circ$, see Fig. 4) for **1**. Clearly, flattening of the ring in **1** is enforced by the sp^2 -hybridized C(2) atom of the keto group. This causes atoms C(1) and C(5) to adopt more of the character of an inverted C atom, thus destabilizing **1**.

As was mentioned in ref. [3], greater folding of the bicyclic molecule does not necessarily mean a reduction of π conjugation of the diene unit. Pyramidalization at C(5) and C(6) keeps tor-

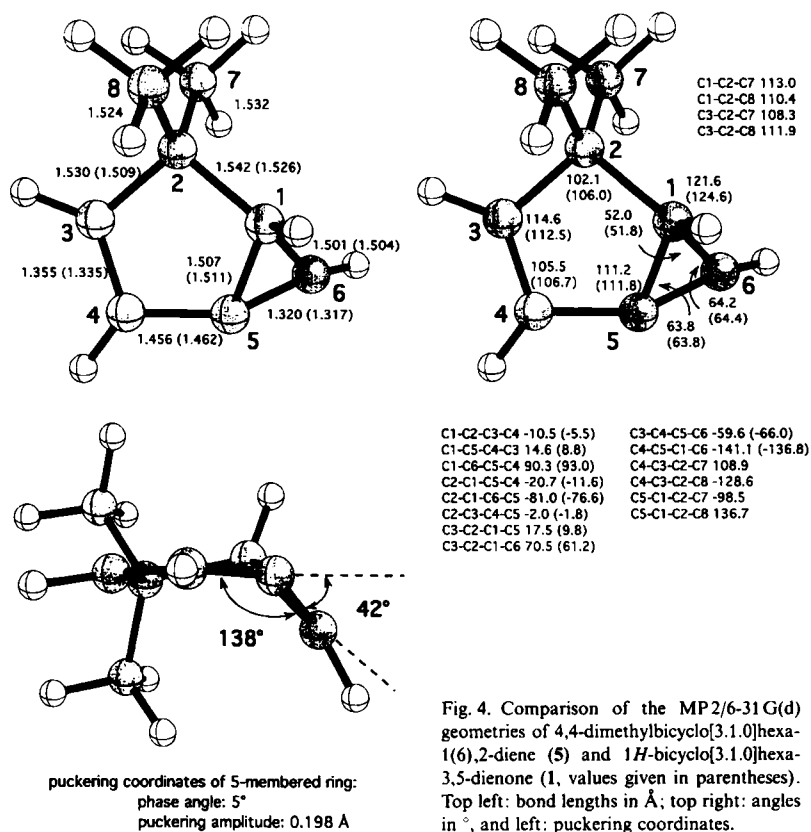


Fig. 4. Comparison of the MP2/6-31 G(d) geometries of 4,4-dimethylbicyclo[3.1.0]hexa-1(6),2-diene (**5**) and 1H-bicyclo[3.1.0]hexa-3,5-dienone (**1**, values given in parentheses). Top left: bond lengths in Å; top right: angles in $^\circ$; and left: puckering coordinates.

sion of the cyclopropene double bond small. If one assumes a POAV arrangement^[18] of the $2p\pi$ orbital at C(5) and C(6) (i.e., the $2p\pi$ orbital forms the same angle with the three bonds; see ref. [18]), then the $2p\pi$ orbitals in **5** are distorted by just 5.4° compared with 9.0° in **1**. Since puckering in the five-membered ring is larger for **5** than for **1**, lower torsion of the cyclopropene bond in **5** can only be obtained by more pyramidalization at C(5) and C(6), which is confirmed by the calculated pyramidalization angles^[18] for **5** (C(5): 22.4° ; C(6): 7.5°) than for **1** (C(5): 19.2° ; C(6): 5.5°).

