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Geometry of the Transition State of the Decarbonylation of Bicyclo[2.2.1]hepta-2,5-dien-7-one. Experimental and ab Initio Theoretical Studies

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Abstract: The geometries of bicyclo[2.2.1]hepta-2,5-dien-7-one (**1**) and of the concerted, synchronous transition state for formation of benzene and carbon monoxide from **1** were obtained from ab initio calculations. A nonsynchronous transition state was not found at the UHF/4-31G level, despite an extensive search. At the MP3/6-31G* level, the calculated activation energy for the decarbonylation is in agreement with experiment. Calculations for synchronous transition states reproduce the experimental correlation between the activation energy and the heat of reaction for a series of allowed thermal reactions. Tentative assignments of the observed IR spectrum for **1** and **1**-d_6 are made based on the RHF/3-21G vibrational frequencies and intensities. The factors contributing to the facile decarbonylation are considered to be the availability of an allowed pathway for the reaction and the exothermicity of the reaction, due to the ring strain of the reactant and the stability of the products.

Since the early 1900's it has been recognized that the bicyclo[2.2.1]hepta-2,5-dien-7-one skeleton is remarkably prone to fragmentation, losing carbon monoxide well below ambient temperature.[1] Over the years there have been many attempts at its synthesis,[1,2] but only a few stabilized derivatives have been made.[3-6] These include the iron tricarbonyl complex[4] (**2**), the dibenzo derivative[5] (**3**), and a substituted derivative[6] (**4**). Compounds **2** and **3** are stable at room temperature, and compound **4** decarbonylates at ca. −40 °C. Despite the continued experimental interest in this system, it was not until recently that the parent system (**1**) was independently synthesized and characterized by Birney and Berson[7] and by LeBlanc and Sheridan.[8] The activation energy for its fragmentation to carbon monoxide and benzene was found to be 15 ± 2.5 kcal/mol.[7,8] For a molecule that obeys the rules of valence, and must suffer the cleavage of two carbon–carbon single bonds during the course of the reaction, this seems a remarkably low barrier for fragmentation.

A number of explanations have been advanced to account for this propensity to lose carbon monoxide. In 1942 Allen and Allan[1c] pointed out the following:

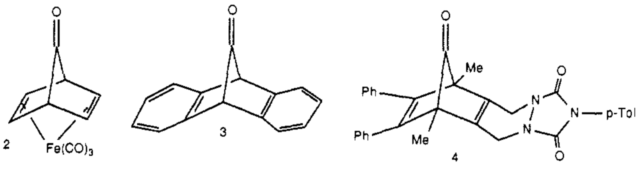
> The loss of carbon monoxide is, in reality, a cleavage of linkages beta, gamma to the double bond, comparable to the production of butadiene from cyclohexene.... (In the case of bicyclo[2.2.1]hepta-2,5-dien-7-ones) there are two such linkages to increase the tendency to cleavage... and so far, in no single instance... has such a substance been isolated.

Landesberg and Sieczkowski[4] suggest that bicyclo[2.2.1]hepta-2,5-dien-7-one is destabilized by electron repulsion between the olefinic and carbonyl π orbitals. Woodward and Hoffmann[9b] discussed the decarbonylation of bicyclo[2.2.1]hepta-2,5-dien-7-one (**1**) as an orbital symmetry allowed cheletropic reaction, which is in turn a class of pericyclic reactions. They highlight it as a prime example of how the availability of an allowed pathway may lower the activation energy of a reaction.

Background

Whether concerted pericyclic reactions occur via synchronous or non-synchronous pathways and which theoretical or experimental criteria should be used to discriminate between them appears to be a question to which no consensual answers have been found.[9-12] McIver[12] and then Dewar[10] have questioned the existence of synchronous reactions, the latter arguing that "multi-bond reactions cannot normally be synchronous."[10] Dewar has presented a series of semiempirical calculations (UHF/MNDO and UHF/MINDO3)[10] as well as some experiments[11a] to support this conclusion. We thank a referee for pointing out that McIver's arguments are weaker for cheletropic reactions;[12]

Scheme I



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the interaction force constants should be greatest when the two breaking bonds are on the same atom. And indeed ab initio calculations on pericyclic reactions have generally found synchronous transition states.[13] Occasionally non-synchronous transition states have been found at low levels of theory, but these have disappeared at higher correlated levels of theory.[13a,b] The obvious response is that at some unspecified higher level of theory the conclusions might change to again favor a nonsynchronous pathway.

A number of experimental results have also been used to argue for synchronous transition states. Among these are the careful and elegant studies of deuterium isotope effects in Diels–Alder reactions recently carried out by Gajewski and co-workers.[11b,c] They conclude that the more symmetrical the reagents are the more nearly synchronous the transition state. Similar conclusions have been criticized by Dewar.[10]

According to the Woodward–Hoffmann rules, the concerted thermal cheletropic fragmentation of a five-membered-ring system is allowed in a linear, suprafacial mode or a nonlinear, antarafacial mode.[9b,14] The suprafacial mode is observed experimentally,[18,19] and thus the linear mode is commonly assumed.[9b,20] Diaz et al. have studied the decarbonylation of the tricyclic ketone **5** using MINDO/3.[24] They find a C_s symmetrical (linear) transition state. In contrast, Dewar et al. have used UMINDO/3 and UMNDO to study a variety of cheletropic reactions[25] and suggest nonsynchronous concerted transition states for them. These alleged asynchronous transition states are not located in any of these calculations, rather two-step biradical processes are found. After an empirical correction since "UMINDO/3 and UMNDO are known to overestimate the stability of singlet biradicals and biradical-like species,"[25b] the potential surfaces appear to indicate non-synchronous, concerted pathways. Specifically, the decarbonylation of bicyclo[2.2.1]hepta-2,5-dien-7-one (**1**) was predicted to be nonsynchronous, and to have an activation barrier of 22.5 kcal/mol (UMINDO/3),[25b] which is within 1 kcal/mol of that similarly calculated for the decarbonylation of norbornenone. Dewar noted that the experimental value was likely to be lower. Experimentally the difference in the activation energies is 14 kcal/mol.[7,8,26]

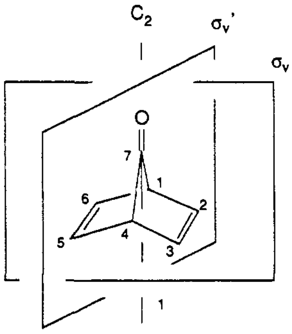

Figure 1. Symmetry elements of bicyclo[2.2.1]hepta-2,5-dien-7-one (**1**).

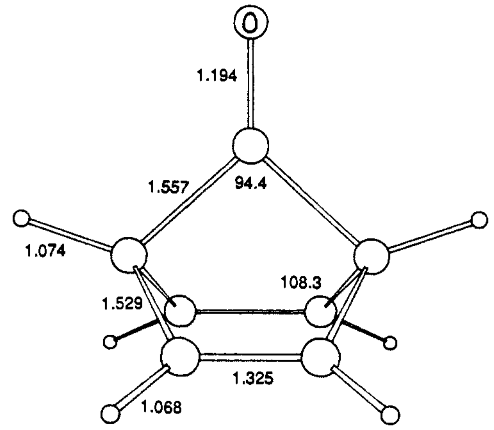

Figure 2. Ground-state geometry (Å and deg) of **1** as calculated at the RHF/4-31G level.

No ab initio calculations on cheletropic fragmentations of five-membered rings had been done prior to this work. In view of the experimental and theoretical interest in the decarbonylation of bicyclo[2.2.1]hepta-2,5-dien-7-one (**1**) to produce benzene, we

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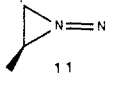
(14) When Woodward and Hoffmann first proposed selection rules for cheletropic reactions, they apparently only considered the linear case and predicted that fragmentations of a three-membered ring, which is constrained to a suprafacial pathway, would be stereorandom because the allowed pathway is antarafacial.[15,16] Shortly thereafter the decomposition of the 1,1-diazine **11** was investigated and found to procede stereospecifically with retention of configuration (suprafacial).[17] It would appear that to accommodate these new data they suggested the nonlinear pathway.[9]



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(20) The only experimental evidence that may be relevant to the mode of departure of a chelefuge is from flash photochemical studies of cyclopentenone and cycloheptadienone by Rosenfeld et al.[21] They examine the vibrational population of CO produced and suggest that since the CO from cyclopentenone is relatively cold, it is produced by a linear pathway. If the CO is produced on the thermal surface this conclusion would be in agreement with theory. They also observe that the CO from cycloheptadienone is hotter, and they suggest it follows a nonlinear pathway. In combination with stereochemical studies of Schuster et al.,[22] which show the reaction is antarafacial on the olefin, these results for cycloheptadienone are in conflict with the predictions of the Woodward–Hoffmann rules. It should be noted that their conclusions rest on several assumptions, including the presumptions that the photochemically induced reactions actually occur on the ground-state surface, and that there should be a difference between the degree of vibrational coupling in a linear vs a nonlinear pathway. There is at present no evidence to support these assumptions, and in fact substantial evidence that the photodecomposition of cyclopentenone occurs on the triplet energy surface,[23] rather than crossing onto the ground state.

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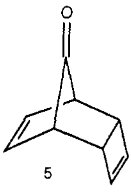

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undertook an ab initio study of the reaction.

The question of synchronicity is in essence a question of geometry of the transition state.[27] Since a transition state has a lifetime of only one molecular vibration, its geometry is only obtainable from a theoretical calculation (though clearly inferences may be drawn from experiments). Because any calculation is based on some level of approximation,[28,29a] it is important to compare at least some results of the calculation with experiment. For a transition state, we will compare the experimental and calculated activation energies.

