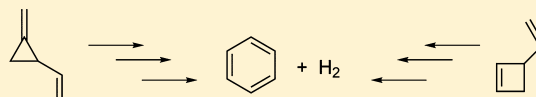


Thermal Aromatizations of 2-Vinylmethylenecyclopropane and 3-Vinylcyclobutene

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S Supporting Information

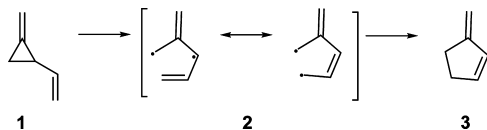
ABSTRACT: A comprehensive theoretical investigation of thermal rearrangements of 2-vinylmethylenecyclopropane and 3-vinylcyclobutene is carried out employing density functional theory and high level ab initio methods, such as the complete active space self-consistent field, multi-reference second-order Møller–Plesset perturbation theory, and coupled-cluster singles and doubles with perturbative triples. In all computations, Pople's polarized triple- ζ split valence basis set, 6-311G(d,p), is utilized. The potential energy surface for the relevant system is explored to provide theoretical insights for the thermal aromatizations of 2-vinylmethylenecyclopropane and 3-vinylcyclobutene. The rate constant for each isomerization reaction is computed using the transition state theory. The simultaneous first-order ordinary-differential equations are solved numerically for the considered system to obtain time-dependent concentrations, hence the product distributions at a given temperature. Our results demonstrate that at high temperatures thermal aromatizations of 2-vinylmethylenecyclopropane (at 700 °C and higher) and 3-vinylcyclobutene (at 500 °C and higher) are feasible under appropriate experimental conditions. However, at low temperatures (at 500 °C and lower), 2-vinylmethylenecyclopropane yields 3-methylenecyclopentene as a unique product, kinetically, and the formation of benzene is not favorable. Similarly, at 300 °C and lower temperatures, 3-vinylcyclobutene can only yield *trans*-1,3,5-hexatriene (major) and *cis*-1,3,5-hexatriene (minor). At 300 < T < 500 °C, 3-vinylcyclobutene almost completely yields 1,3-cyclohexadiene. Hence, our computations provide a useful insight for the synthesis of substituted aromatic compounds. Further, calculated energy values (reaction energies and activation parameters) are in satisfactory agreement with the available experimental results.



1. INTRODUCTION

In a 1968 study, Shields et al.¹ synthesized 2-vinylmethylenecyclopropane (**1**) and reported its thermal rearrangement to 3-methylenecyclopentene (**3**) (Scheme 1). This reaction is

Scheme 1. Rearrangement of **1** to **3**



closely related to vinylcyclopropane rearrangement.^{2–11} Later, Billups et al.¹² determined the activation energy for conversion of 2-vinylmethylenecyclopropane to 3-methylenecyclopentene as 25.8 kcal mol^{−1}. It is proposed that **1** rearranges to a trimethylenemethane (TMM) biradical derivative (**2**) at first, then the biradical undergoes an allylic rearrangement to form **3**.

In 1973, Gilbert and Higley¹³ carried out this rearrangement using deuterium-labeled material. They observed interconversion with ring-labeled material with the activation energy of 24.9 kcal mol^{−1}. This finding is consistent with the existence of intermediate **2** and indicates that the barrier between **2** and **1** is 25.8–24.9 = 0.9 kcal mol^{−1} lower than that between **2** and **3**.

In a 1995 study, Davidson et al.¹⁴ performed a theoretical study of the thermal isomerization of allylidene-cyclopropane to methylenecyclopentene using the complete active space self-

