Thermal Rearrangements of 1-Ethynyl-2-methylcyclopropane: A Computational Study

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Thermal Rearrangements of 1-Ethynyl-2-methylcyclopropane: A Computational Study

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Ⓢ Supporting Information

ABSTRACT: In this research, a comprehensive theoretical investigation of the thermal rearrangements of 1-ethynyl-2-methylcyclopropane is carried out employing density functional theory (DFT), with the B3LYP functional, and high-level ab initio methods, such as the complete active space self-consistent field (CASSCF), multireference second-order Møller–Plesset perturbation theory (MRMP2), and coupled-cluster singles and doubles with perturbative triples [CCSD(T)]. In all computations Pople's polarized triple-ζ split valence basis set, 6-311G(d,p), is utilized. The potential energy surface (PES) for the relevant system is explored to provide a theoretical account of the experiments by Hopf,[1−4] Ellis and Frey,[5] Huntsman et al.,[6] and Berson.[7] The computational results herein on the target system show that the thermal aromatization reaction does not proceed via conversion of 1,2,5-hexatriene (**2**) to 1,3,5-hexatriene (**10a**) as proposed by Hopf.[1−4] Indeed, the reaction proceeds via conversion of **5** and **6** to bicyclo[3.1.0]hexene (**9**) as suggested by Huntsman et al.[6]

INTRODUCTION

Hopf et al. investigated the thermal rearrangements of *cis-* and *trans-*1-ethynyl-2-methylcyclopropane (**1**) in a flow system with 35 s residence times at high temperatures (340−530 °C) (Scheme 1).[1−4] They observed that the cis and trans isomers

Scheme 1. Mechanism Suggested by Hopf
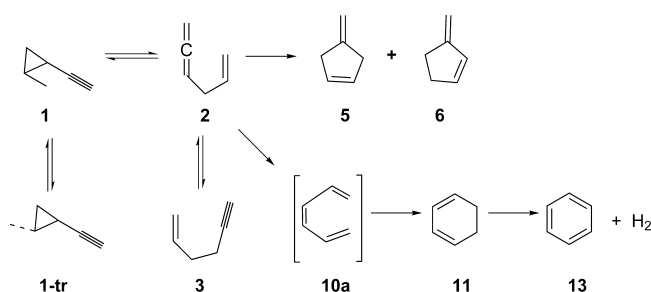
apparently equilibrate rapidly, but the cis isomer undergoes a homo-1,5-hydrogen shift to form **2**. In their experiments, methylenecyclopentenes **5** and **6** were also formed. They also observed that the ratio of methylenecyclopentenes is [**6**]/[**5**] = 1.3, which is consistent with Huntsman et al.'s[8] and Andrews and Baldwin's[9] predictions (Scheme 2).[10] Moreover, it was proposed that **2** undergoes a 1,3-hydrogen shift to form 1,3,5-hexatriene (**10**), which was not observed, but its electro-cyclization product, 1,3-cyclohexadiene (**11**), was isolated. In addition to these products, the benzene (**13**) molecule was observed at high temperatures (Table 1).

In 1966, Ellis and Frey[5] investigated high-temperature thermal rearrangement of bicyclo[3.1.0] hexene (**9**) and observed that **9** rearranges to 1,3- and 1,4-cyclohexadiene, **11** and **12** (Scheme 3). They estimated the activation energies for these reactions as 50.2 kcal mol⁻¹. Further, 1,4-cyclohexadiene
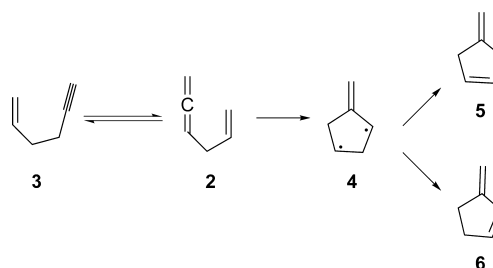
Scheme 2. Huntsman's Mechanism

Table 1. Hopf's Results

temp (°C)	% conversion	2	3	5	6	11	13
340	67	58	20	3	4	15	0
370	74	46	20	5	9	20	0
530	100	0	0	29	38	30	3

