were present. GC analysis gave 8 peaks, the largest of which was identified as 9-$i$-$Pr_2N$-FlH.

GC/MS analysis gave 8 peaks with the retention times, areas, and $m/e$ values shown in Table V.

The structures of the compounds with $m/e$ of 347 and 429 were supported further by the MS fragments associated with them:

$$347 \xrightarrow{(-i\text{-}Pr_2N)} FlCH_2CF_3\ (247,\ 100\%) \xrightarrow{(-CF_3)} FlCH_2\ (178,\ 27.8\%) \xrightarrow{(-CH_2)} HFlH\ (165,\ 4\%)$$

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

**Registry No.** 9-Me-Fl$^-$, 31468-21-0; 9-MeO-Fl$^-$, 71805-70-4; 9-$Me_2N$-Fl$^-$, 83936-70-3; 9-$i$-$Pr_2N$-Fl$^-$, 109495-02-5; 9-$PhCH_2$-Fl$^-$, 53629-11-1; 2-Br-9-$PhCH_2$-Fl$^-$, 103422-01-1; 2,7-$Br_2$-9-$PhCH_2$-Fl$^-$, 109528-77-0; c-$C_6H_{10}(NO_2)Ts$, 41774-12-3; $PhSO_2CH_2Cl$, 7205-98-3; $PhCH_2Cl$, 100-44-7; $i$-BuBr, 78-77-3; $i$-BuI, 513-38-2; $CF_3CH_2I$, 353-83-3.

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# An Experimental and Theoretical Evaluation of the Intramolecular Reactions of Cyclohexyne

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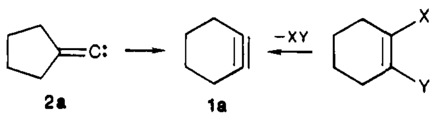
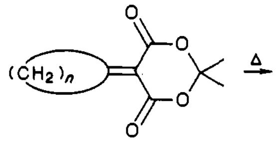
*Received January 28, 1987*

**Abstract:** The intramolecular reactions of cyclohexyne (**1a**) have been explored theoretically by using ab initio calculations at the MP2/6-31G* level and experimentally by examining the ring expansion of cyclopentylidenecarbene (**2a**) at elevated temperatures. The calculations indicate that **1a** is more stable than **2a** by 19.0 kcal/mol and that the barrier for **1a** → **2a** is 26.4 kcal/mol. Carbene **2a** can rearrange to bicyclo[3.1.0]hex-5-ene and thence to cyclohexadiene with a barrier of 38.9 kcal/mol. A higher energy reaction of **1a** is cleavage to ethylene and butatriene in a retro-Diels–Alder reaction, which is calculated to have a barrier of 46.8 kcal/mol. This retro-Diels–Alder reaction is observed experimentally when **2a** is generated by the pyrolysis of the cyclopentylidene adduct of Meldrum's acid.

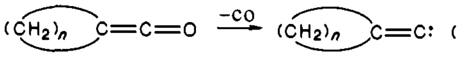
Although cycloalkynes with eight or more carbons[1] and certain substituted cycloheptynes[2] are isolable, the chemistry of the smaller ring cycloalkynes has mainly been inferred from intermolecular trapping reactions.[3] Consequently, there is little known about the intramolecular reactivity of these interesting species. In this paper, we report a theoretical and experimental evaluation of the intramolecular chemistry of cyclohexyne (**1a**). Methods of preparing cyclohexynes include $\beta$-elimination reactions of substituted cyclohexenes[4] and ring expansion of cyclopentylidenecarbene (**2a**) as illustrated in eq 1.[5] Thus, carbene **2a**, when generated by elimination, ring expands to cyclohexyne (**1a**), which may then be trapped with a suitable reagent.[5] An interesting pyrolytic method of preparing cycloalkylidenecarbenes (**2**) in which the cycloalkylidene derivatives of Meldrum's acid (**3**) are thermolyzed via methylene ketenes (**4**) to give **2** (eq 2) has been reported by Baxter and Brown.[6] However, pyrolysis of Meldrum's acid adduct **3a** gave only 1,3-cyclohexadiene (**5**) and benzene (**6**) (from decomposition of **5**). Since ring expansion of **2a** is observed when this carbene is generated at lower temperatures,[5] these data imply that this ring expansion may be reversible and that a low-energy intramolecular pathway for **1a** may simply be ring contraction to carbene **2a** followed by rearrangement to **5**. Rearrangement of **2a** to **5** is thought to involve an initial C–H insertion to give bicyclo[3.1.0]hex-5-ene (**7**), which subsequently ring opens to 2-cyclohexenylidene (**8**) followed by rearrangement to **5** (eq 3).