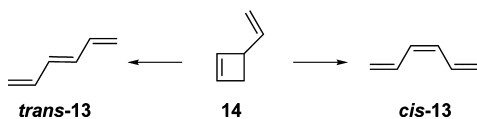
consistent field (CASSCF) method with a six-electron, six-orbital active space [(6e,6o)CASSCF] along with the 6-31G(d) basis set. According to their calculations, the barrier between **2** and **1** is lower by 2.0 kcal mol^{−1} than that between **2** and **3**. They also found that the conrotatory closure of the *cisoid* orthogonal singlet **2** to methylenecyclopentene **3** is favored by 2.8 kcal mol^{−1} over the disrotatory closure. Note, however, that their energies did not include ZPVE corrections and dynamical electron correlation effects. In 1997, Maier and Senger¹⁵ generated the triplet **2** molecule upon irradiation of **1** in a bromine-doped xenon matrix and characterized it by means of infrared (IR) spectroscopy for the first time. Their experimental results indicated that the **1** → **3** isomerization probably proceeds via the singlet biradical (**2**) as an intermediate.¹⁵ Further experimental studies with derivatives of 2-vinylmethylenecyclopropane showed that the major aspects of rearrangements are the same as in the parent system.^{16–18}

3-Vinylcyclobutene rearranges to *trans*-hexatriene (Scheme 2) with an activation energy of 26.8 kcal mol^{−1}.¹⁹ The formation of *cis*-hexatriene is slow and requires significantly higher temperatures.¹⁹ In 1996, Niwayama et al.²⁰ investigated substituent effects on rates and stereoselectivities of conrotatory electrocyclic reactions of cyclobutenes using the restricted Hartree–Fock (RHF) method with the 3-21G basis set. They

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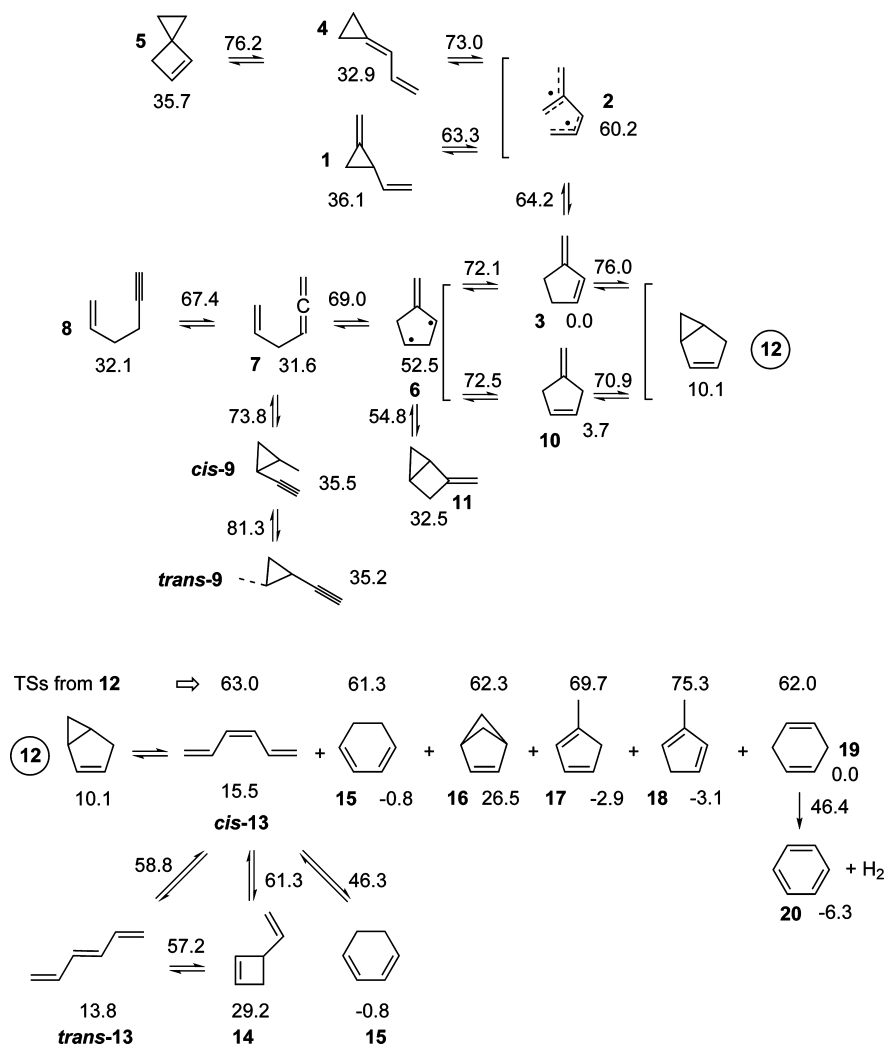
Scheme 2. Rearrangements of 14 to *cis*- and *trans*-Hexatriene