The low torsion of the cyclopropene double bond is also reflected by the fact that the first excited triplet state of **5**, at 49 kcal mol^{-1} , is high above its singlet ground state (at fully spin-projected UMP2/6-31 G(d)). Since a strong distortion of the cyclopropene double bond would increase the biradical character of **5** and thereby decrease the energy difference between singlet and triplet state, a large singlet–triplet splitting confirms that the double bond in the three-membered ring is normal. Calculated C(5)–C(6) bond lengths of 1.320 and 1.317 Å for **5** and **1**^[3] (cyclopropene: 1.301 Å) are in line with this description.

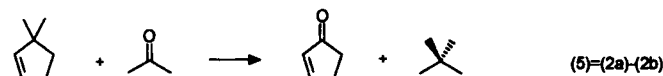
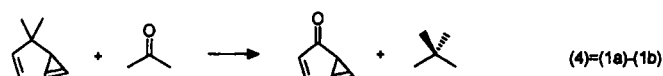
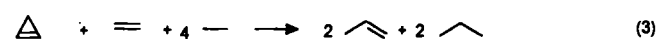
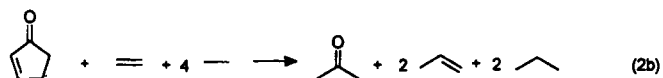
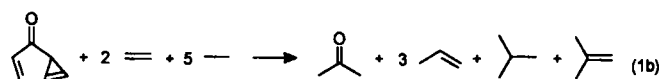
The strain in the bicyclic molecules **5** and **1** can be reduced by π delocalization within the diene unit. MP2/6-31 G(d) bond orders^[16, 19–22] of bonds C(3)–C(4), C(4)–C(5), and C(5)–C(6) for **5** (1.90, 1.19, 1.88) and **1** (1.94, 1.17, 1.94, see Table 3) confirm this and, in addition, show the increase in π delocalization when replacing the keto group (**1**) by a CMe_2 group (**5**). These trends should directly be reflected by the relative stabilities of **5** and **1**.

Table 3. MP2/6-31 G(d) bond orders n of 4,4-dimethylbicyclo[3.1.0]hexa-3,5-dien-2-one (**5**) and 1*H*-bicyclo[3.1.0]hexa-1(6)-2-diene (**1**) [a].

Bond	n [5]	n [1]
C(1)–C(2)	0.999	1.063
C(1)–C(5)	1.001	0.993
C(1)–C(6)	0.932	0.919
C(2)–C(3)	1.035	1.143
C(3)–C(4)	1.904	1.936
C(4)–C(5)	1.194	1.173
C(5)–C(6)	1.884	1.940
C(2)–C(7)	1.006	–
C(2)–C(8)	1.044	–
C(2)–O	–	1.833

[a] The bond order n [19–22] is given by the equation $n = \exp(a(\rho_b - b))$ where ρ_b is the electron density at the bond critical point and the two constants a and b have been determined from ρ_b (ethane) and ρ_b (ethene) at MP2/6-31 G(d) to be 1.075 and 1.657 e Å^{-3} .

Formal reactions (1)–(5) are used to evaluate the relative stabilities of **5** and **1** at the MP2/6-31 G(d) level of theory. The total strain energies of **5** and **1** as obtained from the homodesmotic reaction (1) are 74.7 and $77.6 \text{ kcal mol}^{-1}$,^[23] respectively; this clearly indicates that **5** and **1** are among the most strained bicyclic systems that have been experimentally observed.^[24] The total strain energy covers strain of the five- and three-membered rings as well as the annelation strain. According to reaction (2a), the ring strain energy of 3,3-dimethylcyclopentene is $2.0 \text{ kcal mol}^{-1}$ at MP2/6-31 G(d), while cyclopentenone (reaction 2b) possesses a ring strain energy of $-2.6 \text{ kcal mol}^{-1}$, that is, the molecule is stabilized in its equilibrium form. If one compares these values with the MP2/6-31 G(d) ring strain of cyclopentene ($2.4 \text{ kcal mol}^{-1}$), it becomes clear that cyclopentenone is stabilized by 5 kcal mol^{-1} by π delocalization in the enone unit and 3,3-dimethylcyclopentene