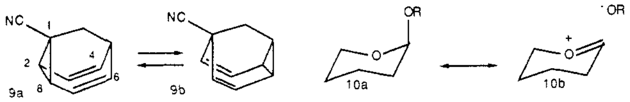
Computational Methods

The ab initio calculations have been carried out with the GAUSSIAN82[30] and GAMESS[31] programs, as installed on a VAX 11-750 at Yale, and GAUSSIAN82-Rev. K[30] as installed on the CRAY X-MP/48 at the Pittsburgh Supercomputing Center. Geometries were fully optimized with C_{2v} symmetry constraints as described, using the gradient techniques in the programs.[32] The basis sets used in this work include STO-3G,[33a] which is a minimal basis set, the 3-21G[33b] and 4-31G[33c] "split-valence" basis sets, and the 6-31G* [33d] basis set, which includes "polarization" functions on carbon and oxygen. Unless otherwise stated, analytical frequencies[30] were only calculated on stationary points, and always at the same level as the optimization. Semiempirical calculations were done with AM1.[34]

To investigate the effects of electron correlation, Møller–Plesset (MP2, MP3) perturbation theory[35] was used, with the RHF/4-31G and RHF/6-31G* wave functions.[36] The results of some limited CI calculations using several different excitations from the RHF/4-31G wave functions are reported in the supplementary material.

We have taken advantage of the symmetry of the system. The highest symmetry possible for **1** and for its suprafacial linear decarbonylation would be C_{2v} where the carbon monoxide would depart along the C_2 axis (see Figure 1). However, if the CO remains in the plane bisecting the olefins (σ_v, Figure 1) then the reaction is still synchronous and still allowed (linear) according to orbital symmetry. The forbidden nonlinear pathway and a stepwise biradical pathway would involve a distortion toward one of the bridgeheads. (Such a distortion could possibly retain the σ_v' plane (Figure 1), but this is not required.) This corresponds to the non-synchronous concerted pathway as described by Dewar for this system.[25b]

Scheme II



Calculated Geometries

Ground State. The optimized geometry of bicyclo[2.2.1]hepta-2,5-dien-7-one (**1**) at various levels of theory is presented in Table I and in Figure 2 (RHF/4-31G). It has been observed that bond lengths are slightly shorter at the RHF/6-31G* level as compared to the RHF/4-31G level[29b] and that at the MP2 level bond lengths are longer than at the RHF level.[29b] These general trends are seen here in the optimized geometries of **1**. Table II presents the geometries of some related molecules, both experimental values, and when available, those calculated at the RHF/4-31G level as well. Although the geometry was optimized under the constraint of C_{2v} symmetry, the Cartesian force constants subsequently obtained for that geometry indicate that it is a local minimum and is stable toward unsymmetric distortions. A less symmetric geometry would have to be significantly distorted in order to reside at a local minimum. This is unlikely in such a rigid molecule. Furthermore compounds **6**, **7**, and **8** are found experimentally to have C_{2v} symmetry.[37,38] And finally, the calculated IR frequencies and intensities of **1** and **1**-d_6 agree well with the experimental ones (see below). Thus the calculated geometry of **1** appears to reproduce both the symmetry and the geometrical features of the ground-state well.

There is a subtle but consistent trend in the calculated geometry of **1** as compared to norbornadiene (**7**) at the RHF/4-31G level. In **1**, the two planes defined by each olefin and the bridgeheads form an angle of 117.7° (the flap angle). This is 2.5° more than the calculated flap angle of **7**[39] (and 1.7° more than the experimental value in **7**). Although small, this difference is larger than expected for errors (±1.0°)[29b] in the calculation. Furthermore, it is in the opposite direction to that expected from strain; compare norbornane[37] (**6**) with norbornanone[38] (**8**) (see Table II). Since it represents a flattening of the incipient benzene ring, this seems to indicate the ground state is distorted toward products. A close comparison of calculated bond lengths between **1** and **7** reinforces this idea (see Table II). The bond alternation around the six-membered ring in **1** (C_1C_2–C_2C_3 = 0.211 Å) is slightly less than that in **7** (C_1C_2–C_2C_3 = 0.222 Å). These comparisons are between atoms that have the same formal hybridization in the two molecules. An RHF/4-31G optimized geometry for 7-norbornanone (**8**) is not available for a direct comparison. When compared to the experimental values for **8**, the C=O bond length in **1** is shorter by 0.02 Å and the C_1–C_7 bond is longer by 0.03 Å. Generally the use of the 4-31G basis set leads to bond lengths that are shorter than experiment but within 0.03 Å.[29b] Thus while the expected errors in the calculation are just large enough to make this comparison approximate, it seems to demonstrate the same distortion seen in the other half of the molecule. A comparison is also possible with the C=O bond length in cyclopropanone,[40,41] where the carbonyl is calculated to be longer, even though it is more strained than in **1**. This suggests that the length of the C=O bond in **1** prefigures the product carbon monoxide as well.

Some slight variation in bond length is expected at different levels of theory.[29b,33,42] However, both ground-state distortions

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(27) Generally, a calculation optimizes to a structure on the potential energy surface which has zero or one negative eigenvalue of the force constant matrix.[28,29] This **structure** does not necessarily correspond to a **state** on the free energy surface. In most cases, the distinction is small, and for simplicity, we will refer to structures obtained from calculations as ground states and transition states.

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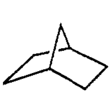
Table I. Calculated Geometries of Norbornadienone, Constrained[a] to C_{2v} Symmetry, As Optimized at Various Levels of Theory

	level of theory						
			RHF				MP2
	MINDO/3[b]	AM1	STO-3G	3-21G	4-31G	6-31G*	4-31G
			Bond Lengths (Å)				
C_7O	1.193	1.213	1.203	1.191	1.194	1.175	1.226
C_1C_7	1.575	1.574	1.572	1.569	1.557	1.553	1.607
C_1C_2	1.528	1.526	1.538	1.534	1.529	1.525	1.533
C_2C_3	1.359	1.357	1.314	1.323	1.325	1.325	1.360
H_1C_1	1.112	1.101	1.086	1.076	1.074	1.079	1.090
H_2C_2	1.098	1.087	1.079	1.069	1.068	1.073	1.084
			Bond Angles (deg)				
$C_1C_7C_4$	c	94.4	93.9	94.0	94.4	94.5	93.4
$C_1C_4H_4$	c	161.3	162.0	161.3	160.8	160.4	160.8
$C_1C_2C_3$	c	108.2	108.4	108.5	108.3	108.3	108.6
$C_2C_1C_4C_5$[d]	c	114.2	116.0	116.6	117.7	118.5	119.0

[a] Although the optimization was constrained to C_{2v} symmetry, the frequencies calculated at the RHF/4-31G geometry have no negative eigenvalues indicating that the C_{2v} structure is a minimum. (See the text for further discussion.) [b] From ref 25b. [c] Values not reported. [d] "Flap angle".

Table II. Experimental and Calculated Geometries of Reference Compounds Related to Norbornadienone (1)[g]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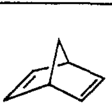
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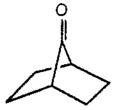

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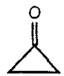

	6		7		8		
	exptl[a]	4-31G[b]	exptl[c]	4-31G[b]	exptl[d]	exptl[e]	4-31G[f]
			Bond Lengths (Å)				
C_1C_7	1.560	1.540	1.573	1.562	1.527		
C_7O					1.213	1.200	1.198
C_1C_2	1.539	1.545	1.535	1.543	1.569		
C_2C_3	1.557	1.560	1.343	1.321	1.539		
			Bond Angles (deg)				
$C_1C_7C_4$	93.1		94.1	94	99.5		
$C_1C_4H_4$				162	150.2		
$C_2C_1C_4C_5$	113.1		115.6	115.2	110.0		

[a] Reference 37. [b] Reference 39. [c] Reference 37. [d] Reference 38. [e] Reference 40. [f] Reference 41. [g] The numbering is based on that of norbornadienone, as in Figure 1.

are also seen in the geometries obtained at the RHF/6-31G* and the MP2/4-31G levels (Table I). At the MP2/4-31G level, the C_1C_7 bond is longer, just over 1.6 Å, and the flap angle of 119.0° is flatter than at the RHF/4-31G level. In summary, although the absolute lengths of these bonds do change when structure is optimized at different levels, these distortions are consistently observed at reliable levels of theory. Thus it appears that the ground-state geometry of **1** is distorted toward the product geometry.[43] If so, the ground-state structure provides a unique experimental probe of the reaction coordinate for a generalized decarbonylation and an indication of the degree of synchronicity of this cheletropic reaction.

There may be some experimental precedent for this distortion toward products. In the crystal structure of 1-cyanosemibullvalene (**9a**), at −45 °C, the C_2–C_8 distance is lengthened and the C_4–C_6 nonbonded distance is shortened relative to model systems.[44] Christoph and Beno suggest that the geometry is distorted along the reaction coordinate of the Cope rearrangement toward **9b** and attribute this to either a resonance contribution of the rearranged material or homoaromaticity.[44] From X-ray data, Kirby and co-workers[45] find that the length of the axial C–OR bond in cyclic acetals **10a** parallels the ease of hydrolysis; the more electronegative R is, the longer the C–OR bond. They suggest this is due to the resonance contribution of **10b**, in which the bond is broken. Dunitz and co-workers have observed a related phenomenon in the X-ray crystal structures of carbonyl compounds and a number of nucleophiles.[46] The position of the nucleophiles relative to the carbonyl is suggested to reflect the trajectory of nucleophilic additions to carbonyl groups in general. In all these cases it seems that ground-state geometries can indeed prefigure the reaction pathway. The fact that such distortions are not observed more often may simply reflect the paucity of studies of reactive species with such low barriers to unimolecular reactions.