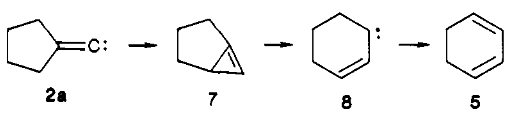
**2a** **1a** (1)



**3a**, $n = 4$
**b**, $n = 5$
**c**, $n = 6$
**d**, $n = 7$



**4** **2** (2)



**2a** **7** **8** **5** (3)

In order to investigate the feasibility of rearrangement of **1a** to 1,3-cyclohexadiene, we have carried out an ab initio molecular orbital study of the energetics of this system. Since these calculations predict an additional first-order pathway for **1a**, we have also reinvestigated the pyrolysis of **3a** in order to search for this process.

## Results

**Molecular Orbital Calculations.** In these ab initio calculations, which utilized the GAUSSIAN 82 program,[7] geometries were optimized with the 3-21G basis set and single-point calculations were made at the 6-31G, the 6-31G*, the MP2/6-31G, and the

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**Table I.** Energies (hartrees) of Relevant Species along the $C_6H_8$ Surface at Various Computational Levels

| molecule | 3-21G | 6-31G | MP2/6-31G | 6-31G* | MP2/6-31G* | ZPE (NEV)[a] |
|---|---|---|---|---|---|---|
| **1a** ($C_{2v}$) | -230.43876 | -231.62822 | -232.17792 | -231.72110 | -232.49775 | 81.93 (1) |
| **1a** ($C_2$) | -230.45034 | -231.63936 | -232.19178 | -231.73365 | -232.51316 | 82.08 (0) |
| **2a** ($C_2$) | -230.45586 | -231.64868 | -232.15875 | -231.74157 | -232.48170 | 81.29 (0) |
| TS1-B+E ($C_{2v}$) | -230.36742 | -231.55665 | -232.12258 | -231.63649 | -232.43302 | 78.57 (1) |
| TS1-2 ($C_1$) | -230.41635 | -231.60477 | -232.13648 | -231.70780 | -232.46894 | 80.73 (1) |
| TS2-BY ($C_1$) | -230.35592 | -231.54998 | -232.10499 | -231.65813 | -232.44492 | 78.15 (1) |
| === + = | -230.43983 | -231.64245 | -232.16304 | -231.72174 | -232.46820 | 75.67 (0) |
| **13** ($C_s$) | -230.43129 | -231.63058 | -232.13669 | -231.72371 | -232.46162 | 79.84 (1)[b] |

[a] Zero-point energy in kcal/mol and the number of negative eigenvalues of the force constant matrix in parentheses. [b] The negative eigenvalue indicates a favorable out-of-plane distortion of the five-membered ring.

**Table II.** Relative Energies (kcal/mol) of Relevant Species along the $C_6H_8$ Surface at Various Computational Levels

| molecule | 6-31G | MP2/6-31G | 6-31G* | [MP2/6-31G*][a] | MP2/6-31G* | MP2/6-31G* + ZPC |
|---|---|---|---|---|---|---|
| **1a** ($C_{2v}$) | 6.99 | 8.70 | 7.88 | 9.59 | 9.67 | 9.52 |
| **1a** ($C_2$) | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| **2a** | -5.85 | 20.73 | -4.97 | 21.61 | 19.75 | 18.96 |
| TS1-B+E | 51.92 | 43.44 | 60.99 | 52.51 | 50.30 | 49.79 |
| TS1-2 | 21.71 | 34.71 | 16.23 | 29.23 | 27.76 | 26.41 |
| TS2-BY | 56.10 | 54.48 | 47.40 | 45.78 | 42.83 | 38.90 |
| === + = | -1.94 | 18.04 | 7.48 | 27.46 | 28.22 | 21.81 |
| **13** ($C_s$) | 5.51 | 34.58 | 6.24 | 35.31 | 32.35 | 30.11 |