by just $0.4 \text{ kcal mol}^{-1}$, probably because of small hyperconjugative interactions of the two exocyclic C–C bonds with the double bond. The ring strain energy of cyclopropene was estimated to be between 53 and 55 kcal mol^{-1} .^[24, 25] From homodesmotic reaction (3) we calculate a value of $53.8 \text{ kcal mol}^{-1}$ at the MP2/6-31 G(d) level. From these values it becomes clear that the total strain energies of **5** and **1** are basically determined by the cyclopropene strain energy and some 20 to 25 kcal mol^{-1} of annelation strain (where the higher value applies to **1**, which is more destabilized by ring annelation than **5**). The ring annelation energy covers the distortion strain of the three- and five-membered rings caused by annelation and the π delocalization energy of the newly formed diene (**5**) and triene (**1**) units. Distortion of cyclopropene from its equilibrium geometry to the geometry it possesses in **5** and **1** costs 25.4 and $28.0 \text{ kcal mol}^{-1}$, respectively. The corresponding values for the five-membered rings are 6.5 and $6.8 \text{ kcal mol}^{-1}$. If one evaluates the ring annelation energy from the difference reaction (1) – (2) – (3) one obtains 18.9 (**5**) and $26.4 \text{ kcal mol}^{-1}$ (**1**), respectively. Comparing these values with the sum of distortion energies for three- and five-membered rings resulting from annelation (31.9 and $34.8 \text{ kcal mol}^{-1}$), a π delocalization energy of -13.0 and $-8.4 \text{ kcal mol}^{-1}$ can be estimated for **5** and **1**, respectively.^[26] The difference in the stabilities of **5** and **1** (reaction 4) is determined by this $4.6 \text{ kcal mol}^{-1}$ higher cyclopropene–cyclopentene π delocalization energy of **5** and enhanced by a $2.6 \text{ kcal mol}^{-1}$ smaller distortion energy of the cyclopropene unit of **5**. These stabilizing factors compensate for the lower stability of the five-membered ring in **5** ($4.6 \text{ kcal mol}^{-1}$ according to reaction 5) and lead to a $2.9 \text{ kcal mol}^{-1}$ higher overall stability of **5** [reaction (4)]. The stabilizing effect of π delocalization in **5** is reflected by the calculated bond lengths and bond orders, and results from the larger puckering in the five-membered ring, a smaller folding between the three- and five-membered rings, and a consequently smaller distortion of the $2p\pi$ orbitals as discussed above.

According to IR polarization measurements, the triplet carbene **3** has C_{2v} symmetry, which is in line with UMP2 calculations. Olivella and co-workers^[5] found that the triplet state of cyclohexa-2,5-dienylidene **2** is more stable than **1** by

19.1 kcal mol⁻¹, according to CASPT2/6-31 G(d) and CISD/6-31 G(d) calculations at CASSCF/6-31 G(d) geometries. It is easy to see that this energy difference decreases considerably (according to UMP2/6-31 G(d) energies by 11 to about 8 kcal mol⁻¹) for the isomers **3** and **5**, since **5** is more stable than **1**, and **3** less stable than **2**.

Carbene **2** is stabilized by π delocalization involving the keto group, thus forming an aromatic 6 π unit (resonance structure **2b**). The importance of resonance form **2b** can be assessed from the calculated bond lengths in the six-membered ring of **2** and **3** (Fig. 5) as well as from the calculated spin density distribution based on UMP2/6-31 G(d) response densities (Fig. 6). A spin density of 0.171 (Fig. 6) is obtained for the O atom, which is

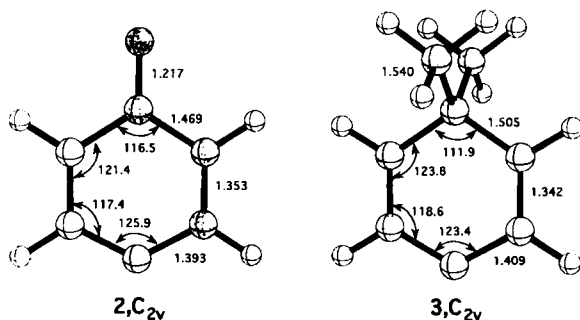


Fig. 5. UMP2/6-31 G(d) geometries of 4-oxocyclohexa-2,5-dienylidene (**2**) and 4,4-dimethylcyclohexa-2,5-dienylidene (**3**). Bond lengths in Å and angles in °.