Synchronous Transition State. By definition, the synchronous transition state lies on the σ_v plane (Figure 1). Consistent with the distortion of the ground-state geometry, a transition state for the decarbonylation of **1** was found that had C_{2v} symmetry. The geometries are reported in Table III and Figure 3, and the energies in Table IV. A frequency calculation on the RHF/4-31G geometry subsequently showed that this was a true transition state, with only one negative eigenvalue of the Hessian (force constant) matrix, i.e., one imaginary frequency (638i cm^{-1}). The transition vector (the displacements calculated for the negative eigenvector) is shown in Figure 3A. They indicate that the fragmentation occurs as expected, smoothly distorting toward products. Thus it appears that a synchronous linear pathway is permissible for this cheletropic fragmentation. The lowest real vibrations at the transition state are shown in Figure 3, B and C. The 98-cm^{-1} mode corresponds to bending in the σ_v plane. A fragmentation distorted in this direction remains synchronous and orbital symmetry allowed. The 208-cm^{-1} mode corresponds to bending toward the nonsynchronous pathway. From the point of view of reaction

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(43) Preliminary calculations (RHF/3-21G) by J. Reynolds and J. A. Berson indicate that diazabarrelene may be more dramatically distorted toward benzene and nitrogen, reflecting the greater exothermicity of this fragmentation.

(44) Christoph, G. C.; Beno, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 3156.

(45) (a) Allen, F. H.; Kirby, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 6197. (b) Briggs, A. J.; Glenn, R.; Jones, P. G.; Kirby, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 6200. (c) Jones, P. H.; Kirby, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 6207. (d) Jones, P. G.; Sheldrick, G. M.; Kirby, A. J.; Briggs, A. J. *Acta Cryst. Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 1380. (e) Edwards, M. R.; Jones, P. G.; Kirby, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 7067.

(46) (a) Schweizer, W. B.; Procter, G.; Kaftory, M.; Dunitz, J. D. *Helv. Chim. Acta* **1978**, *61*, 2783. (b) Burgi, H. D.; Dunitz, J. D.; Schefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065.

Table III. Calculated Geometries of C_{2v} Stationary Points[a] for the Decarbonylation of Norbornadienone, As Optimized at Various Levels of Theory. At the RHF/4-31G and MP2/4-31G Levels, These Structures Were Shown To Be Transition States

	level of theory					
		RHF				MP2
	AM1[b]	STO-3G[c]	3-21G	4-31G[d]	6-31G*	4-31G[e]
			Bond Lengths (Å)			
C_7O	1.187	1.161	1.152	1.155	1.136	1.193
C_1C_7	1.937	2.047	1.985	1.970	1.974	1.980
C_1C_2	1.453	1.446	1.454	1.454	1.453	1.470
C_2C_3	1.371	1.345	1.341	1.341	1.342	1.372
H_1C_1	1.098	1.088	1.074	1.074	1.078	1.091
H_2C_2	1.093	1.081	1.070	1.070	1.074	1.087
			Bond Angles (deg)			
$C_1C_7C_4$	82.1	76.6	78.8	79.1	78.7	80.0
$C_1C_4H_4$	162.6	169.4	167.1	166.8	167.2	167.0
$C_1C_2C_3$	113.8	114.4	113.7	113.7	112.9	113.5
$C_2C_1C_4C_5$	134.8	138.0	134.6	134.6	134.7	133.2

[a] The optimizations were constrained to C_{2v} symmetry. [b] This structure has two imaginary frequencies, −684 cm^{-1} (similar to Figure 3A) and −222 cm^{-1} (similar to Figure 3C). [c] This structure has two imaginary frequencies, −767 cm^{-1} (similar to Figure 3A) and −91 cm^{-1} (similar to Figure 3B). [d] This structure has only one imaginary frequency, −638 cm^{-1} shown in Figure 3A, and therefore is a true transition state. [e] It appears that this is a true transition state. (See text for further discussion.)

Table IV. Energies of Norbornadienone (**1**), the C_{2v} Transition State, and the Derived Energy of Activation[f]

level of theory	ground-state energy (au)	transition-state energy (au)	energy of activation (kcal/mol)[a]	error[b]
1 RHF/3-21G	−341.443 878	−341.410 384	19.0	+3
2 RHF/4-31G	−342.847 045	−342.811 537	20.3	+4
3 RHF/4-31G//RHF/6-31G*	−342.846 155	−342.810 714	20.2	+4
4 RHF/4-31G//MP2/4-31G	−342.838 992	−342.804 293	19.8	+4
5 RHF/6-31G*//RHF/4-31G	−343.355 919	−343.317 530	22.1	+6
6 RHF/6-31G*	−343.356 843	−343.318 396	22.1	+6
7 MP2/4-31G(FC)//RHF/4-31G	−343.592 504	−343.577 630	7.3	−9
8 MP2/4-31G(FU)	−343.612 179	−343.596 355	7.9	−8
9 MP2/4-31G(FC)	−343.600 103	−343.584 418	7.8	−8
10 MP2/6-31G*(FC)//RHF/6-31G*	−344.420 737	−344.399 040	11.6	−4
11 MP3/6-31G*(FC)//RHF/6-31G*	−344.446 065	−344.414 188	18.0	+2
12 RHF/STO-3G	−339.078 882	−339.003 528	45.3[c]	+29
13 RAM1			22.6[c]	+7
exptl			E_a = 15 ± 2.5[d] 17 ± 2[e]	

[a] These energies include a −2.0 kcal/mol zero-point energy correction based on the RHF/4-31G calculated vibrational frequencies. [b] Relative to the average experimental value for the E_a of 16 kcal/mol. [c] This structure is a stationary point, but has two imaginary frequencies. See text. The energies are not corrected for the zero-point vibrational energy. [d] Reference 7. [e] Reference 8. [f] The geometries were optimized at several levels of theory. Single point energies were then obtained at those geometries. The RHF/STO-3G and RAM1 structures are not transition states (see text).

dynamics, the more important distortion should be the more facile 98-cm^{-1} mode.

There is one caveat to this optimistic picture. Geometries of ground states or transition states can sometimes be altered fairly drastically by the inclusion of electron correlation. Cases in point would be the bends in the ground-state geometries of carbon suboxide[47] and propadienone[48] which can only be reproduced at the MP2 level. Transition states may be even more sensitive to correlation effects.[13] Therefore, it is important to verify that this C_{2v} geometry for the decarbonylation of **1** is a transition state at a correlated level as well.

The geometry of the transition state was optimized at the MP2/4-31G level in C_{2v} symmetry (see Table III). Unfortunately calculation of the second derivatives at the MP2/4-31G level would require at least 30 h on the CRAY, and so was not undertaken. Instead, we made a numerical estimate of the curvature of the surface. From the MP2/4-31G optimization it is clear that this surface has an imaginary frequency in C_{2v} symmetry, corresponding to the fragmentation. If there is a second imaginary frequency, this seems likely to involve one of the two real normal modes (RHF) in Figure 3, B and C. Therefore, the MP2/4-31G optimized structure was displaced (0.2 times the normal coordinate) following each of these two normal modes.[49] Single-point MP2/4-31G energies were higher than that calculated at the C_{2v} geometry by 0.1 kcal/mol (98-cm^{-1} mode) and 1.3 kcal/mol (208-cm^{-1} mode), respectively. Thus the C_{2v} structure is almost certainly a transition state at the MP2/4-31G level as well.

The bond lengths of the breaking bonds are only 1.980 Å at the RHF/4-31G level. This is somewhat shorter than breaking bonds in transition states calculated for less exothermic reactions (the Cope reaction of 1,4-hexadiene (2.023 Å, RHF/3-21G),[13a] the Diels–Alder reaction of butadiene and ethylene (2.244 Å, CAS1/4-31G),[13b] and the 1,3-dipolar addition of acetylene and fulminic acid (2.185, 2.210 Å)[50]). This is in accord with the Hammond postulate,[51] which suggests that the transition state for a more exothermic reaction such as this decarbonylation should be earlier than for a less exothermic one.

We note that at the RAM1 and RHF/STO-3G levels the stationary points with C_{2v} symmetry are not transition structures, but have two imaginary frequencies. In both cases the largest imaginary frequency corresponds to fragmentation along the C_{2v}

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(47) (a) Lozes, R. L.; Sabin, J. R.; Oddershede, J. *J. Mol. Spectrosc.* **1981**, *86*, 357. (b) Weber, W. H.; Ford, G. W. *J. Mol. Spectrosc.* **1976**, *63*, 445.

(48) Brown, R. D.; Godfrey, P. D.; Champion, R.; McNaughton, D. *J. Am. Chem. Soc.* **1981**, *103*, 5711.

(49) As confirmation of the validity of this approach, if one starts at the RHF/4-31G geometry and does a series of MP2/4-31G single points following the RHF/4-31G transition vector, the energy rises and then falls. In this case at least, the RHF normal mode reproduces the gross contour of the MP2 surface.

(50) Kormornicki, A.; Goddard, J. D.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1980**, *102*, 1763.

(51) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

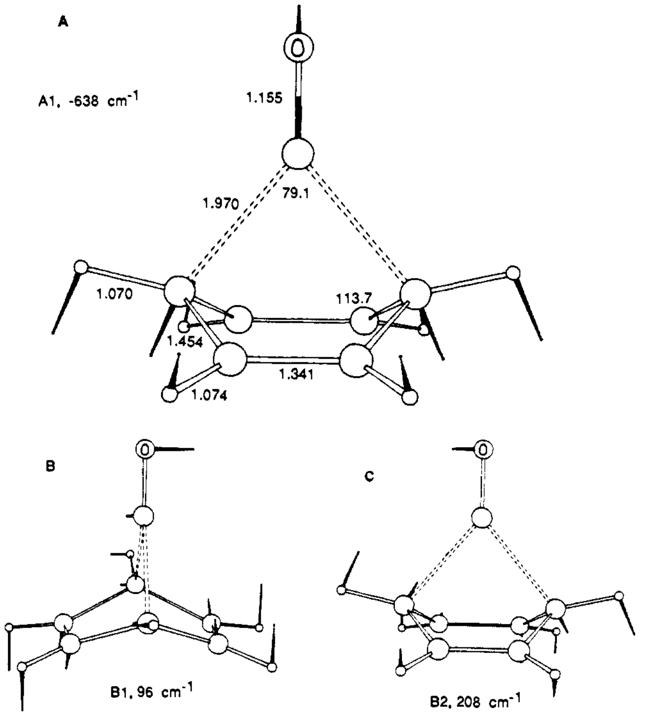

Figure 3. Geometry (Å and deg) and lowest frequency normal modes of the synchronous (C_{2v}) transition state for the decarbonylation of **1**, as calculated at the RHF/4-31G level. The displacement vectors are shown. A is the transition vector connecting the reactants with products. B is the first B1 vibration and C is the first B2 vibration.