[a] Additivity approximation.[8]

MP2/6-31G* levels. Geometries calculated for relevant species along the $C_6H_8$ energy surface are shown in Figure 1 along with their energies relative to the $C_2$ symmetry structure of **1a**. Absolute energies and zero-point energies of relevant species are given in Table I while relative energies in kcal/mol are given in Table II.

Correlation and polarization effects are both important in determining relative energies of species on the $C_6H_8$ potential energy surface. A comparison of the energies of **1a** and **2a** shows that polarization has little effect, while correlation causes a 25 kcal/mol difference in energies. At the 6-31G* level **2a** is predicted to be 5.0 kcal/mol more stable than **1a**, while at the MP2/6-31G* level **1a** is 19.8 kcal/mol more stable than **2a**. We have also estimated the effects of correlation and polarization by using the additivity principle ([MP2/6-31G*], Table II), in which the effects of polarization and correlation on a 6-31G calculation are simply added.[8] Since this approximation yields energies within 3 kcal/mol of those obtained by an actual MP2/6-31G* calculation, its use provides a convincing demonstration that accurate results can be obtained by combining the results of two relatively inexpensive calculations. Unless otherwise stated, energetics in the subsequent discussions are derived from energies at the MP2/6-31G* level, including zero-point corrections.

The lowest energy conformer of **1a** is nonplanar with $C_2$ symmetry and carbons 4 and 5 out of the plane of the triple bond by 24.4°. A planar cyclohexyne is calculated to be less stable by 9.5 kcal/mol. A recent theoretical study of cyclopentyne has found that a structure of $C_s$ symmetry is 0.04 kcal/mol more stable than the $C_{2v}$ structure.[9] As expected, the triple bond in **1a** is stronger than that in cyclopentyne, as indicated by the triple-bond stretching frequency, which is calculated to be 341 $cm^{-1}$ higher in **1a** (1828 $cm^{-1}$, $C_5H_6$; 2169 $cm^{-1}$, $C_6H_8$; 0.89 scaling factor), and the triple-bond distance, which is 0.042 Å shorter in **1a** (1.238 Å, $C_5H_6$; 1.196 Å, $C_6H_8$).

The HOMO of **1a** is predicted to be the symmetric $\pi$ orbital of the triple bond lying in the pseudo plane of the ring. The optimum geometry of **2a** is also of $C_2$ symmetry with carbons 3 and 4 twisted about the symmetry axis by 25.5°. The lowest energy intramolecular reaction of **2a** is calculated to be rearrangement to **1a**, a process that has a barrier of only 7.4 kcal/mol via transition state TS1-2. The rather long breaking and forming C–C bonds in TS1-2 are indicative of a species in which the migrating $CH_2$ group is weakly complexed to the unsaturated carbon–carbon linkage (Figure 1). The transition state for intramolecular C–H insertion by **2a** (TS2-BY) to give bicyclo[3.1.0]hex-5-ene (**7**) has been located, and this process, depicted in eq 3, is calculated to have a barrier of 19.9 kcal/mol.[10]

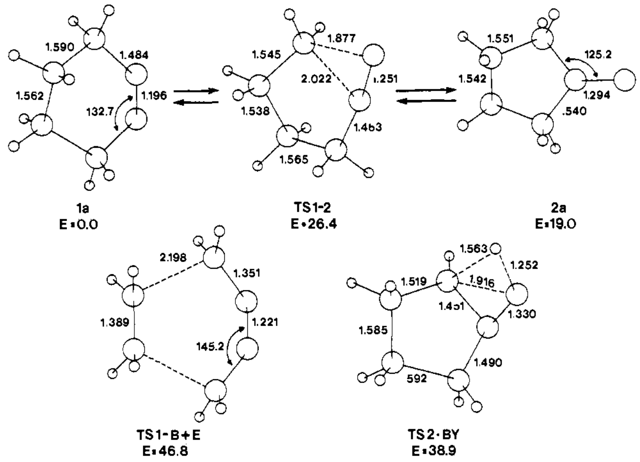
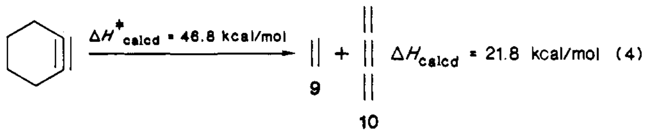