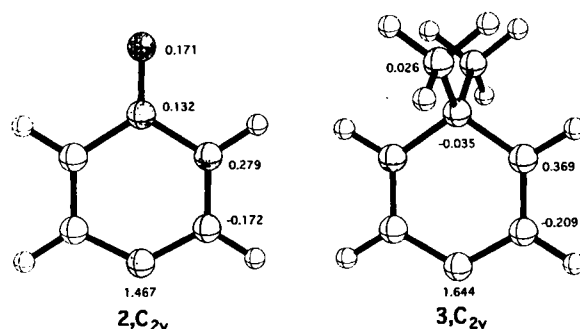


Fig. 6. UMP2/6-31 G(d) spin densities of 4-oxocyclohexa-2,5-dienylidene (**2**) and 4,4-dimethylcyclohexa-2,5-dienylidene (**3**).

similar to that calculated at the MCSCF/6-31 G(d) level (0.205).^[51] The spin density at the formal carbene center C(4) is lower in **2** (1.467 at UMP2/6-31 G(d); 1.390 at MCSCF/6-31 G(d)^[51]) than in **3** (1.644 at UMP2/6-31 G(d), Fig. 6), indicating a better delocalization of the unpaired π electron in the former carbene. The spin density at C(4) in **2** was estimated to be 1.4 from ESR data;^[127] this value is in reasonable agreement with the calculated spin densities.

Conclusions

1: Irradiation of diazomethane **4** in argon at 10 K produced triplet-ground-state carbene **3**, which was characterized by IR, UV/Vis spectroscopy and oxygen trapping. The carbene was photolabile and on 515 nm irradiation rearranged to the highly strained cyclopropene **5**. If the spin state is conserved during the ring-closure process, it is unlikely that the triplet ground state of carbene **3** (T-3) plays a role in this rearrangement. At 10–30 K the thermal energy is not sufficient to populate the singlet state, unless the singlet and triplet state are almost degenerate. Thus,

the most reasonable pathway is the photochemical formation of S-3 (via excited triplet states), which subsequently rearranges to **5**. Alternatively, the rearrangement might occur on the triplet surface, producing triplet **5** as the primary product of the ring-closure. However, this requires the rearrangement of excited triplet states of **3**, since the ground state of **3** is expected to lie energetically far below T-5.

2: In contrast to other similar carbene rearrangements^[31] the **3** → **5** rearrangement is irreversible under the conditions of low-temperature matrix isolation. This is in line with our theoretical results, which indicate that this rearrangement is still exothermic. However, the energy difference is reduced from 19 to 8 kcal mol⁻¹ compared with the reversible **2** → **1** rearrangement. Thus, the transition state is later and the activation barrier now obviously large enough to inhibit the back-reaction at cryogenic temperatures. At room temperature the **5** → **3** rearrangement is expected to be fast, which explains the lack of trapping products of **5** in earlier studies.^[6]

3: The calculated strain energy of **5** is 75 kcal mol⁻¹, which is 20 kcal mol⁻¹ larger than the strain of cyclopropene (53.8 kcal mol⁻¹ at MP2/6-31 G(d)). The additional strain results from distortion of the three- and five-membered rings (ca. 32 kcal mol⁻¹) by ring annelation, diminished by a π delocalization energy of 13 kcal mol⁻¹.^[26]

4: Despite a torsional angle of 60° at the formal single bond of the diene unit and of 90° at the cyclopropene double bond, the actual torsional angles between the 2 π orbitals of the diene unit are just 5 and 30°. The molecule avoids larger $p\pi$ – $p\pi$ torsional angles by significant pyramidalization at C(4) (2.6°), C(5) (22.4°), and C(6) (7.5°). In this way, biradical character is avoided and the molecule is stabilized by π delocalization in the diene unit.