Table V. Energies of the Nonsynchronous Transition State for the Decarbonylation of **1**

level of theory	transition-state energy (au)	energy of activation (kcal/mol)[a]
1 UMINDO3[b]		22.5
2 UMNDO[b]		26.7
3 UHF/STO-3G	-339.031 716	29.6
4 UHF/4-31G partial optimization[c]	-342.808 373	24.3
5 RHF/4-31G//UHF/4-31G partial optimization[c]	-342.796 559	31.7
6 RHF/6-31G*//UHF/4-31G partial optimization[c]	-343.303 829	32.7
7 MP2/6-31G*(FC)//UHF/4-31G partial optimization[c]	-344.394 425	16.5

[a] These values are relative to the corresponding RHF energies of the C_{2v} ground-state molecule. They are not corrected for zero-point vibrational energy, and hence are not directly comparable to the activation energies in Table IV. [b] Reference 25b. [c] R_1 and R_2 fixed at the UHF/STO-3G lengths, the remainder of the molecule was optimized. This corresponds to point A in Figure 5.

axis. At the RAM1 level the smaller imaginary frequency corresponds to a distortion in the $\sigma_v{}'$ plane toward a nonsynchronous geometry. (This normal mode is similar to that in Figure 3C.) At the RHF/STO-3G level, the smaller imaginary frequency corresponds to a distortion in the σ_v plane which remains an orbital symmetry allowed fragmentation (see Figure 3B). Since at the higher levels the C_{2v} structure is a true transition state, we conclude that these results are artifacts of these more limited theoretical treatments.[52]

Is There a Nonsynchronous Transition State? If there is a synchronous (C_{2v}) transition state even at this correlated level, is there also a nonsynchronous[53] one? If there is another one, which is the experimental one, i.e. which is of lower energy? We restricted our search for a nonsynchronous transition state to the $\sigma_v{}'$ plane (Figure 1). The search was carried out at the UHF level since this method recovers some electron correlation.[54] This and spin contamination in the UHF method both tend to favor a biradical-like transition structure.[13c,54b] Indeed, a nonsynchronous transition state with C_s symmetry ($\sigma_v{}'$ in Figure 1) and with one imaginary frequency (440i cm^{-1}) is found at the UHF/STO-3G level, as reported in Figure 4 and in Table V. This geometry is quite similar to that found by Dewar[25b] at the UMINDO level. The UHF wave function is stable at this geometry. The S^2 value of 1.722 indicates substantial spin contamination. The transition vector indicates that only one of the bridgehead to carbonyl bonds is breaking. At 2.186 Å this bond is quite similar in length to that found at the UMNDO level[25b] (2.144 Å). The other bond, 1.586 Å, is stretching only slightly (UMNDO 1.535 Å). Thus

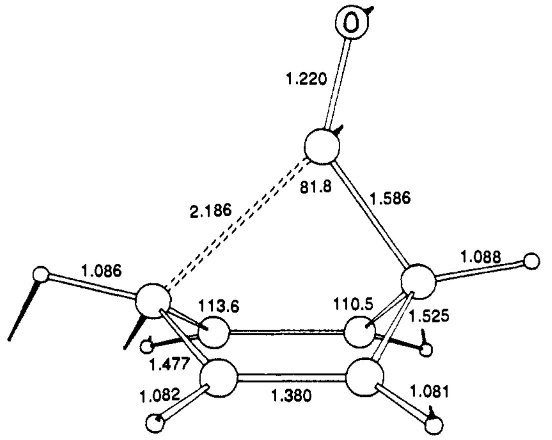

Figure 4. Geometry (Å and deg) and transition vector for the UHF/STO-3G nonsynchronous transition state for the decarbonylation of **1** (C_s symmetry, $\sigma_v{}'$ plane in Figure 1). This transition state does not persist at higher levels of theory.

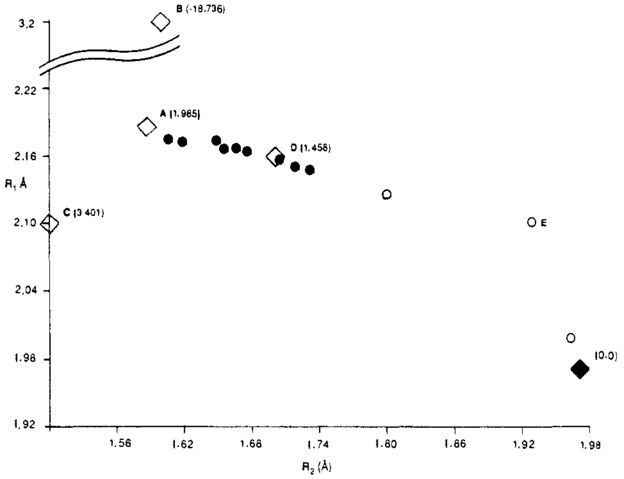

Figure 5. The barrier on the two-dimensional UHF/4-31G potential energy surface for the nonsynchronous decarbonylation of **1**. The reaction coordinate is taken to be the length of the two breaking bonds and C_s symmetry ($\sigma_v{}'$ plane in Figure 1) is maintained. Energies (in parentheses) are in kcal/mol. The values of R_1, R_2, and S^2 and the energies are reported in supplemental Table I. Structures optimized with constrained bond lengths are indicated as ◇. The other points are intermediate geometries from optimizations attempting to find a transition state. Those structures marked as ● have a maximum force of less than 0.003 hartrees/bohr or hartree/deg, and so are close to being optimized. Those marked as ○ have larger forces. The RHF/4-31G synchronous transition state is indicated as ◆. The energy of points closer to the synchronous transition state is uniformly lower in energy than those further away. The exceptions are points B and E, which are past the barrier and hence are much lower in energy. Frequencies at A and D indicate that on this surface, distortions orthogonal to the barrier lower the energy.

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[52] Schroeder, S.; Thiel, W. *J. Am. Chem. Soc.* **1985**, *107*, 4422.

[53] We did not search elsewhere in the σ_v plane for another synchronous transition state.

[54] (a) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *21*, 571. (b) McKee, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1900.

it appears that this transition state is for formation of a biradical intermediate and not for concerted formation of benzene and carbon monoxide.

We were unable to reoptimize this transition state at the UHF/4-31G level. Since the existence of a proposed transition state is in question, we will describe in some detail how we searched for it at the UHF/4-31G level. The results of this extensive search are summarized in Figure 5 and discussed below. The lengths of the two breaking bonds are taken as a two-dimensional-reaction coordinate. The barrier separating reactants and products then corresponds to a ridge on this potential energy surface. Points along this ridge have a negative second derivative corresponding to crossing the ridge. The forces at a point on the crest of the ridge can be used in an optimization to follow the crest down in energy toward a transition state.

The geometry was first optimized at the UHF/4-31G level with R_1 and R_2 fixed at the STO-3G lengths (point A, Figure 5). The energy was 2 kcal/mol higher than that of the C_{2v} geometry at the RHF/4-31G level, and the S^2 value was 0.888, indicating substantial spin contamination. Starting from this partially optimized geometry and using the second derivative matrix (Hessian) calculated at the UHF/STO-3G level, all of the bond lengths were allowed to optimize toward a transition state. The geometry slowly moved toward C_{2v} symmetry. The intermediate geometries are indicated by circles in Figure 5. A filled circle indicates the maximum force is less than 0.003 hartree/bohr or hartree/deg. These structures are fully optimized except for the distorting force along the crest of the ridge.[55] The energies and the S^2 values smoothly decreased from the values at point A as the structure became more symmetrical (see supplemental Table I). This is all consistent with an optimization along a potential ridge, as described above.

To further explore the surface, several other optimizations were performed with fixed lengths for the two breaking bonds (points A, B, C, and D). Points B and E have energies lower than A or the C_{2v} structure, suggesting that they are past the barrier separating reactants and products. The length of the one bond at point C is shorter than in the starting material, so this compression leads to a higher energy. A frequency calculation at point D (bond lengths of 1.700 and 2.160 Å, $S^2 = 0.690$) showed two imaginary frequencies. Because the forces at point D are not zero, the calculation does *not* indicate a second-order maximum *nor* imply the existence of two transition states. However, it is close enough to being optimized (maximum force of 0.025, RMS force of 0.008 hartree/bohr) that it may be instructive to examine the normal modes. The largest imaginary frequency (474i cm^{-1}) corresponds to cleavage of both bonds. The smaller one (170i cm^{-1}) corresponds to the trajectory being followed in the optimization, namely moving along the ridge toward the synchronous transition state. This point is not a second-order maximum because following the 170i-cm^{-1} mode toward C_{2v} symmetry lowers the energy, but in the opposite direction raises it. Distortions out of the σ_v' plane raise the energy, as indicated by the non-imaginary vibrations which break the symmetry. Therefore, this point is on the crest of the ridge.

The UHF/4-31G energies of various partially optimized structures along the crest of this ridge (points A, C, D, and the intermediate points) are above the RHF/4-31G energy for the C_{2v} transition state. (The RHF/3-21G wave function is stable with respect to UHF at the C_{2v} geometry.) This is despite the fact that UHF theory recovers some of the correlation energy, and hence tends to give lower energies than RHF.