(**12**) undergoes dehydrogenation reaction to give benzene (**13**) with the activation energy of 42.7 kcal mol⁻¹.[5] This reaction occurs via a syn elimination by a retro Diels−Alder-like mechanism.[11] However, 1,3-cyclohexadiene (**11**) gives benzene (**13**) only at very low pressures (<0.04 torr) with the activation energy of 61.7 kcal mol⁻¹.[12−14]
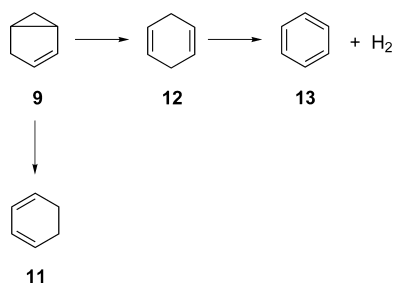
In a 1988 study, Huntsman et al.[6] proposed an alternative path to formation of 1,3- and 1,4-cyclohexadiene (**11** and **12**) (thus to benzene, **13**) via bicyclo[3.1.0]hexene, **9** (Scheme 4). According to this mechanism, methylenecyclopentenes (**5** and **6**) first rearrange to biradical intermediates (**7** and **8**). These intermediates then form bicyclo[3.1.0]hexene (**9**), which
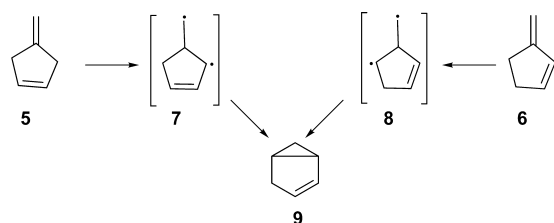
Scheme 3. Ellis's Mechanism

Scheme 4. Proposed Mechanism for the Formation of 9 from 5 and 6

subsequently rearranges to cyclohexadienes **11** and **12** (Scheme 3).

The 1-ethynyl-2-methylcyclopropane (**1**) molecule is an important species; its thermal aromatization reaction is closely related to several interesting systems, such as the Huntsman−Baldwin−Roth mechanism[8−10,15] and Berson trimethylene-methanes (Berson-TMMs).[7,16−40] In this study, a comprehensive theoretical investigation of the thermal rearrangements of 1-ethynyl-2-methylcyclopropane is carried out employing density functional theory (DFT) and high-level ab initio methods. The potential energy surface (PES) for the relevant

system (Scheme 1) is explored to provide a theoretical account of experiments by Hopf,[1−4] Ellis and Frey,[5] Huntsman et al.,[6] and Berson.[7] Since the conversion of **1** to **5** and **6** has been discussed in our previous study,[10] in this research the main focus will be on the explanation of the thermal aromatization part (formation of benzene).

■ COMPUTATIONAL METHODS

The computations in this study have mostly been carried out by using GAUSSIAN 03 (RevD.01) program[41] and the GAMESS package.[42] GAUSSIAN 03 is used for the density functional theory and coupled-cluster (CC) computations, whereas GAMESS is used for the complete active space self-consistent field (CASSCF)[43−54] and multireference second-order Møller−Plesset perturbation theory (MRMP2)[54−61] computations. For three-dimensional chemical drawings, the CHEMVP program is used.[62]