**Figure 1.** Geometries calculated at the 3-21G level for relevant species along the $C_6H_8$ energy surface. Energies are in kcal/mol, bond lengths in angstroms, and angles are in degrees.

Further investigation of the energetics of **1a** revealed that a higher energy reaction of this species is cleavage to ethylene (**9**) and butatriene (**10**) in the retro-Diels–Alder reaction in eq 4. The



(4)

transition state for this process (TS1-B+E) is 20.4 kcal/mol higher in energy than that for rearrangment to **2a**. The energy difference between the two transition states TS1-B+E and TS2-BY is also very sensitive to the inclusion of correlation and polarization. At the 6-31G level TS1-B+E is favored by 4.2 kcal/mol over TS2-

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[10] A Referee has suggested that an alternate route to **5** from **1a** could involve the intermediacy 1,2-cyclohexadiene. We have carried out calculations at the MNDO level[11] to test this hypothesis and have found that the transition state (without CI) is 76 kcal/mol higher than TS1-2 (also calcualted by MNDO). Since the 1,3-sigmatropic shift is a forbidden reaction, while the formation of **2a** occurs via an allowed reaction, further calculations at the ab initio level were not done.

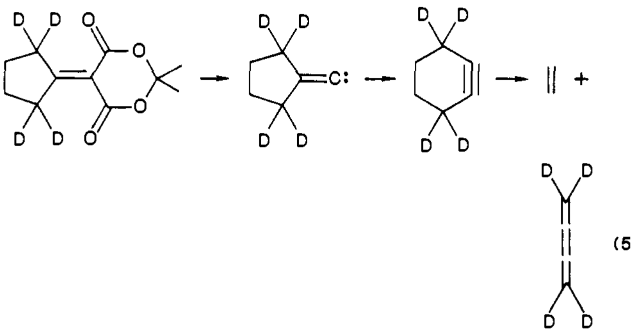
**Table III.** Product Yields (%) at Various Temperatures in the Pyrolysis of **1a** Product

| product | temp, °C | | | |
|---|---|---|---|---|
| | 550 | 575 | 600 | 650 |
| acetone | 101.9 | 102.8 | 89.0 | 100.3 |
| $CO_2$ | 100.0 | 100.1 | 100.0 | 101.0 |
| 1,3-cyclohexadiene (**5**) | 39.2 | 50.5 | 53.1 | 28.1 |
| benzene (**6**) | 3.3 | 3.4 | 4.4 | 3.8 |
| ethylene (**9**) | 11.9 | 19.5 | 20.7 | 17.0 |
| butatriene (**10**) | 4.0 | 5.1 | 4.5 | 4.4 |
| **9**/(**5** + **6**) | 0.28 | 0.36 | 0.36 | 0.53 |

BY. This difference becomes 7.9 kcal/mol, favoring TS2-BY over TS1-B+E at the MP2/6-31G* level.

These calculations predict that the lowest energy intramolecualr reaction of cyclohexyne is rearrangement to 1,3-cyclohexadiene via carbene **2a**. However, a higher energy cleavage to ethylene and butatriene is predicted to compete with this pathway at elevated temperatures. In order to test this possibility, we have reexamined the pyrolysis of **3a**.