In conclusion, we have explored the potential surface of the σ_v' plane in great detail, and at the UHF/4-31G level we can trace the crest of the potential ridge separating reactants and products. Any decarbonylation in this symmetry must cross this ridge. The synchronous transition state is the lowest point on the crest of the ridge, and is indeed the *only* transition state that we can find. Semiempirical AM1 calculations and ab initio calculations with the STO-3G basis set are both unable to reproduce the gross features of the potential surface as described at higher levels of theory.

There can be little doubt that at the UHF/4-31G level, distortions toward a nonsynchronous transition state raise the energy of the system. It still could be argued that correlation energy should be accounted for in a more consistent way than with UHF theory. Because point A was obtained by UHF/4-31G partial optimization of the UHF/STO-3G transition state, this geometry was chosen for the MP2/6-31G*(FC) single point calculation. The energy of this nonsynchronous geometry remains higher than the synchronous transition state, 2.9 kcal/mol above the MP2/6-31G*(FC)//RHF/6-31G* value. The data in Table IV suggest that further geometry optimization might lower the energy of point A by no more than 0.5 kcal/mol, but the conclusion remains that the synchronous transition state is favored.

Calculated Energetics

The Activation Energy for the Decarbonylation of 1. Setting aside the hypothetical nonsynchronous pathway, how well does the calculated activation energy of the C_{2v} pathway compare with experiment? At the RHF/4-31G level it is calculated to be 22.3 kcal/mol. The zero-point vibrational energy correction (−2.0 kcal/mol, from the frequency calculations) lowers this to 20.3 kcal/mol. This is only slightly closer to the experimental value than the MINDO/3 value of 22.5 kcal/mol,[25b] which was undoubtedly obtained at a fraction of the cost.

RHF theory using the 4-31G basis set is reasonably accurate for determining ground-state geometries.[29b] But higher level single point calculations are needed to obtain reliable energies.[29c,d,56,57] Therefore we performed single-point calculations on the ground-state and transition-state geometries optimized at various levels of theory. The calculated energies are reported in Tables IV and V and in Figure 6. An initially disturbing trend is that the RHF/6-31G* level gives a calculated energy difference in worse agreement with experiment than RHF/4-31G. This trend is seen in other reactions,[56] and reflects the fact that while better basis sets more accurately describe the ground state they do not provide a corresponding large improvement in the description of the transition state.

The application of a second-order Møller–Plesset perturbation treatment makes the activation energy too low (Table IV, entries 7–10). This type of behavior has been observed before.[29e,56] It has been suggested that the effects of better basis sets and of CI are roughly additive.[29f] Thus based on entries 2, 5, and 7 an MP2/6-31G* calculation might be expected to give an activation energy close to 11 kcal/mol. The calculated MP2/6-31G*(FC)//RHF/6-31G* energy is in fact 11.6 kcal/mol (entry 10).

The calculated activation energy for the decarbonylation of bicyclo[2.2.1]hepta-2,5-dien-7-one depends on the basis set and the level of correlation, but not on the level at which the geometries were obtained. In Table IV entries 2, 3, and 4 are single-point energies on geometries obtained at the RHF/4-31G, RHF/6-31G*, and MP2/4-31G levels. These calculated activation energies are all within 0.5 kcal/mol of each other. Similarly entries 5 and 6, which are RHF/6-31Gσ single points are two different geometries, give the same activation energies, and finally, the MP2/4-31G energies (entries 7, 8, and 9) are within 0.5 kcal/mol of each other, at different geometries and whether or not the frozen core approximation (FC) is used. It is therefore reasonable to expect that single-point calculations at higher levels will be adequate descriptions of the potential surface.

The MP3/6-31G*(FC)//RHF/6-31G* activation energy of 18 kcal/mol (entry 11) agrees well with the experimental values of 15 ± 2.5 or 17 ± 2 kcal/mol[7,8] and is superior to the results

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(55) Point D ($R_1 = 1.699$ Å, $R_2 = 2.160$ Å, constrained optimization) and the overlapping point in Figure 5 (Supplemental Table I, point 10, $R_1 = 1.705$ Å, $R_2 = 2.155$ Å, intermediate in the optimization) differ by only 0.008 kcal/mol.

(56) (a) Jensen, F.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 3139. (b) Spellmeyer, D.; Houk, K. N., submitted for publication. (c) Ruelle, P.; Kesselring, U. W.; Nam-Tran, H. *J. Am. Chem. Soc.* **1986**, *108*, 371.

(57) (a) Hehre, W. J. *Acc. Chem. Res.* **1976**, *9*, 399. (b) Schaefer, H. F., III *Science* **1986**, *231*, 1100.

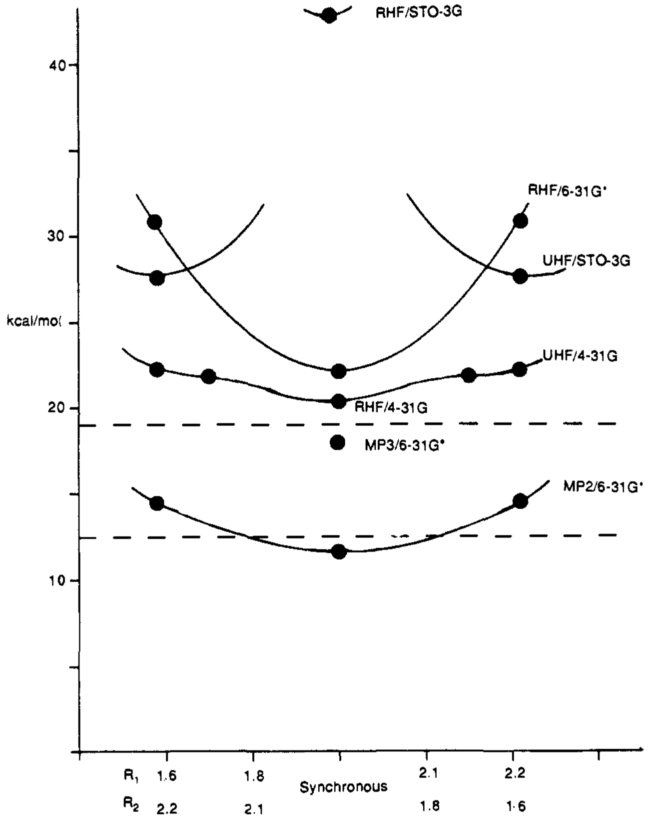

Figure 6. The barrier to decarbonylation of **1** as calculated at various levels of theory. C_s symmetry (σ_v' plane in Figure 1) is maintained. The area within the dotted lines corresponds to the experimental activation energy with the reported error bars.[7,8] Calculated energies are indicated as ● and the shape of the potential surfaces is based on frequency calculations. Synchronous structures are calculated at the RHF or RMP2 levels (see Table V) and are corrected for zero-point vibrational energies (−2.0 kcal/mol). The nonsynchronous ones are calculated at the UHF or RMP2 levels (see Table VI). Although the zero-point vibrational energy correction is based on the synchronous transition state, and is not directly applicable to the nonsynchronous transition state, the values from Table VI were reduced by 2.0 kcal/mol to make them more directly comparable to the energies for the synchronous structures.

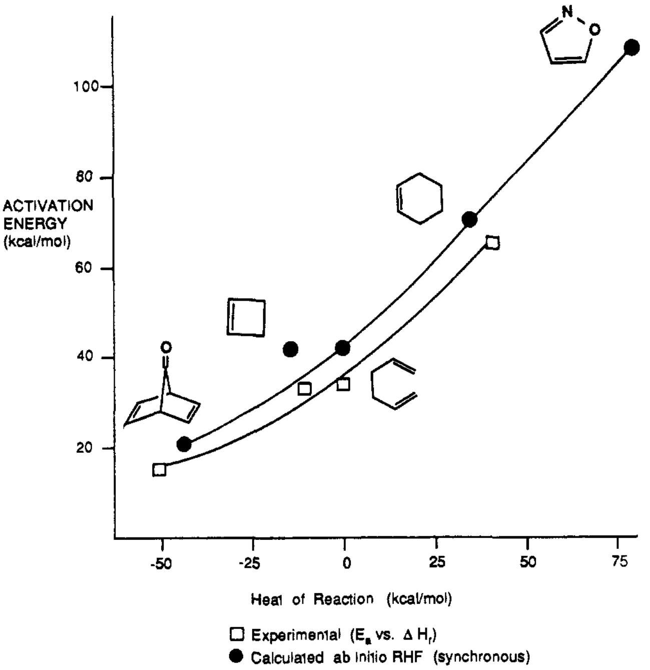

Figure 7. The activation energy vs the heat of reaction for a series of pericyclic reactions. The calculated energies are all at the RHF/3-21G or RHF/4-31G levels, are for synchronous transition states, and are not corrected for the zero-point vibrational energy. The curves are fitted to the points by inspection. References: fragmentation of bicyclo[2.2.1]hepta-2,5-dien-one, experimental activation energy;[7] heat of reaction from group equivalents;[7,60] calculated, this work; ring opening of cyclobutene, experimental,[58a] calculated;[56b,58b] Cope reaction of 1,5-hexadiene, experimental,[58c] calculated;[13a] retro-Diels–Alder reaction of cyclohexane, experimental,[58d] calculated[13b–l] (RHF/3-21G energy of cyclohexene = −231.729152 hartrees); retro 1,3-dipolar addition of fulminic acid and acetylene, experimental,[11d] calculated.[50]

of semiempirical calculations (E_a = 22.5 kcal/mol, MINDO/3).[25b] Furthermore, this number is not expected to change drastically at higher levels. Calculations on other systems suggest that activation energies calculated at the MP2, MP3, and MP4 (STDQ) levels oscillate, with the MP2 value lower, the MP3 value higher, and the MP4 (STDQ) value in between the two;[29e,56] thus one would expect the MP4/6-31G* (FC) activation energy to be between 12 and 18 kcal/mol, and probably around 15 kcal/mol. This predicted value remains within the experimental error for the observed reaction.