noted that substituents connected to the C₃ carbon atom can rotate either inward or outward to form a *cis* and a *trans* product, respectively. Niwayama et al.²⁰ calculated the activation energy for the rearrangement of 3-vinylcyclobutene to *cis*- and *trans*-hexatriene as 45.3 and 40.4 kcal mol⁻¹, respectively, at the RHF/6-31G**/3-21G level. Their result of 40.4 kcal mol⁻¹ is too high relative to the experimental value¹⁹ of 26.8 kcal mol⁻¹. However, it is not surprising to observe such failures of the RHF method. It is well-known that for accurate computation of activation energies one needs to take into account electron correlations.

The thermal cycloaromatization of dienes has been one of the interesting topics among physical organic chemists, as emphasized by two recent reviews by Hitt and O'Connors²¹ and Zimmermann.²² Diene aromatization ensures a reliable

method to synthesize substituted aromatic systems from easily available starting materials.²¹ Recently, we have explored^{23–25} the potential energy surface (PES) for thermal rearrangements of 1-hexen-5-yne, 1,2,5-hexatriene, and 2-methylenecyclo[2.1.0]pentane^{26–29} and 1-ethynyl-2-methylcyclopropane.^{30–32} Our computational results demonstrated that the mentioned molecules can yield the aromatization product (benzene) at sufficiently high temperatures.

Although thermal rearrangement of 2-vinylmethylenecyclopropane to 3-methylenecyclopentene was carried out experimentally^{1,12,13,15} and studied theoretically,¹⁴ its thermal rearrangement to benzene has not been explored experimentally yet. Similarly, although thermal rearrangement of 3-methylenecyclopentene to hexatriene is known,^{19,33,34} the aromatization of 3-vinylcyclobutene has not been experimentally investigated yet. Hence, in this research, we will theoretically demonstrate that 2-vinylmethylenecyclopropane and 3-vinylcyclobutene may rearrange to benzene under suitable experimental conditions. For this purpose, a comprehensive theoretical investigation for thermal aromatizations of 2-vinylmethylenecyclopropane and 3-vinylcyclobutene

Scheme 3. Reaction Pathways in the C₆H₈ Chemical System Considered for the Kinetic Simulations of This Work^a

^aZPVE-corrected energies (kcal mol⁻¹) of stationary structures on the PES are shown. Values below the species refer to minima, while those near the reaction arrows are for the TSs. All energies are relative to 3.

is carried out employing density functional theory (DFT) and high level ab initio methods.

2. COMPUTATIONAL METHODS

The computations in this study were mostly carried out by using the Gaussian 03 program³⁵ and the GAMESS package.³⁶ Gaussian 03 was used for DFT and coupled-cluster (CC) computations, whereas GAMESS was used for CASSCF^{37–40} and multi-reference second-order Møller–Plesset perturbation theory (MRMP2).^{41–44} For three-dimensional chemical drawings, the CHEMVP program is used.⁴⁵

Geometry optimizations for the closed-shell and high-spin open-shell structures were performed with the DFT method, B3LYP functional.^{46,47} Vibrational frequencies were computed to characterize each stationary structure. Intrinsic reaction coordinate (IRC)^{48–52} computations were carried out when necessary. In order to improve the computed energies, single-point frozen-core coupled-cluster singles and doubles with perturbative triples [CCSD(T)]^{53–60} computations were carried out at optimized DFT geometries. In all computations, Pople's polarized triple- ζ split valence basis set, 6-311G(d,p), was employed.^{61–63} For the biradical minima **2**, **6**, and the π bond rotation TS connecting *cis*-**13** to *trans*-**13**, geometry optimization and frequency computations were performed with the CASSCF method. For the biradical **2** and the π bond rotation TS, a six-electron, six-orbital active space, which consisted of six π orbitals of methylene groups, was used in the CASSCF computations, while for the biradical **6** a four-electron, four-orbital active space was used. At optimized geometries, single-point frozen-core MRMP2 computations were carried out to improve the energy values.