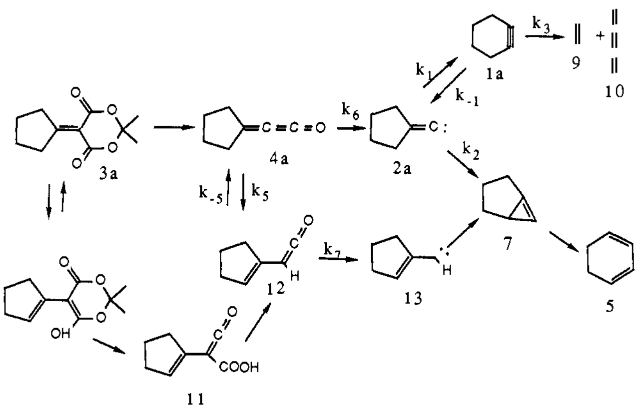
**Pyrolysis of 3a.** The pyrolysis of **3a** was examined over temperatures ranging from 450 to 650 °C. All attempts to trap cyclohexyne by passing the pyrolysate into a cold trap containing such reagents as methanol, isobutene, and 2,5-diphenylisobenzofuran failed. The yields of volatile products observed upon pyrolysis of **1a** at temperatures between 550 and 650 °C are shown in Table III. Under the conditions of these pyrolyses, loss of both $CO_2$ and acetone is essentially quantitative above 550 °C. In addition to the two previously reported hydrocarbon products, cyclohexadiene and benzene (**5** and **6**),[6] two new products, ethylene and butatriene (**9** and **10**), are observed. These latter two products are most easily rationalized as arising via the retro-Diels–Alder reaction in eq 4. The fact that less **10** than **9** is detected is undoubtedly due to the lability of butatriene under the high-temperature reaction conditions.[12] The butatriene has been unambiguously identified from its $^1H$ and $^{13}C$ NMR spectra.[13] The use of 2,2,5,5-tetradeuterio-**3a**, a precursor of 2,2,5,5-tetradeuterio-**2a**,[5,14] led to butatriene-$d_4$ and ethylene-$d_0$, whose IR spectra showed only a trace of ethylene-$d_2$ (eq 5).



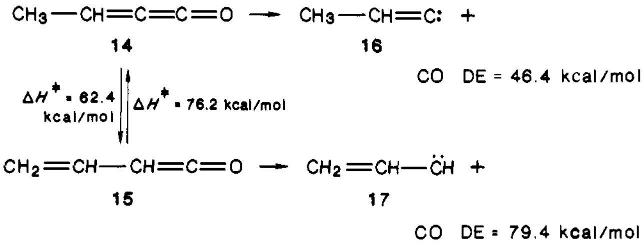
## Discussion

The results of theory and experiment agree in predicting competing intramolecular pathways in the thermal decomposition of **1a**. One path leads to cyclohexadiene while the other generates butatriene + ethylene. However, a competing route to cyclohexadiene in the pyrolysis of **3a** was recently uncovered by Wentrup, Gross, Berstermann, and Lorenčak,[14] who found that, in addition to methylene ketene **4a**, vinyl ketenes **11** and **12** are generated. Vinyl ketene **12** may then lose CO to give vinyl carbene **13**, which may rearrange to **7** and thence to cyclohexadiene. The various pathways to **5**, **9**, and **10** are shown in Scheme I.

**Scheme I**



**Scheme II**



Wentrup, Gross, Berstermann, and Lorenčak[14] were able to observe the IR spectra of ketenes **4a**, **11**, and **12** in the pyrolysis of **3a** by trapping them on a window at 77 K. They were also able to trap all ketenes by the addition of methanol to the pyrolysate. While it is clear that ketenes **4a**, **11**, and **12** are formed in the pyrolysis of **3a**, the relative importance of carbenes **2a** and **13** as precursors to **6** is not known. In order to assess the energetics of the formation of carbenes **2a** and **13** in the pyrolysis of **3a**, we have calculated the energy of **13** and have estimated the bond dissociation energies (DE) and barriers to 1,3-hydrogen migration in ketenes **4a** and **12**.