Geometry optimizations for the closed-shell and high-spin open-shell molecules are performed with the DFT method (B3LYP functional[63,64]) using the GAUSSIAN 03 program. Vibrational frequencies are computed to characterize each stationary structure. After locating a TS, intrinsic reaction coordinate (IRC)[65−69] computations are carried out. In order to improve the computed energies single-point frozen-core coupled-cluster singles and doubles with perturbative triples [CCSD(T)][70−78] computations are carried out at optimized DFT geometries. In all computations Pople's polarized triple-ζ split valence basis set, 6-311G(d,p), is employed.[79−81] For the biradicals and transition states (TSs) that have large spin contaminations, geometry optimization and frequency computations are performed with the CASSCF method using the GAMESS program package. At optimized geometries, single-point MRMP2 computations are carried out to improve the energy values.
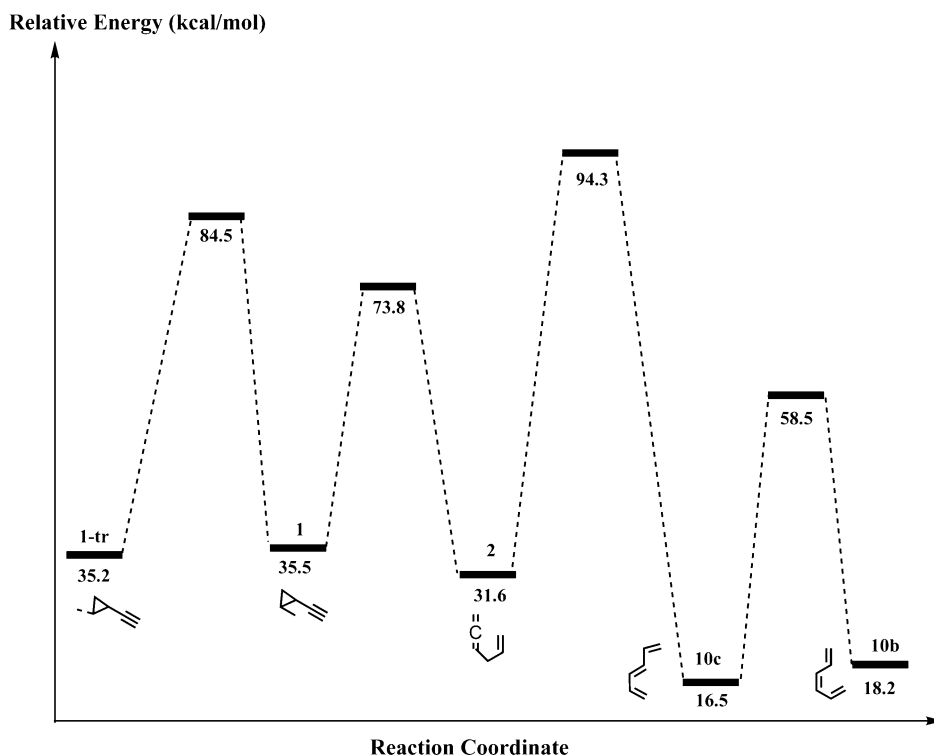

Figure 1. Relative energy profile for the Hopf mechanism (part I).

In order to obtain a unique energy scale at the CCSD(T)/6-311G(d,p) level for the biradical structures, vertical singlet−triplet energy differences obtained via MRMP2 computations are used with CCSD(T) energies of the corresponding triplet states to obtain final energy of the singlet biradical structures. This approximation can be formalized by

$$E(^1X) = E_{CCSD(T)}(^3X) + E_{MRMP2}(^1X) - E_{MRMP2}(^3X)$$

(1)

where X is a biradical species and $E(^1X)$ is the final energy of species ^1X.

Among the singlet TSs, largest values of $\langle S^2 \rangle = 0.98$ and $\langle S^2 \rangle = 1.59$ for the TS between **1** and **1-tr**, and the TS connecting **10b** to **10c**, respectively, which are optimized with the CASSCF method, for all remaining TSs value of $\langle S^2 \rangle \leq 0.50$. Further, when we optimized TSs (for which $\langle S^2 \rangle \leq 0.50$) with the CASSCF method and performed single-point MRMP2 computations, we did not observe significant differences from CCSD(T) predictions in relative energies. Hence, for TSs with small spin contaminations, we can still trust single-reference methods such as DFT and CCSD(T).

RESULTS AND DISCUSSION

Throughout this research, energies of all structures are presented relative to the species **5**. Energies of all closed-shell singlets are from the CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) level, while for open-shell singlets they are from MRMP2/6-311G(d,p)//CASSCF/6-311G(d,p). Zero-point vibrational energy (ZPVE) corrections are all at the DFT level. In the text only the ZPVE-corrected relative energies are discussed, whereas total energies and ZPVEs are provided in Tables S1−S3 of the Supporting Information. For the transition state between species **A** and **B**, the **A/B** notation is used throughout the whole article.

Hopf Mechanism. Relative energy profiles for Hopf et al.'s[1] suggested mechanism (Scheme 1) are provided in Figures 1 and 2. Thermal rearrangement of **2** to **1** occurs via simultaneous 1,3-cyclization and 1,6-hydrogen shift. The conversion frame requires a syn orientation; thus, only the cis isomer can be formed. The calculated reaction energy and barrier are 3.9 and 42.2 kcal mol^{-1}, respectively. The cis isomer (**1**) transforms to the trans isomer (**1-tr**) with a reaction energy

of −0.3 kcal mol^{-1} and a barrier of 49.0 kcal mol^{-1}. The relative energy of **1/1-tr**, 84.5 kcal mol^{-1}, is high compared with other relative energies. Thus, formation of **1-tr** is not expected, except for very high temperatures. The computed geometries of structures **1** and **1/2** are shown in Figure 3, while **1-tr** and **1/1-tr** are shown in Figure 4.
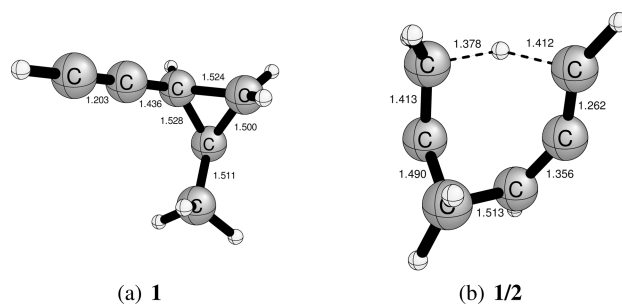