In conclusion, although fairly high level (MP3/6-31G*) single-point calculations are required here to reliably reproduce the experimental activation energy, the geometry of the transition state and the gross features of the potential surface seem to be well reproduced at the RHF/4-31G level. Although it was prudent to search for a nonsynchronous pathway, it is only found at low levels of theory and does not persist at higher levels.

Activation Energies for Other Pericyclic Reactions. A corollary of the Hammond postulate[51] suggests that within a series of similar reactions, the more exothermic ones should have lower activation energies. Recently, it has been demonstrated that this is observed experimentally for a series of allowed pericyclic fragmentations.[7] Ab initio calculations, even at the RHF level, do in fact reproduce the experimental results[7,11d,58] over a wide range of exothermicities, as shown in Figure 7. These results are for RHF calculations with split-valence basis sets and without corrections for zero-point energies and Boltzmann distribution (heat capacity). The E_a seems to be consistently overestimated by about 5 kcal/mol. It should be recognized that these calculated activation energies are all for the synchronous pathways.

The Hammond postulate applies only to similar reactions. These reactions are quite diverse, including three different types of fragmentations, an electrocyclic ring opening, and a sigmatropic rearrangement. Thus there is no necessity that they be so well correlated. However, the RHF calculations based on a synchronous model reproduce the experimental trends. *This strongly supports the contention that all of these reactions are in fact synchronous.*

Heat of Reaction for the Decarbonylation of 1. Heats of reaction are particularly hard to accurately derive from ab initio data.[29g,59] The situation is more difficult when hybridization changes accompany the reaction. To minimize problems associated with rehybridization, comparisons are often made by using isodesmic or homodesmic reactions to obtain heats of reaction. In this way an effort is made to compare molecules with the same type and number of bonds in an attempt to obtain the greatest cancellation of errors. For calculations done at the MP2/6-31G* level this approach works well for most molecules.[59] Unfortunately even this approach does not reproduce the heat of formation of benzene well.[59]

When a reaction such as the decarbonylation of bicyclo[2.2.1]hepta-2,5-dien-7-one is considered, the situation may be even worse. Not only is benzene a product, but the hybridization of the atoms is changing drastically. This is more pronounced for the heat of reaction than for the activation energy, for which

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[58] (a) Cooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220. (b) Houk, K. N.; Rondan, N. *J. Am. Chem. Soc.* **1985**, *107*, 2099. (c) Doering, W. v. E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971**, *27*, 5299. (d) Sauer, J.; Sustman, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

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Table VI. Heat of Reaction for the Decarbonylation of Bicyclo[2.2.1]hepta-2,5-dien-7-one (**1**) As Calculated at Various Levels of Theory[e]

level of theory	ΔH_r (kcal/mol)	references CO	references C_6H_6
group equivalents	−51	7	7
MINDO/3	−38.9	25b	25b
MINDO	−40.8	25b	25b
AM1	−20.7	34	34
RHF/3-21G	−43.2	*a*	42b
RHF/4-31G	−52.3	33c	*b*
RHF/6-31G*//RHF/4-31G	−53.1	*c*	*c*
RHF/6-31G*	−52.8	*d*	42b
MP2/6-31G*(FC)//RHF/6-31G*	−33.7	*a*	59
MP3/6-31G*(FC)//RHF/6-31G*	−35.4	*a*	*c*

[a] Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2792. [b] Unpublished results. [c] This work. The energy for CO is RHF/6-31G*/RHF/4-31G = −112.737 337 hartrees. The energies for benzene are RHF/6-31G*/ /RHF/4-31G = −230.070 305, MP3/6-31G*(FC)//RHF/6-31G* = −231.485 222 hartrees. [d] Whiteside, R. A.; Frisch, M. J.; Pople, J. A. *The Carnegie-Mellon Quantum Chemistry Archive*; Carnegie-Mellon University: Pittsburgh, PA, 1986. [e] The ab initio values have not been corrected for the zero-point energy. There is no experimental heat of formation of **1** for comparison.

the calculation appears to reproduce the experimental results.

The heat of reaction as calculated at various levels of theory is presented in Table VI. Those values from the ab initio calculations have not been corrected for differences in zero-point energies. Note that the RHF and MP energies are different, but that the MP2 and MP3 energies are fairly close. The latter values suggest that the reaction is somewhat less exothermic than calculated from group equivalents.[60] The caveats discussed above, and especially the lack of an experimental value for comparison, leave some ambiguity about the calculated *heat of reaction*. However, this should *not* detract from the agreement between the calculated and experimental *activation energies*.

Calculated and Experimental Infrared Spectra of 1 and 1-d_6

In principle, analysis of the experimental infrared and Raman spectra of a large number of isotopic variants of a molecule allows the assignment all of the bands and the derivation of a set of force constants (not necessarily unique) to describe the molecule.[61] In practice, laborious syntheses are needed just to obtain the necessary molecules for spectroscopic study. For bicyclo[2.2.1]hepta-2,5-dien-7-one (**1**), this would indeed be a formidable task, given the multistep synthesis and the final low-temperature photolysis required. The synthesis of bicyclo[2.2.1]hepta-2,5-dien-7-one-d_6 (**1**-d_6) required a substantial revision of the synthetic approach,[7] and several more isotopic variants would be required for a full vibrational analysis in the conventional manner. Furthermore, no Raman spectrum of **1** has yet been obtained. This is technically more difficult than obtaining a matrix-isolated IR spectrum. Thus a vibrational assignment of **1** is not likely solely from the experimental data.

Nevertheless, such an analysis would in fact be quite useful. It would demonstrate the symmetry of the molecule, which is of some relevance to the symmetry of the transition state. Furthermore, the observed IR spectrum of **1** apparently exhibits a splitting of the carbonyl band which may be due to Fermi resonance.[7] A determination of the symmetries of the bands possibly involved would increase the level of confidence in that assumption. The exclusion of other potential photoproducts (i.e., ethylenedione) rests in turn on the assignment of all the observed carbonyl bands to **1**. Accordingly, we have made use of theoretical frequencies and intensities calculated by ab initio methods in analogy to similar calculations in the literature.[62]

Table VII. Fundamental Harmonic Vibrational Frequencies of Bicyclo[2.2.1]hepta-2,5-dien-7-one (**1**) As Calculated at the RHF/4-31G Level[f]

calcd freq (cm^{-1})	symm	IR intens.	Raman intens.	corrected[a] freq (cm^{-1})	obsd IR freq (cm^{-1})	error
193.5	B1	2	2	172		
437.5	B2	7	12	389		
452.1	A1	7	9	402		
503.1	A2	0	4	448		
628.9	B2	0	2	560		
656.0	A1	7	5	584	575	+9
804.6	B1	48	0	716	716	0
813.5	A1	38	3	724	722[b]	+2
820.4	A2	0	3	730		
877.2	B1	0	2	781		
918.5	B2	28	0	817	791	+26
938.0	A1	58	3	835	809	+26
963.8	B2	0	0	858		
1010.7	B1	0	6	900		
1028.1	A1	9	17	915	937	−22
1029.9	A2	0	0	917		
1120.3	A2	0	0	997		
1139.7	B2	2	1	1014	1026	−12
1180.1	B2	11	0	1050	1039[c]	
1213.8	B1	0	2	1080		
1255.4	A1	3	30	1117	1112	+5
1320.1	A1	1	8	1175	1160[d]	+15
1325.4	B2	0	3	1180		
1369.1	B1	9	1	1218	1207	+11
1414.2	A2	0	11	1259		
1446.9	A2	0	1	1288		
1488.4	B2	12	0	1325	1317	+8
1758.3	B1	1	7	1565		
1797.5	A1	0	22	1600		
1972.1	A1	466	8	1755	1808[e]	−53
3337.2	B2	21	33	2970		
3339.5	A1	5	146	2972		
3406.6	A2	0	126	3032		
3408.5	B2	4	36	3034		
3434.7	B1	15	57	3057		
3438.1	A1	4	230	3060		

[a] This is the calculated frequency time 0.89; see the text for the justification. [b] In a nitrogen matrix the 716-cm^{-1} band appears to be split into two bands. [c] This region of the spectrum is obscured by starting material. [d] Tentatively identified in the spectra; a very weak band. [e] Estimated in the absence of Fermi resonance; see the text for an explanation. [f] Correlation of the calculated vibrations with the observed infrared absorptions of **1**.

A set of force constants is obtainable from an ab initio calculation by evaluating the analytical second derivatives of the wave function.[29h,62] Harmonic vibrational frequencies can be derived from the force constants. These were obtained for bicyclo[2.2.1]hepta-2,5-dien-7-one at the RHF/4-31G level and used above to obtain the zero point energy corrections. They are reported in Table VII, along with the symmetry descriptions of the modes, the calculated IR and Raman intensities, and the observed IR frequencies. To facilitate comparison, the observed spectrum is presented graphically in Figure 8A and those calculated bands between 2000 and 600 cm^{-1} which have integrated IR intensities above 3 km/mol are similarly in Figure 8B. It is evident from inspection of these figures that while the calculated band locations differ significantly from the experimental ones, the patterns are similar. It appears that the band positions are all shifted to higher frequencies, while the band intensities seem reasonably well reproduced.

Systematic investigations of calculated harmonic vibrational frequencies at the HF level with split valence basis sets and for

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(62) (a) Raine, G. P.; Schaefer, H. F., III; Haddon, R. C. *J. Am. Chem. Soc.* **1983**, *105*, 194. (b) Hess, A. B., Jr.; Schaad, L. J.; Polavarapa, P. L. *J. Am. Chem. Soc.* **1984**, *106*, 4348. (c) Hout, R. F., Jr.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *3*, 234. (d) Hess, B. A., Jr.; Schaad, L. J.; Carsky, P.; Zahradnik, R. *Chem. Rev.* **1986**, *86*, 709. (e) Pulay, P. *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977; Vol. 4, pp 153–185.