At the MP2/6-31G* level, carbene **13** was calculated to be less stable than **2a** by 11.2 kcal/mol (Tables I and II). In order to estimate the DE in ketenes **4a** and **12** and the barrier to their interconversion, we have calculated these values for model ketenes **14** and **15** at the MP2/6-31G* level. If we make the assumption that the DE of ketenes **14** and **15** approximates the activation enthalpy for carbene formation, the results of these calculations, shown in Scheme II, indicate that in methylene ketene **14** dissociation is favored over rearrangement by 16.0 kcal/mol. However, the DE of **15** is larger than that of **14** by 33.0 kcal/mol and in this vinyl ketene, rearrangement is favored over dissociation by 3.2 kcal/mol. It is interesting that ketene **15** is more stable than **14** by 13.8 kcal/mol while in the corresponding carbenes the stabilities are reversed, with carbene **16** more stable than **17** by 19.2 kcal/mol. It is undoubtedly these factors that contribute to the low DE of **14** relative to **15**. These DE's may be compared to the experimental[15] and calculated[16] DE of ketene to CO and $^1CH_2$ of 89.1 and 83.4 kcal/mol. If the energetics calculated for model ketenes **14** and **15** can be extrapolated to ketenes **4a** and **12** in Scheme I, we expect that $k_6 > k_5$ and $k_{-5} > k_7$. Hence, the predominate pathway to hydrocarbon products in the pyrolysis of **3a** should be via ketene **4a**.

The cleavage of **1a** in eq 4 is a higher energy process than its rearrangement to **5** in eq 3 but will be entropically favored. Therefore we expect the **9**:(**5** + **6**) ratio to increase with increasing

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(14) Wentrup, C.; Gross, G.; Berstermann, H.-M.; Lorenčak, P. *J. Org. Chem.* **1985**, *50*, 2877.

(15) The experimental $\Delta H_f$ of $^1CH_2$ is taken as 103.1 kcal/mol from the measured $H_f$ of the triplet (Hayden, C. C.; Neumark, D. M.; Shobatake, K.; Sparks, R. K.; Lee, Y. T. *J. Chem. Phys.* **1982**, *76*, 3607) and the observed singlet–triplet splitting (Bunker, P. R.; Jensen, P.; Kaemer, W. P.; Breadsworth, R. *J. Chem. Phys.* **1986**, *85*, 3724). The $\Delta H_f$ of ketene and CO Wiley-Interscience: New York, 1976.

(16) Bouma, W. J.; Nobes, R. H.; Radom, L.; Woodward, C. E. *J. Org. Chem.* **1982**, *47*, 1869

temperature. The data in Table III show that this is the case. Assuming that both **9** and **5** arise only from the equilibrium mixture of **1a** and **2a** ($k_{-5} > k_7$) leads to eq 6 and 7, in which $E_{a5}$

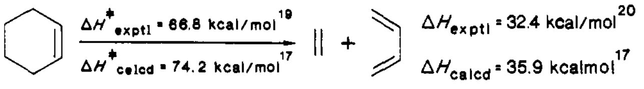
$$\mathbf{9}/(\mathbf{5} + \mathbf{6}) = k_2k_1/k_3k_{-1} \tag{6}$$

$$\ln (\mathbf{9}/(\mathbf{5} + \mathbf{6})) = \ln(A_9/A_5) + (E_{a5} - E_{a9} - \Delta G)/RT \tag{7}$$

and $E_{a9}$ are the activation energies for the formation of **5** and **9** from **2a** and **1a**, respectively, and $\Delta G$ is the free energy change in going from **1a** to **2a**. Thus, a plot of ln (**9**/(**5** + **6**)) vs. $1/T$ should be linear with a slope that will allow an evaluation of $E_{A5} - E_{A9} - \Delta G$ and an intercept that yields $\Delta S^{\ddagger}_9 - \Delta S^{\ddagger}_5$.

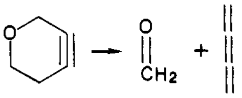
The data in Table III yield such a plot with a correlation coefficient of 0.97, from which $E_{a5} - E_{a9} - \Delta G = -9.1 \pm 1.7$ kcal/mol may be calculated. If the rate-determining step in the formation of **5** is C–H insertion by **2a** to give **7**, this experimental $\Delta E_a - \Delta G$ value may be compared to the theoretically calculated value of −10.4 kcal/mol, in which $\Delta G$ is evaluated by using $\Delta S$ calculated from 3-21G frequencies. The data in Table III also indicate that the entropy of the transition state for the cleavage in eq 4 is more positive than that of the transition state for C–H insertion by **2a** by 8.6 ± 2.0 eu. This entropy difference is significantly underestimated theoretically, where a value of 0.3 eu is calculated by using 3-21G frequencies. Although the remarkable agreement between theory and experiment for $E_{a5} - E_{a9} - \Delta G$ observed above may be somewhat fortuitous, both theory and experiment provide convincing evidence for the existence of competing first-order pathways to the decomposition of **1a**.