Figure 3. Selected interatomic distances (Å) for structures **1** and **1/2**.
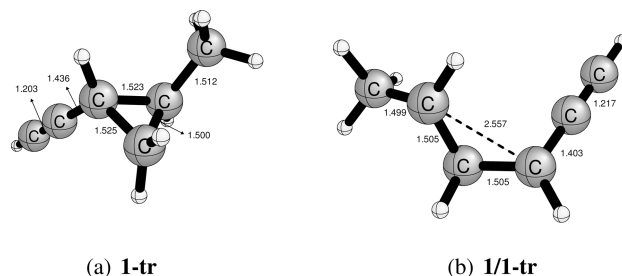

Figure 4. Selected interatomic distances (Å) for structures **1-tr** and **1/1-tr**.

Hopf et al. suggested that the triene **10a** (Scheme 1) might be formed from **2**. Then, triene can yield benzene by several consecutive reactions. At first, the possibility of formation of triene from **2** has been investigated. The results obtained show that the allene **2** rearranges to triene **10c** by a 1,3-hydrogen shift. The reaction energy and barrier are calculated as −15.1 and 62.7 kcal mol^{-1}, respectively. Further, the relative energy of TS that connects **2** to **10c**, **2/10c** is 94.3 kcal mol^{-1}, too high compared with other relative energies. Thus, our results demonstrate that Hopf et al.'s[1] suggested mechanism for the formation of **10c** from **2** is kinetically unfavorable. Hence, in the following subsection an alternative path will be considered for the formation of benzene (**13**). The computed geometries of **10c** and **2/10c** are shown in Figure 5.

The triene **10c** isomerizes to **10b** via a π-bond rotation, and then **10b** rearranges to **10a** with a reaction energy of 4.4 kcal mol^{-1} and an activation barrier of 5.3 kcal mol^{-1}. Then, the triene **10a** rearranges to 1,3-cyclohexadiene, **11**, via a well-known electrocyclic ring closure. For the **10a** → **11** conversion, the calculated reaction energy and barrier are −23.4 and 23.7 kcal mol^{-1}, respectively. Our results, −23.4 and 23.7 kcal mol^{-1}, are consistent with Rodriguez−Otero's computation of −23.0 and 24.8 kcal mol^{-1} at the QCISD(T)/6-31G(d,p)//MP2/6-31G(d,p) level for the reaction energy and barrier, respectively.[82] The computed geometries of **10b** and **10b/10c** are shown in Figure 6, **10a** and **10a/10b** in Figure 7, and **11** and **10a/11** in Figure 8.

The **11** molecule further rearranges to the bicyclic intermediate **9** via an initial 1,2-hydrogen shift followed by ring closure. That bicyclic intermediate, **9**, plays a prominent
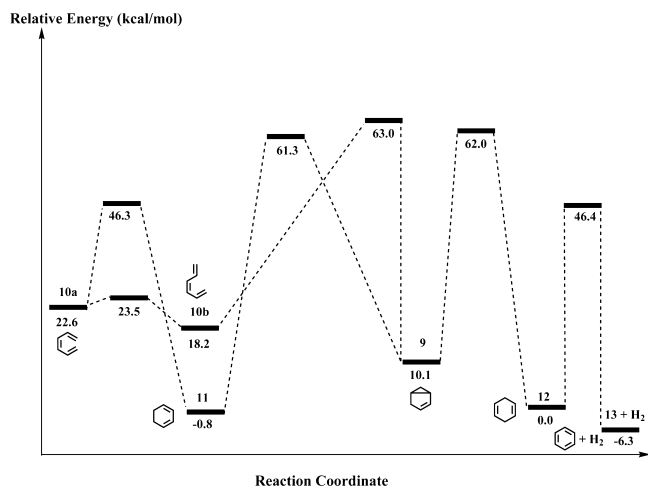