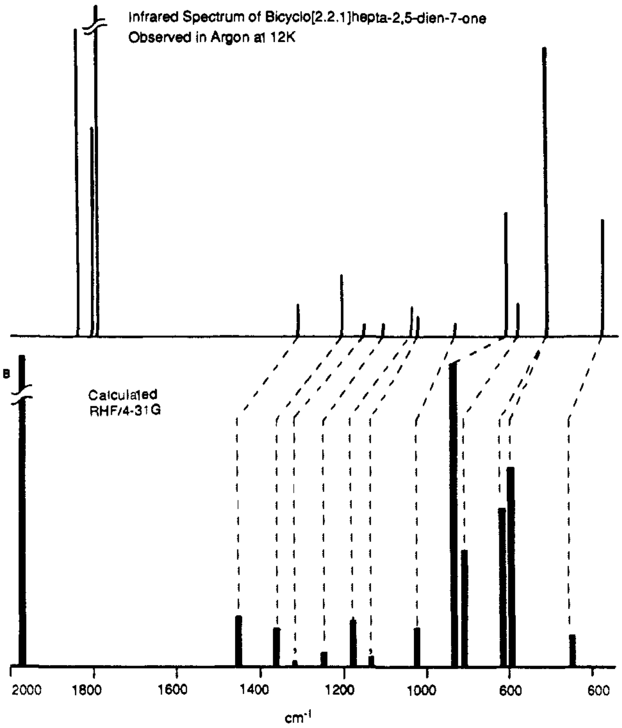

Figure 8. (A) The infrared spectrum of bicyclo[2.2.1]hepta-2,5-dienone observed in an argon matrix at 12 K.[7] The approximate intensities are estimated from peak heights. (B) The infrared spectrum as calculated at the RHF/4-31G level. Note the close correspondence between the calculated and observed band locations and intensities (although the locations are consistently calculated at higher frequencies). See the text and Table VII for further discussion of the assignments.

a variety of molecules have amply demonstrated that this is a consistent trend.[62] Although elaborate scaling schemes have also been proposed,[62e] the use of a single empirical scaling factor (between 0.9 and 0.85) gives close agreement between the calculated (harmonic) and experimental (anharmonic) band locations.[29h,63] Since absolute intensity data are less often obtained from experiment, it is not clear if those data also require scaling. Although such an empirical scaling means that the results are not strictly ab initio, this particular application is general and well precedented, as well as being useful.[62]

Therefore the corrected vibrational frequencies (after multiplication by 0.89) are also reported in Table VII. When these are compared to the experimental values, a much better agreement is observed, and most assignments are readily apparent. The observed bands at 575, 781, 809, 937, 1026, 1112, 1207 cm^{-1} and the carbonyl absorption (whose fundamental is estimated to be at 1808 cm^{-1}) can all be assigned with some confidence. The band locations and relative intensities both agree between theory and experiment. There are only a few difficulties. The calculation predicts two bands close together at 724 and 732 cm^{-1}, but in argon only one is observed at 716 cm^{-1}. This seems attributable to an accidental degeneracy in the experimental spectra. Support for this interpretation may be found in the spectrum of **1** generated in a nitrogen matrix, where the band seems to be split into two, at 722 as well as 716 cm^{-1}. This must be considered a tentative assignment.[7c] Finally, it should be noted that there is a band predicted to occur around 1060 cm^{-1} that is not observed. There are several absorptions from the photochemical precursor in this region,[7] and they would obscure a weak band from **1**. Spectral subtraction seems to suggest the presence of a band, but it is simply not possible to say whether there is a band there or not.[7c]

With these two minor caveats, the IR spectrum can be assigned to symmetry classes as in Table VII. The remaining error in the corrected band locations is also indicated. The agreement between

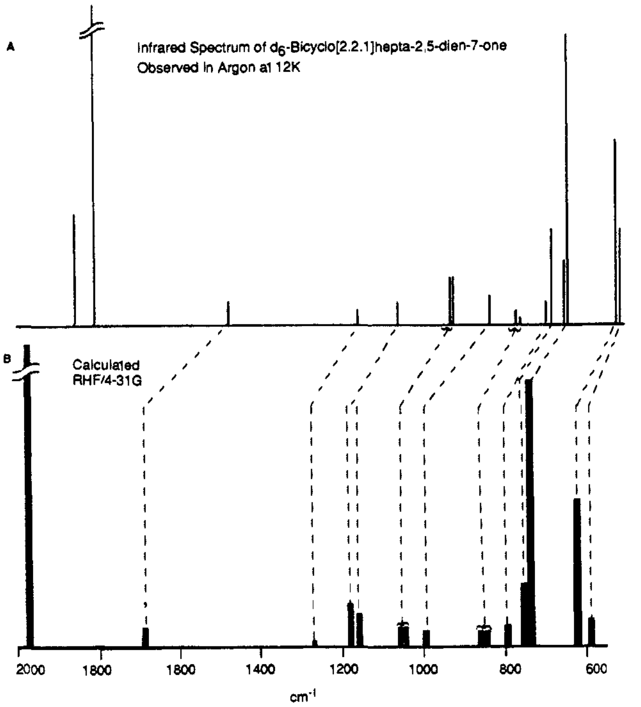

Figure 9. (A) The infrared spectrum of bicyclo[2.2.1]hepta-2,5-dien-one-d_6 observed in an argon matrix at 12 K.[7] (B) The infrared spectrum as calculated at the RHF/4-31G level. See Figure 8 for explanation; see text and Table VIII for further discussion.

the experimental and theoretical band locations and intensities is remarkable; the reader is reminded that the only assignments possible without the calculation were the carbonyl stretch and the CH wag.[7a,b]

It was suggested in the original identification of **1** that Fermi resonance might lead to the multiple carbonyl bands observed.[7a,b] The assignment of the frequencies here allows this. Resonance is possible between the combination band of the 722- and 1112-cm^{-1} bands (1834 cm^{-1}) and the carbonyl (1808) since all the bands are of A_1 symmetry, but at least two other combination bands might also be involved. The bands at 1092 (calculated) and at 716 cm^{-1} (observed) are both of B_1 symmetry; their combination band would be around 1808 cm^{-1} and of A_1 symmetry. The B_2 bands observed at 1026 and 781 cm^{-1} could also lead to an A_1 combination band at 1807 cm^{-1}. Thus it would seem any or all of these three bands might contribute to the observed splitting of the "carbonyl stretching" absorption into three. The spectrum is clearly more complicated than expected just from a single resonance, and it seems likely that more than one interaction leads to the observed splitting. However, it is not now possible to assign the observed bands at 1846, 1801, and 1795 cm^{-1} to any particular set of possible Fermi resonances.

The IR spectrum of bicyclo[2.2.1]hepta-2,5-dien-7-one-d_6 has also been reported.[7] The force constant matrix obtained for the protio compound should be equally valid for any symmetrically substituted isotopic variant, and for the hexadeuterio compound in particular.[61] On the basis of the RHF/4-31G force constant matrix for the ground state of bicyclo[2.2.1]hepta-2,5-dien-7-one (**1**), the frequencies[64] and IR intensities[65] of the vibrations of bicyclo[2.2.1]hepta-2,5-dien-7-one-d_6 were obtained. They are reported in Table VIII and graphically in Figure 9B and compared to the experimentally observed IR absorptions in Figure 9A. Once again the agreement is quite good.

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(64) Chapman, O. L.; Miller, M., University of California, Los Angeles, California, ISO, a program for calculation of vibrational frequencies of isotopically substituted molecules. Based on GAUSSIAN82, ref 43a.

(65) Chapman, O. L.; Miller, M., University of California, Los Angeles, California, INTEN, a program for calculation of IR intensities from applied external electric fields. Based on ref 66.

(66) Komornicki, A.; McIver, J. W., Jr. *J. Chem. Phys.* **1979**, *70*, 2014.

Table VIII. Fundamental Harmonic Vibrational Frequencies of Bicyclo[2.2.1]hepta-2,5-dien-7-one-d_6 (**1**-d_6) As Calculated at the RHF/4-31G Level[d]

calcd freq (cm^{-1})	symm	IR intens.	corrected[a] freq (cm^{-1})	obsd IR freq (cm^{-1})	error
184.6	B1	2	164		
385.2	A1	11	343		
406.2	B2	7	362		
439.8	A2	0	391		
542.5	B2	0	483		
598.7	A1	5	533	516.6	+16
626.8	B1	27	558	521.8	+36
754.8	A1	50	672	641.3	+31
				652.2[b]	
756.2	B2	12	673	684.1	−11
764.0	A2	0	680		
791.9	A1	4	705	698.3	+7
824.5	A1	0	734		
834.6	A2	0	743		
839.9	B1	0	748		
863.0	B2	3	768	760	+8
869.8	B1	3	774	765	+9
882.0	B2	0	785		
914.6	A2	0	814		
997.7	B2	13	888	839.2	+49
1054.0	A1	4	938	926.1	+12
1059.2	B2	4	943	932.4	+11
1100.0	A1	0	979		
1114.6	A2	0	992		
1159.8	B1	6	1032	1058.7[c]	
1181.3	B2	8	1051	1058.7[c]	
1268.9	A2	0	1129		
1272.3	B2	1	1132	1159.6	−28
1684.7	B1	4	1499	1478.9	+20
1733.3	A1	1	1543		
1968.3	A1	463	1752	1808	−56
2463.5	B2	12	2193		
2470.3	A1	4	2199		
2511.7	A2	0	2235		
2513.6	B2	1	2237		
2569.7	B1	7	2287		
2573.4	A1	1	2290		

[a] This is the calculated frequency times 0.89; see the text. [b] This observed absorption may be due to Fermi resonance of the observed band at 641.3 cm^{-1} and the overtone of the first A1 band at 343 cm^{-1} (calculated, scaled). [c] This assignment is ambiguous. Only one of the predicted bands is observed; the other may be obscured by starting material. [d] Correlation of the calculated vibrations with the observed infrared absorptions of d_6-**1**.