In order to obtain a unique energy scale at CCSD(T)/6-311G(d,p) level for the biradical minima **2**, **6**, and the π bond rotation TS connecting *cis*-**13** to *trans*-**13**, the vertical singlet–triplet energy difference obtained via MRMP2 computations was used with CCSD(T) energy of the corresponding triplet state to obtain the final energy of the singlet biradical, as suggested in previous studies.^{23,24,64} This approximation can be formalized by

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

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

3. THEORETICAL KINETIC MODELING

The rate constant for each isomerization reaction is computed using the transition state theory (TST).^{65,66} The TST rate constant is

$$k_{\text{TST}} = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (2)$$

where k_B is the Boltzmann constant, h is Planck's constant, ΔG^\ddagger is the Gibbs free energy of TS relative to reactant, R is the ideal gas constant, and T is the temperature. Then, simultaneous first-order ordinary-differential equations are solved numerically for the 2-vinylmethylenecyclopropane and 3-vinylcyclobutene rearrangements to obtain time-dependent concentrations, hence the product distributions at a given temperature. The MATLAB 7.0.4 program package⁶⁷ is employed to solve the coupled rate equations. Simultaneous first-order ordinary-differential rate equations can be written as follows⁶⁸

$$\frac{dy_i}{dt} = -k_i y_i + \sum_{j \neq i} k_{ji} y_j \quad (3)$$

$$k_i = \sum_{j \neq i} k_{ij} \quad (4)$$

where y_i is the concentration of the i th species, k_{ij} is the rate constant for the $i \rightarrow j$ reaction, and t is the time.

4. RESULTS AND DISCUSSION

Throughout this research, energies of all structures are presented relative to species **3**. Energies of all closed-shell

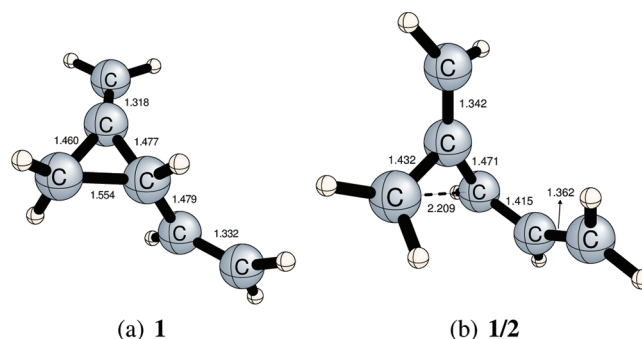


Figure 1. Selected interatomic distances (Å) for structures **1** and **1/2**.

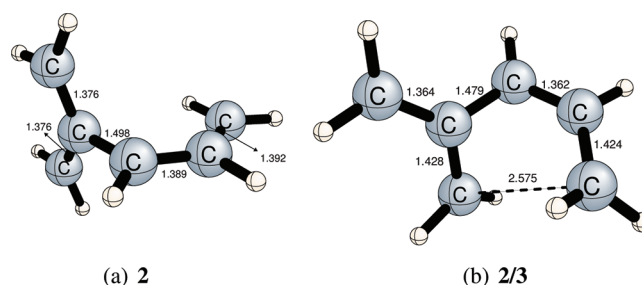


Figure 2. Selected interatomic distances (Å) for structures **2** and **2/3**.