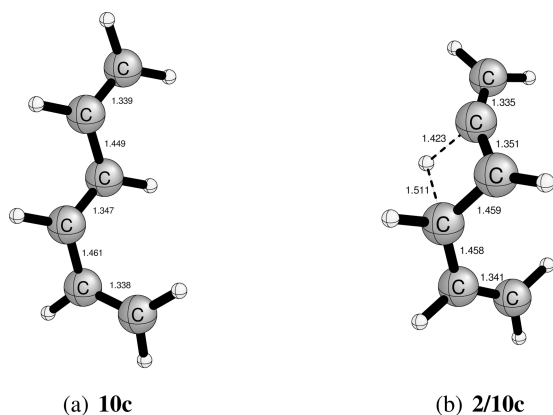**Figure 2.** Relative energy profile for the Hopf mechanism (part II).

(a) **10c**   (b) **2/10c**

Figure 5. Selected interatomic distances (Å) for structures **10c** and **2/10c**.

(a) **10b**

(b) **10b/10c**

Figure 6. Selected interatomic distances (Å) for structures **10b** and **10b/10c**.

(a) **10a**   (b) **10a/10b**

Figure 7. Selected interatomic distances (Å) for structures **10a** and **10a/10b**.

role for connecting methylenecyclopentenes **5** and **6** to the benzene molecule. For the process **11 → 9**, the reaction energy and barrier are calculated as 10.9 and 62.1 kcal mol⁻¹, respectively. The calculated activation energy for the reverse reaction (**9 → 11**) is 51.2 kcal mol⁻¹, which is in good agreement with the experimental value of 50.2 kcal mol⁻¹.[5] Further, Roth et al.[83] determined formation enthalpies of **9** and

(a) **11**   (b) **10a/11**

Figure 8. Selected interatomic distances (Å) for structures **11** and **10a/11**.

6 as 37.8 and 27.6 kcal mol⁻¹, respectively, by calorimetry hydrogenation method. Hence, the experimental relative energy of **9** is 10.2 kcal mol⁻¹, which is in excellent agreement with our result of 10.1 kcal mol⁻¹. Moreover, the experimental formation enthalpy of **11** was reported as 25.4 kcal mol⁻¹;[84] thus, the experimental relative energy of **11** is −2.2 kcal mol⁻¹. The computed relative energy is 1.4 kcal mol⁻¹ higher than experiment. The computed geometries of **9** and **9/11** are shown in Figure 9.

(a) **9**   (b) **9/11**

Figure 9. Selected interatomic distances (Å) for structures **9** and **9/11**.

The **9** intermediate rearranges to 1,2-cyclohexadiene (**12**) via a 1,2-hydrogen shift. The calculated values for the reaction energy and barrier are −10.1 and 51.9 kcal mol⁻¹, respectively. The experimental activation energy for this reaction is 50.2 kcal mol⁻¹.[5] Thus, the calculated value of 51.9 kcal mol⁻¹ is in good agreement with experiment. Further, the experimental formation enthalpy of **12** was reported as 26.1 kcal mol⁻¹ by Roth et al.;[83] thus, the experimental relative energy of **11** is −1.5 kcal mol⁻¹. Hence, the computed relative energy is 1.5 kcal mol⁻¹ higher than experiment. The **9** molecule can also rearrange to **10b** with a reaction energy of 8.1 and reaction barrier of 51.2 kcal mol⁻¹, respectively. The computed geometries of **12**, **9/10b**, and **9/12** are shown in Figure 10.

The **12** molecule decomposes to the benzene + H₂ via a syn elimination by a retro Diels−Alder-like mechanism.[11] The computed reaction energy and barrier are −6.3 and 46.4 kcal mol⁻¹, respectively. The experimental reaction and activation energy for this dissociation have been reported as −6.3 and 42.7 kcal mol⁻¹, respectively.[5] Hence, while the calculations reproduced the experimental reaction energy, the computed barrier is too high by 3.7 kcal mol⁻¹. The geometries of **13** and **12/13** are shown in Figure 11.