There are a few differences between the calculated and observed spectra of the d_6 compound. The experimental spectrum has an absorption at 652.2 cm^{-1} which cannot be accounted for directly in the calculated spectrum. This may, however, be due to Fermi resonance between the observed band at 641.3 cm^{-1} and the overtone of the first A_1 band at 343 cm^{-1} (calculated and scaled by 0.89). Similarly, there are two carbonyl absorptions, a strong one at 1808 cm^{-1}, and a weak one at 1891 cm^{-1}. The overtone of either the A_1 band at 926.1 cm^{-1} (observed) or the B_2 band at 932.4 cm^{-1} (observed) might be involved in Fermi resonance with the carbonyl. Two absorptions are calculated at 1032 and 1051 cm^{-1}, but only one is observed at 1058.7 cm^{-1}. This band is close to several absorptions in the starting material. The other predicted band may be obscured.[7c]

Two other general comments about the calculated versus observed spectra are in order. First, the assignments in Tables VII and VIII must be considered tentative. Particularly when two or more bands are closely spaced, there is no guarantee that the closest match between the calculated and observed spectra is the best assignment. Nonetheless, as assigned, the average error in the scaled frequencies for **1** is 16 cm^{-1}, and for **1**-d_6 it is 22 cm^{-1}. This is in reasonably close agreement with experiment. Second, the only bands not observed in the experimental spectra which are expected and are predicted calculationally are the C–H and C–D stretches, between 3060 to 2970 and 2290 to 2193 cm^{-1}, respectively. Experimental difficulties may have contributed to their not being observed.[7c]

Although the detailed description of the vibrational spectrum of **1** and **1**-d_6 is still not complete, the use of the calculated harmonic frequencies has greatly extended the understanding of the experimental IR spectra. Conversely, the reasonable agreement between the calculated and observed spectra provides the only direct experimental validation of the geometry calculated for the ground state of **1**. While the calculated geometry is similar to analogous molecules, and there is every reason to expect that a Hartree–Fock calculation with the 4-31G basis set should give a reasonable geometry, that is not a guarantee that **1** in fact has the calculated geometry. However, if the calculated geometry were significantly different than the actual one, either in terms of symmetry or overall bonding, then the calculated IR spectra would not have been expected to match the experimental ones as well.[29b,62e] In fact since the calculation after correction appears to underestimate the strength of the C=O stretch (1755 cm^{-1} corrected, 1808 cm^{-1} experimental) and overestimate the strength of the bridgehead C—C stretch (835 cm^{-1} corrected, 809 cm^{-1} experimental), it may be that the ground state is even more distorted toward products than the RHF/4-31G calculations indicate. Thus, the IR spectra vindicate the initial assumption of C_{2v} symmetry and provide indirect support for the contention that the geometry is distorted toward products.

Discussion

Bicyclo[2.2.1]hepta-2,5-dien-7-one has a remarkably low activation energy for decarbonylation. This is reproduced by ab initio calculations that indicate it follows a synchronous concerted pathway. In terms of the Woodward–Hoffmann rules this is a linear suprafacial mechanism. The question remains, is such a low barrier to be expected? There are several factors that are involved. The first is simply that there is an orbital symmetry allowed pathway that is accessible to the molecule. Furthermore, the orbitals are aligned so that they may overlap to take full advantage of this mechanism.

Clearly this is not a sufficient explanation. There is an experimental correlation between the overall exothermicity of allowed pericyclic fragmentations and the observed activation energies.[7a,b,67] A retro Diels–Alder reaction to give acetylene and cyclopentadienone is also allowed by orbital symmetry, but the much more exothermic fragmentation to benzene and carbon monoxide is observed. On the basis of the above correlation, and an estimate of the exothermicity of the decarbonylation of **1**, an activation energy of ≈18 kcal/mol was suggested.[7b] This value is the same as calculated at the MP2/6-31G* level. Clearly, the large exothermicity for the decarbonylation of **1** manifests itself in the observed low activation energy.

Depending upon structure, product stabilization or reactant destabilization may make the major contribution to changes in the exothermicity along a series of reactions. MM2 calculations[68] suggest that **1** is more strained than bicyclo[2.2.1]hept-2-en-7-one by 5 kcal/mol.[7c] Landesberg and Sieczkowski[4] have suggested that electron donation from the olefins into antibonding orbitals of the carbonyl contributes to the instability of **1**. This may be, but then a similar effect should also destabilize the dibenzannelated compound **3**; this is not observed.

Product stability must also play a major role in the case of **1**, as the reaction produces two very stable fragments, benzene and carbon monoxide. Recently, Grimme[67] has demonstrated that in a series of retro-Diels–Alder reactions the gain in resonance energy is correlated with a decrease in the activation energy, in analogy to the more general correlations in Figure 7 and ref 7a,b. Because the gain in resonance energy obtained by aromatization of the central ring of anthracene is less than that for benzene, it is to be expected that **3** is kinetically 8 kcal/mol more stable than **1**.[67] Furthermore, the stability of **2** relative to **1** might be at-

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tributed to larger resonance energy in benzene as opposed to benzene iron tricarbonyl.

Conclusions

The ab initio calculations seem to represent the ground state and transition state of bicyclo[2.2.1]hepta-2,5-dien-7-one reasonably well. The ground-state geometry with C_{2v} symmetry seems reasonable when compared to similar molecules whose geometry is known, and leads to calculated IR spectra of bicyclo[2.2.1]-hepta-2,5-dien-7-one and bicyclo[2.2.1]hepta-2,5-dien-7-one-d_6 which closely match the experimental ones. This geometry appears distorted toward products, which in turn suggests that the transition state is symmetrical. A transition state with C_{2v} symmetry is indeed found. This appears to be a transition state when correlation effects are included at the MP2/4-31G level as well. Furthermore, the activation energy at the MP3/6-31G* level agrees quite closely with the experimental value, and reasonable extrapolation to the MP4/6-31G* level suggests that one should expect even better agreement there. While a nonsynchronous transition state is found at the UHF/STO-3G level, this does not persist at higher levels. The C_{2v} geometry is lower in energy than the nonsynchronous ones with the 4-31G basis set at both RHF and UHF levels, and at the MP2/6-31G* level. The synchronous transition state explains the observed pattern of reactivity of **1** and other norbornenones. Furthermore, it completes a correlation of the exothermicity and reactivity for a series of pericyclic concerted reactions that ab initio calculations suggest all follow synchronous pathways. In the case of bicyclo[2.2.1]hepta-2,5-dien-7-one (**1**), even the ground-state geometry prefigures a symmetrical transition state. Thus while no mechanism can ever be "proven", the synchronous mechanism as reflected by the ab initio calculations provides the best available explanation of the experimental trends of these widely disparate reactions.

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Supplementary Material Available: Energies of points in Figure 5, optimized geometries for **1**, synchronous and nonsynchronous transition states, and details of CI calculations (4 pages). Ordering information is given on any current masthead page.

Rotational Barriers in Aldehydes and Ketones Coordinated to Neutral Lewis Acids

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Abstract: Calculations of the energies and geometries of complexes of some aldehydes and ketones with neutral Lewis acids have been performed in order to characterize the conformations and rotational barriers of the Lewis acid–carbonyl complexes and of substituents at the carbonyl. The 6-31G* basis set was used to obtain energies for geometries optimized at 6-31G* or 3-21G, and correction for electron correlation with use of the Møller–Plesset perturbation method was made where practical. Complexes of H_2CO with BH_3, BF_3, AlH_3, and $AlCl_3$ all had bent, C_s symmetry structures as minima, with linear structures 6–10 kcal/mol higher in energy and out-of-plane structures higher still in energy. The effect of BH_3 and BF_3 coordination upon the rotational barriers about the C–C bond adjacent to the carbonyl group of propanal was minimal, while the effect upon the conformational preferences of acetone was pronounced. Rotation about the donor–acceptor bond in the C_s structures of the aldehydes had a barrier of 0.8 to 1.4 kcal/mol with the syn (eclipsed) conformation the minimum for all of the Lewis acids studied, while for acetone the gauche conformations of both the Lewis acid and methyl hydrogens with respect to the carbonyl were lowest in energy.

Lewis acid complexation of carbonyl compounds can have a dramatic effect on the rates and selectivities of reactions at carbonyl centers.[1] There has been much discussion of the mechanisms of Lewis acid catalyzed reactions of carbonyl compounds, and much ambiguity remains. An understanding of the conformations of the Lewis acid–carbonyl complexes and their relative energies and steric requirements is a necessary prerequisite to determining the origin of selectivities and stereochemical preferences in these reactions. In previous papers, we have calculated the conformations and barriers to rotation of some aldehydes, ketones, carboxylic acids, and esters.[2-4] Here we extend these studies to the conformations of aldehydes and ketones coordinated to neutral main group Lewis acids.

Few experimental data are available on the equilibrium geometry of complexes of organic carbonyl compounds with main group Lewis acids. Thus a calculational study should be valuable in elucidating the most stable conformations of the complexes. In addition, calculational methods offer data on conformational energies, rotational barriers, and models for transition states that are difficult or impossible to obtain by experimental measurements. One might hope to get structural and energetic data from molecular mechanics calculations, but parameters for Lewis acid complexes are not well established, so molecular mechanics results would not be reliable. We report here the results of ab initio calculations on conformations and energies of BH_3, BF_3, and AlH_3,

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