Scheme 4. Resonance Structures of **2**

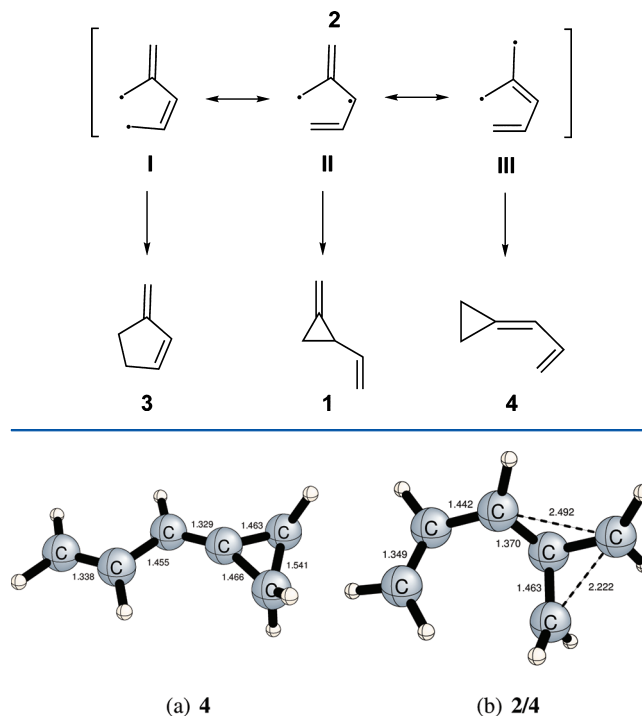


Figure 3. Selected interatomic distances (Å) for structures **4** and **2/4**.

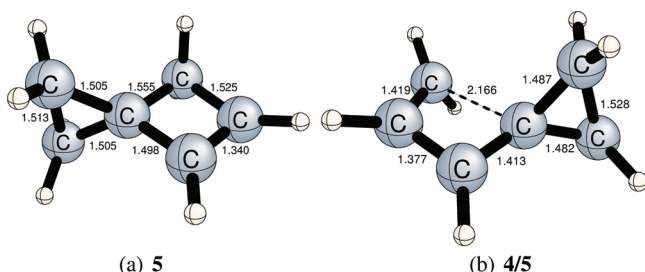


Figure 4. Selected interatomic distances (Å) for structures 5 and 4/5.

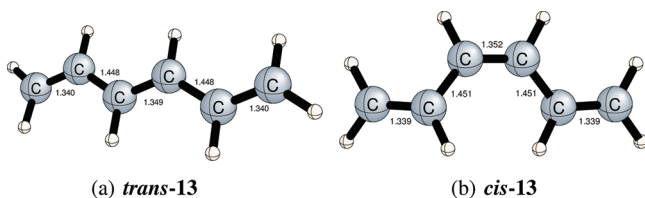


Figure 5. Selected interatomic distances (Å) for *trans*-13 and *cis*-13.

singlets are from CCSD(T)/6-311G(d,p)//B3LYP/6-311G(d,p) level, and open-shell singlets are from MRMP2/6-311G(d,p)//CASSCF/6-311G(d,p). Zero-point vibrational energy (ZPVE) corrections are all at the DFT level. Among the TSs considered in this research, the highest value of T_1 diagnostics^{69,70} is 0.019 for the TS connecting 2 to 4. Hence, the CCSD(T) method is quite reliable for our system. In the text, only the ZPVE-corrected relative energies are discussed, whereas total energies, ZPVEs, and relative free energies are provided in the Supporting Information. For the transition state between species A and B, the notation A/B is used throughout the article.

4.1. Energetics. The considered reaction mechanism for rearrangements of 2-vinylmethylenecyclopropane and 3-vinylcyclobutene is provided in Scheme 3. The minimum energy paths (MEPs) connecting many of the species in this scheme have already been discussed at length in our recent publications.^{23,24} Suffice it to point out here that the pathways of Scheme 3 are in conformity with all available experimental

data about the species involved. Molecules new to the present work are 1, 2, 4, 5, 14, and the minimum energy conformers of *cis*-13 and *trans*-13. We will, therefore, concentrate mainly on the MEPs involving these molecules.