An Alternative Path to Formation of Cyclohexadienes. A relative energy profile for the methylenecyclopentenes route (Scheme 4) is provided in Figure 12. As discussed in the previous subsection, the path connecting **2** to **10** has a high-energy TS. In this subsection, an alternative path to
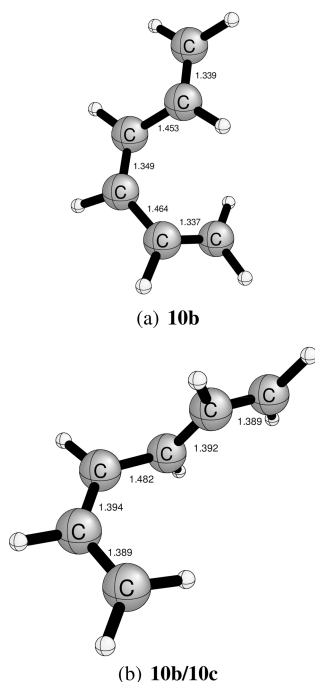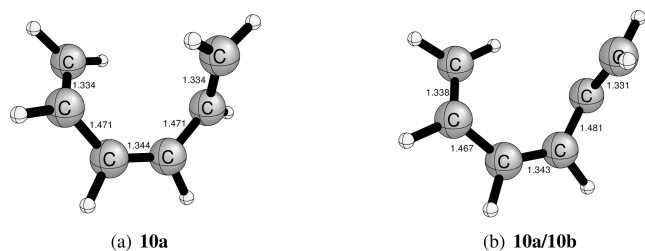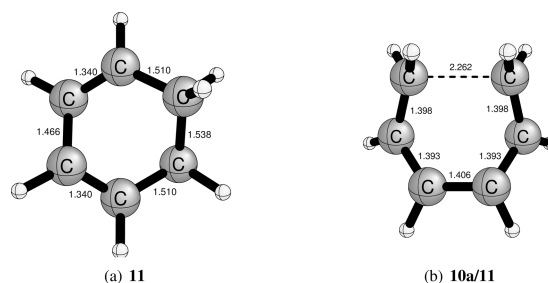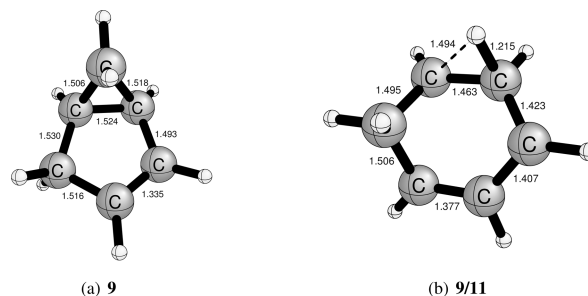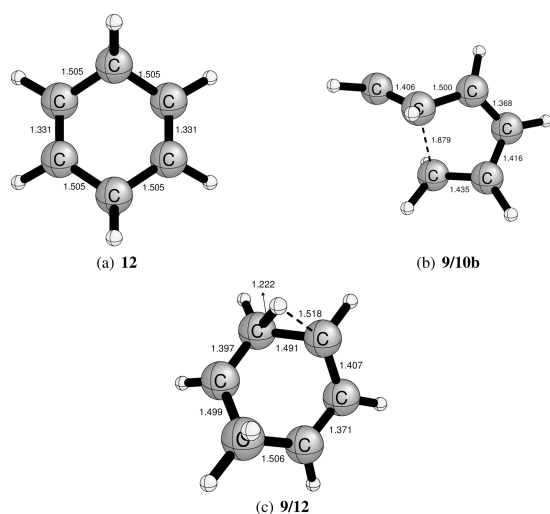
Figure 10. Selected interatomic distances (Å) for structures 12, 9/10b, and 9/12.
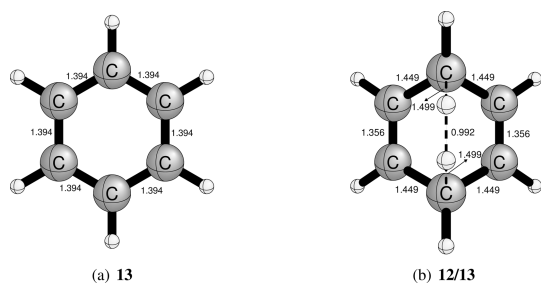

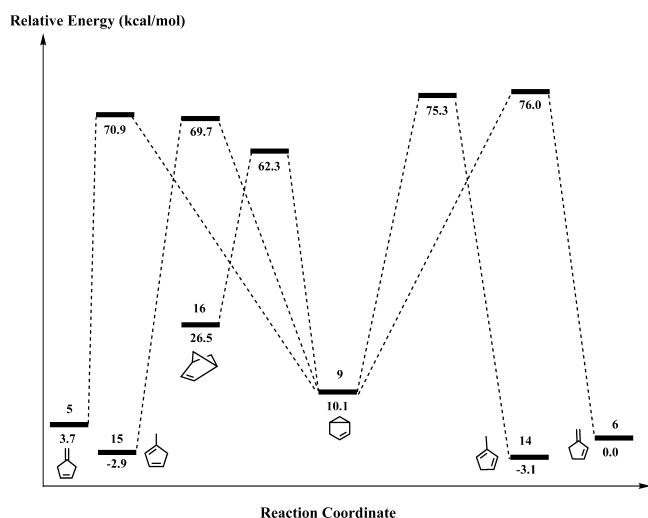Figure 11. Selected interatomic distances (Å) for structures 13 and 12/13.