It is interesting to compare the cleavage of **1a** in eq 4 with the retro-Diels–Alder reaction of cyclohexene to ethylene and butadiene at eq 8. Both reactions are calculated to be endothermic and to require substantial activation energies. The fact that the activation energy for the reaction in eq 4 is calculated to be lower than that calculated in eq 8 by some 27 kcal/mol may be ascribed to the higher energy of **1a** as compared to cyclohexene. These calculations indicate that the reaction in eq 4 involves a synchronous transition state as do ab initio calculations of the transition state for the reaction in eq 8.[17,18] TS1-B+E is characterized by breaking C–C bond lengths of 2.19 Å and a C–C bond length of 1.38 Å in the developing ethylene (Figure 1). These values may be compared to bond lengths of 2.24 and 1.39 Å recently calculated for the transition state of the reaction in eq 8.[18]



(8)

In a reaction analogous to the retro-Diels–Alder reaction proposed here, Baxter and Brown have reported the cleavage of 4-oxacyclohexyne to **10** and formaldehyde (eq 9).[6]



(9)

The fact that the reverse of the cleavage in eq 4 is calculated to have an activation enthalpy of only 25.0 kcal/mol raises the possibility that cyclohexynes may be synthesized and trapped by the addition of suitable dienophiles to butatriene. We are currently attempting to carry out such reactions.

## Experimental Section

**Pyrolysis of 5-Cyclopentylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (3a).** Compound **3a**[21] was sublimed at 180 °C into a vertical pyrolysis tube 25 cm × 6 mm i.d.) that was heated with an external heating coil. The temperature was measured with a thermocouple placed on the external wall of the pyrolysis tube. The pressure measured at the top of the pyrolysis tube was typically 0.6 mm. Products were passed directly into traps at −78 and −196 °C. The contents of the −196 °C trap were analyzed by IR spectroscopy for ethylene and carbon dioxide, using a standard calibration curve. The contents of both traps were then combined and analyzed by NMR spectroscopy for 1,3-cyclohexadiene, benzene, and butatriene, using dioxane as an internal standard. Product yields at various pyrolysis temperatures are given in Table III.

In order to confirm the presence of butatriene, this compound was synthesized[12] and its NMR measured. The spectra of the synthetic product were the same as those reported in the literature:[13] $^1$H NMR ($CDCl_3$) $\delta$ 5.37 (s); $^{13}$C NMR ($CDCl_3$) $\delta$ 95.6, 170.9. The NMR spectra of the pyrolysis products showed NMR signals identical with those of authentic butatriene.

**Pyrolysis of 5-(2,2,5,5-Tetradeuteriocyclopentylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione.**[6,14] Tetradeuterio-**3a** was prepared by dissolving **3a** (0.5 g) in 10 mL of $D_2O$ with 10 mL of dioxane with several drops of pyridine. After 48 h of stirring and removal of the solvents, the deuteriated product showed a singlet in the $^2$H NMR at $\delta$ 3.1 and peaks in the $^1$H NMR at $\delta$ 1.82 and 1.71 in a 2:3 ratio. When this compound was pyrolyzed as described above, the IR of the contents of the −196 °C trap showed the characteristic C–H bending at 949 cm$^{-1}$ for ethylene-$d_0$ with a very weak absorption at 751 cm$^{-1}$, representing a trace of *asym*-ethylene-$d_2$.[22] The $^2$H NMR of the combined traps showed a singlet at $\delta$ 5.3 for butatriene and peaks at $\delta$ 5.8–5.9 for 1,3-cyclohexadiene.

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