5: The bicyclic molecule **1** is less stable than **5** by 2.9 kcal mol⁻¹, which is the result of three opposing stability factors: distortion of the cyclopropene unit in **1** owing to ring annelation is more destabilizing by 2.6 kcal mol⁻¹, while π delocalization in the acrolein unit leads to a relative energy gain of 4.6 kcal mol⁻¹. The cyclopropene/cyclopentene π delocalization is decisive; it is 4.6 kcal mol⁻¹ less stabilizing in the case of **1**.

Experimental Section

General methods and materials: ¹H and ¹³C NMR spectra were recorded in CDCl₃ solutions with TMS as internal standard on a Bruker AM 200 instrument. IR spectra were obtained with a Bruker IFS66 FTIR spectrometer.

4,4-Dimethylcyclohexadienone (8): Ketone **8** was synthesized according to a published procedure [28]. The spectroscopic data are in agreement with that reported by Zimmermann and his coworkers.

Diazo-4,4-dimethylcyclohexa-2,5-diene (4): **4** was prepared by a Bamford–Stevens reaction with a modified version of a procedure published by Jones, Harrison and Rettig [6]. 4,4-Dimethylcyclohexadienone tosylhydrazone was prepared by a standard procedure and recrystallized from dry methanol. The lithium salt was prepared by treating the tosylhydrazone, dissolved in dry CH₂Cl₂, with LiH (1.05 equiv). After removing the solvent under vacuum, the residue was washed thoroughly with dry pentane. The diazo compound was generated by heating the salt to 100 °C in a vacuum. The deep purple diazo compound was distilled in a cold trap or sublimed directly onto the cold window; the IR spectrum obtained from direct deposition was identical with that of a sample that was isolated before deposition. The isolated diazo compound was stored at –80 °C in an inert gas atmosphere. If it was exposed to temperatures > –70 °C, quantitative formation of the azine was observed. ¹H NMR (400 MHz, CDCl₃): δ = 1.09 (s, 6H), 5.14 (d, 2H), 5.92 (d, 2H); IR (Ar, 10 K): $\tilde{\nu}$ = 3046.3 (m), 2972.4 (s), 2960.3 (s), 2951.0 (m), 2942.7 (s), 2920.4 (m), 2870.3 (m), 2860.0 (m), 2097.6 (s), 2053.8 (vs), 2013.8 (vs), 1667.8 (m), 1646.6 (vs), 1593.9 (s), 1471.4 (s), 1456.3 (s), 1425.6 (s), 1374.8 (m), 1361.5 (w), 1356.7 (m), 1283.5 (w), 1196.5 (w), 1141.3 (m), 1119.9 (w), 969.5 (w), 918.0 (vs), 740.0 (vs), 732.1 (w), 671.6 (w), 605.5 (w) cm⁻¹; UV/Vis (Ar, 10 K): λ_{max} = 285.580 nm.

[D₂]4,4-Dimethylcyclohexa-2,5-dienone ([D₂]8): 4,4-Dimethylcyclohexa-2,5-dienone **8** (400 mg, 3.3 mmol) was dissolved in a mixture of D₂O (2 mL) and CD₃OD (2 mL). Then K₂CO₃ (160 mg) was added. The mixture was stirred to bring about dissolution and placed in an oil bath maintained at 85°C. The reaction progress was monitored by NMR spectroscopy. After the deuterium exchange was completed, the reaction mixture was diluted with 2 mL of D₂O and thoroughly extracted with ether. The combined ether extracts were washed subsequently with H₂O and saturated aqueous solutions, dried over MgSO₄, filtered, and concentrated to give an oily yellow residue. The residue was distilled under high vacuum to give 200 mg (49%) of [D₂]8 as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ = 1.2 (s, 6H; CH₃), 7.1 (s, 2H; CH); ¹³C NMR (100 MHz, CDCl₃): δ = 26.7 (2C, CH₃), 39.8 (C), 127.1 (2C, CH), 169.7 (2C, CH), 189.7 (C); MS (EI, high resolution): calcd 124.085, found 124.085.