Figure 12. Relative energy profile for the methylenecyclopentenes route.

formation of cyclohexadienes (thus benzene) is investigated. For this purpose, Huntsman et al.'s[6] mechanism is considered (Scheme 4). Formation of bicyclic intermediate 9 from methylenecyclopentenes route is studied. The 5 molecule rearranges to 9 via a radical mechanism (Scheme 4). First, the biradical intermediate 7 is formed via 1,2-hydrogen shift, and then 7 cyclizes to 9 (Scheme 4). We first consider formation of biradical intermediate 7 (Scheme 4). However, structure 7 does

not correspond to any stationary point. Since structure 7 includes a primary radical center, it is not expected to be stable. However, it still plays an important role in the rearrangement of 5. When IRC calculations are carried out starting with the TS connecting 5 to 9, it is observed that the reaction path passes through structure 9. For the 5 → 9 conversion, the reaction energy and barrier are calculated as 6.4 and 67.2 kcal mol⁻¹, respectively. Similarly, the 6 molecule rearranges to 9. Again, IRC computations showed that the reaction path through the TS connecting 6 to 9 (6/9) passes through structure 8 (Scheme 4). For this conversion, the reaction energy and barrier are calculated as 10.1 and 76.0 kcal mol⁻¹, respectively. Compared with the allene (2) route to formation of 9 (2 → 11 → 9), the methylenecyclopentenes route includes lower energy TSs. The relative energy of 2/10b is 23.4 and 18.3 kcal mol⁻¹ higher than that for 5/9 and 6/9 TSs, respectively. Therefore, formation of 9 (thus benzene) proceeds by a methylenecyclopentenes route. The computed geometries of 5/9 and 6/9 are shown in Figure 13.

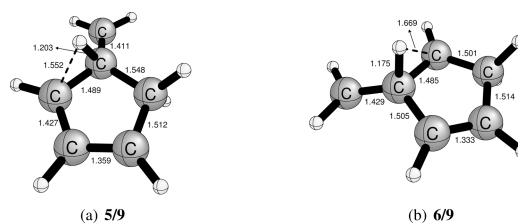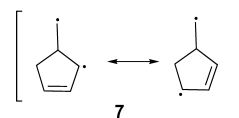
Figure 13. Selected interatomic distances (Å) for structures 5/9 and 6/9.

Another remarkable point is that 5/9 is 5.1 kcal mol⁻¹ lower in energy than 6/9. Since 7 has two resonance hybrids (Scheme 5) while 8 has only one, the 5 route proceeds via a relatively

Scheme 5. Resonance Structures of 7

more stable biradical structure, 7, than the 6 route. Therefore, the 5 route has a lower energy TS. One of the resonance hybrids of 7 cyclizes to 9, while the other one cyclizes to bicyclic 16 molecule. Hence, structure 7 also connects 16 to 9. Since 8 has only one resonance structure, it can only cyclize to 9 molecule. The calculated reaction energy and barrier for conversion of 9 to 16 via structure 7 are 16.4 and 52.2 kcal mol⁻¹, respectively. Further, the experimental value of activation energy for the 16 → 9 conversion was reported as 35.2 kcal mol⁻¹.[85,86] Thus, our result, 62.3 − 26.5 = 35.8 kcal mol⁻¹, is in good agreement with experiment.

Moreover, the experimental formation enthalpy of 16 was reported as 60.0 kcal mol⁻¹ again by Roth et al.;[83] thus, the experimental relative energy of 16 is 32.4 kcal mol⁻¹. The computed relative energy of 26.5 kcal mol⁻¹ is 5.9 kcal mol⁻¹ lower than experiment. Apparently there is a discrepancy between our result and experiment. Although the computed reaction barrier for the 16 → 9 conversion is in good agreement with experiment,[85,86] the reason why the computed relative energy of 16 is so different is unclear. Further, we carried out CCSD(T) computation at optimized MP2

geometries instead of B3LYP geometries in order to show whether this discrepancy is related to the computed geometries or not. However, we obtained almost the same result which indicates that the problem is not related to the geometries. Then, we performed completely renormalized coupled-cluster lambda (CR-CCL) computations,[87,88] which are much more expensive than CCSD(T) but work better in problematic cases, at B3LYP geometries and calculated a relative energy of 26.3 kcal mol^{-1}, which is no improvement. Then, we included core electrons in CCSD(T) computations and obtained a relative energy of 26.2 kcal mol^{-1}, again showing no improvement. Finally, we decided to use a much larger basis set, cc-pVTZ, to investigate whether the problem is related to the basis set, and we calculated the relative energy as 28.6 kcal mol^{-1} at the CCSD(T)/cc-pVTZ level, which is somewhat better than the CCSD(T)/6-311G(d,p) result but still not in a good agreement with experiment. The computed geometries of **16** and **9/16** are shown in Figure 14.
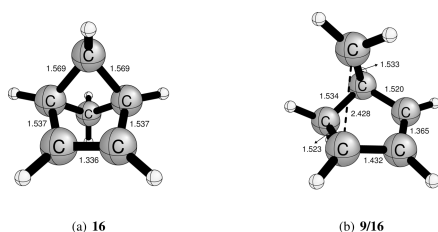

(a) **16**

(b) **9/16**

Figure 14. Selected interatomic distances (Å) for structures **16** and **9/16**.

The **9** molecule also rearranges to **14** via structure **7** and to **15** molecule via structure **8**. The calculated reaction energy and barrier are −13.2 and 65.2 kcal mol^{-1} for conversion to **14**, while −13.0 and 59.6 kcal mol^{-1} for conversion to **15**, respectively. The computed geometries of **14** and **9/15** are shown in Figure 15, while **15** and **9/16** are shown in Figure 16.
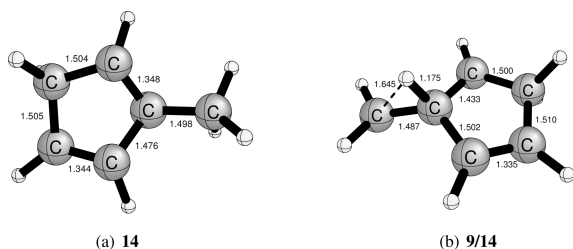

(a) **14**

(b) **9/14**

Figure 15. Selected interatomic distances (Å) for structures **14** and **9/14**.
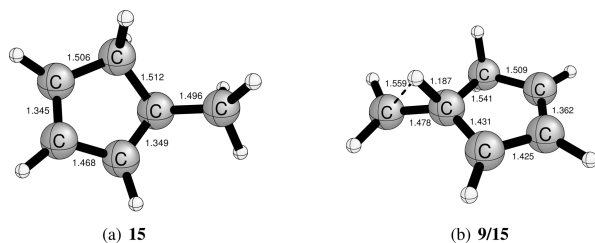

(a) **15**

(b) **9/15**

Figure 16. Selected interatomic distances (Å) for structures **15** and **9/15**.

CONCLUSIONS

In this research, thermal rearrangements of 1-ethynyl-2-methylcyclopropane and several other isomers connected to it by chemical reaction pathways have been investigated employing the highest level of theory available within our computational facilities. The relevant portions of the lowest-energy, singlet-spin potential energy surface of the C_6H_8 chemical systems have been explored in order to determine the reaction energies and activation parameters accurately, with the ultimate objective of providing a theoretical account of pyrolysis experiments by Hopf,[1−4] Ellis and Frey,[5] Huntsman et al.,[6] and Berson[7] on the target system.

Our computational results are in accord with the experimental observations of Hopf,[1−4] Ellis and Frey,[5] Huntsman et al.,[6] and Berson.[7] Further, calculated energy values (reaction energies and activation parameters) are in agreement with the available experimental results. The computational results herein on the target system show that the thermal aromatization reaction does not proceed via conversion of 1,2,5-hexatriene (**2**) to 1,3,5-hexatriene (**10a**) as proposed by Hopf.[1−4] Indeed, our calculations indicate that the reaction proceeds via conversion of **5** and **6** to bicyclo[3.1.0]-hexene (**9**) as suggested by Huntsman et al.[6] It is interesting that **9** is centrally involved in the interconversions of nine different molecules.

ASSOCIATED CONTENT

S **Supporting Information**

Cartesian coordinates, total energies, and ZPVE values for all stationary structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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