[D₂]Diazo-4,4-dimethylcyclohexa-2,5-diene ([D₂]4): [D₂]4 was prepared by the procedure described above [6]. IR (Ar, 10 K): $\tilde{\nu}$ = 3046 (m), 2960.8 (s), 2941.8 (s), 2913.7 (m), 2866.3 (m), 2114.1 (m), 2087.2 (s), 2048.2 (vs), 2039.1 (vs), 2003.2 (vs), 1668.2 (m), 1626.6 (vs), 1581.8 (s), 1470.9 (s), 1454.5 (m), 1387.8 (s), 1375.1 (m), 1304.0 (w), 1282.2 (w), 1175.9 (s), 1134.1 (s), 1004.1 (vs), 948.2 (w), 863.3 (m), 831.7 (m), 662.9 (vs), 650.7 (w), 583.4 (m) cm⁻¹.

Matrix spectroscopy: Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Linde, 99.9999%) at 30 K on top of a CsI (IR) or sapphire (UV/Vis) window at a rate of approximately 0.15 mmol min⁻¹. The samples were produced by co-deposition of Ar with streams of diazo-4,4-dimethylcyclohexa-2,5-diene (**4**) and [D₂]4 generated by sublimation at -37°C. The sample temperature at deposition was -37°C. Irradiation was carried out with Osram HBO 500 W mercury high-pressure arc lamps in Oriol housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10 cm path of water and by a Schott KG1 filter. For broad-band irradiation Schott cut-off filters were used (50% transmission at the wavelength specified), and for narrow-band irradiation, interference filters in combination with dichroic mirrors and cut-off filters were used. Partially oriented matrices were obtained by the method of photoselection. Linearly polarized light was generated by means of a linear polarizer in combination with the filters described above.

Infrared spectra were measured by a Bruker IFS66 FTIR spectrometer with a standard resolution of 1 cm⁻¹ in the range 400–4000 cm⁻¹. Polarized IR spectra were recorded by a Specac aluminum grid polarizer (Cambridge Physical Sciences, Ltd). To avoid photolysis by UV light, all spectra were run with a polished Ge filter with 50% transmission at 5000 cm⁻¹. IR dichroism was evaluated by comparison of the integrated IR bands.

UV/Vis spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer with a resolution of 2 nm.

4,4-Dimethyl-2,5-cyclohexadienyldiene (3): Photolysis of matrix-isolated diazo-4,4-dimethylcyclohexa-2,5-diene (**4**) yielded 4,4-dimethyl-2,5-cyclohexadienyldiene (**3**). UV/Vis (Ar, 10 K): λ_{max} = 277, 288, 299 nm.

4,4-Dimethyl-2,5-cyclohexadienone-O-oxide (6): Oxidation (Ar/1% O₂, 45 K) of matrix-isolated 4,4-dimethyl-2,5-cyclohexadienyldiene (**3**) produced carbonyl oxide **6**. IR (Ar, 10 K): $\tilde{\nu}$ = 3247.0 (41), 2979.5 (10), 2947.7 (4), 1668.2 (3), 1615.1 (3), 1472.5 (5), 1447.1 (7), 1420.0 (5), 1379.2 (4), 1360.5 (3), 1360.5 (4), 1333.3 (1), 1314.9 (3), 1255.3 (8), 1196.2 (5), 1154.7 (4), 1111.8 (3), 984.1 (4), 928.1 (17), 913.5 (3), 892.8 (100), 869.3 (38), 816.3 (16), 762.8 (1), 721.7 (9), 588.7 (16) cm⁻¹ (rel. int.); UV/Vis (Ar, 10 K): λ_{max} = 444 nm.

6,6-Dimethyl-1,2-dioxaspiro[2.5]octa-4,7-diene (7): Photolysis (Ar/1% O₂, λ = 500 nm) of matrix-isolated 4,4-dimethyl-2,5-cyclohexadienone-O-oxide (**6**) yielded a mixture of 6,6-dimethyl-1,2-dioxaspiro[2.5]octa-4,7-diene (**7**) and 4,4-dimethyl-2,5-cyclohexadienone (**8**). **7**: IR (Ar, 10 K): $\tilde{\nu}$ = 2985.8 (3), 2974.5 (1), 2935.8 (1), 1743.8 (100), 1723.1 (16), 1678.0 (11), 1466.3 (6), 1448.2 (3), 1395.6 (6), 1363.7 (6), 1295.8 (13), 1232.1 (4), 1187.6 (27), 1177.0 (13), 1132.1 (17), 1073.8 (16), 952.8 (1), 914.1 (1), 865.4 (3), 810.3 (7), 803.9 (11), 752.1 (7), 744.0 (9), 729.7 (7), 657.1 (7) cm⁻¹ (rel. int.).

8: IR (Ar, 10 K): $\tilde{\nu}$ = 3045.8 (3), 2980.5 (20), 2949.2 (9), 2938.2 (8), 2878.5 (6), 1693.2 (51), 1673.6 (100), 1641.6 (23), 1614.7 (29), 1473.8 (22), 1462.6 (8), 1448.8 (6), 1399.2 (18), 1359.9 (8), 1250.6 (17), 1157.5 (5), 1126.0 (23), 1118.5 (14), 1102.1 (15), 1051.6 (3), 963.8 (14), 916.9 (6), 878.0 (15), 865.7 (32), 861.1 (30), 765.3 (6), 746.3 (12), 701.6 (11) cm⁻¹ (rel. int.); UV/Vis (hexane): λ_{max} = 225 nm.

5,5-Dimethyl-5H-oxepin-2-one (9): Irradiation (λ > 395 nm, Ar, 10 K) of matrix-isolated 6,6-dimethyl-1,2-dioxaspiro[2.5]octa-4,7-diene (**7**) generated 5,5-dimethyl-5H-oxepin-2-one (**9**). IR (Ar, 10 K): $\tilde{\nu}$ = 2985.8 (3), 2974.5 (1), 2935.8 (1), 1743.8 (100), 1723.1 (16), 1678.0 (11), 1466.3 (6), 1448.2 (3), 1395.6 (6), 1363.7 (6), 1295.8 (13), 1232.1 (4), 1187.6 (27), 1177.0 (13), 1132.1 (17), 1073.8 (16), 952.8 (1), 914.1 (1), 865.4 (3), 810.3 (7), 803.9 (11), 752.1 (7), 744.0 (9), 729.7 (7), 657.1 (7) cm⁻¹ (rel. int.).

Computational methods: Ab initio calculations were performed with restricted, unrestricted, and spin-projected second-order Møller-Plesset perturbation theory

(RMP2, UMP2, PUMP2), employing the 6-31 G(d) basis set of Pople and co-workers [29]. MP2/6-31 G(d) vibrational frequencies were scaled by a factor of 0.95. Furthermore, the CIS method was utilized to calculate the UV/Vis spectrum of **5**. Calculations were carried out on a CRAY-YMP/416 with the COLOGNE 94 [30] and GAUSSIAN 92 [31] program packages.

The following RMP2/6-31 G(d)//RMP2/6-31 G(d) energies were used in the calculations of reaction energies for Equations (1)–(5): ethylene - 78.29429; ethane - 79.50397; propane - 118.67441; propene - 117.46653; isobutene - 156.64640; isobutane - 157.84777; acetone - 192.54087; neopentane - 197.02326; cyclopropene - 116.21957; 3,3-dimethylcyclopentene - 272.99184; 2-cyclopentenone - 268.51675; **5** - 309.68952; **1** - 305.20256 Hartree.

The analysis of the electron density distribution was carried out with MP2/6-31 G(d) response densities by a method described elsewhere [19–22]. Mode and degree of ring puckering in the two bicyclic compounds was determined by means of the Cremer-Pople puckering coordinates with the computer program RING88 [15–17].

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