The molecule 1 rearranges to the biradical intermediate 2 by a well-known vinylcyclopropane rearrangement.¹⁹ Both radical centers in the intermediate 2 are allylic radicals; hence the intermediate 2 is stabilized by resonance effects. For the 1 → 2 conversion, the reaction energy and barrier are 24.1 and 27.2 kcal mol^{−1}, respectively. Further, Billups et al.¹² determined the activation energy as 25.8 kcal mol^{−1} for the 1 → 2 isomerization reaction. Hence, our computed activation energy of 27.2 kcal mol^{−1} is in good agreement with experiment. The biradical 2 rearranges to 3 with a reaction energy of −60.2 kcal mol^{−1} and an activation barrier of 4 kcal mol^{−1}, which is reasonable since it is well-known that radical recombination reactions have small barrier heights. Further, our calculations correctly reproduce the difference between the energies of TS 1/2 and TS 2/3 as 64.2 − 63.3 = 0.9 kcal mol^{−1}. The computed geometries of structures 1 and 1/2 are shown in Figure 1, while those of 2 and 2/3 are given in Figure 2.

The biradical 2 also rearranges to 4, again via recombination of radical centers. For the 2 → 4 conversion, the reaction energy and barrier are −27.3 and 12.8 kcal mol^{−1}, respectively. Structure 2 has three different resonance hybrids, as shown in Scheme 4. The cyclization of 2 via resonance structures I, II, and III yields 3, 1, and 4, respectively. The structure 4 further rearranges to 5 via a well-known electrocyclic ring closure reaction.⁷¹ The reaction energy and barrier are 2.8 and 43.3 kcal mol^{−1}, respectively. The computed geometries of structures 4 and 2/4 are shown in Figure 3, while 5 and 4/5 are depicted in Figure 4.

As discussed in our previous study,²⁴ the structure 3 rearranges to benzene + H₂ via several consecutive steps passing through the bicyclic intermediate 12. Another possible path³⁰ passing through 7 → 13 was ruled out due to too high of an activation barrier for 7 → 13 conversion.²⁴ Thus, the aromatization of 1 can be rationalized via reaction path given in Scheme 3. Considering the MEP for the 1 → 20 + H₂ conversion, the highest barrier (72.5 kcal mol^{−1}) belongs to

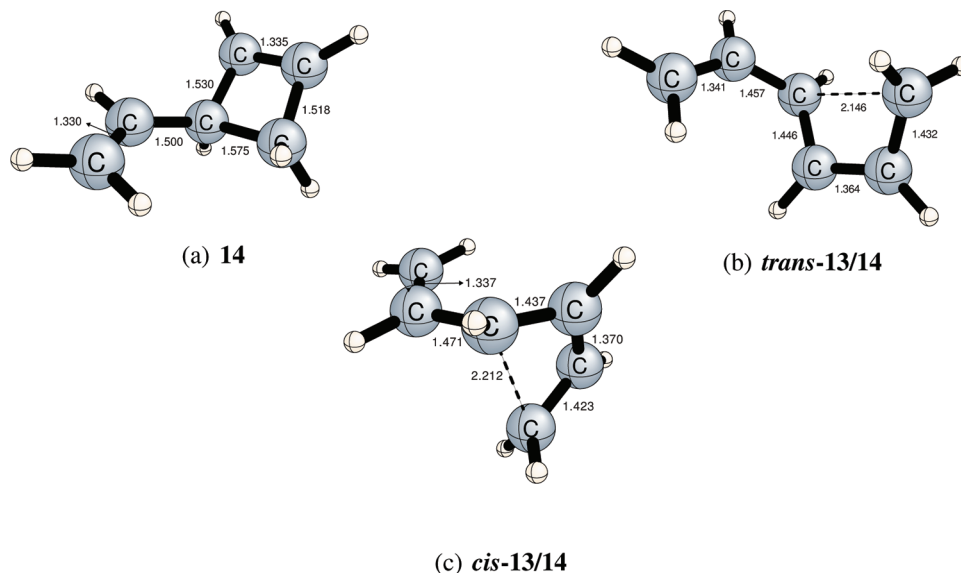


Figure 6. Selected interatomic distances (Å) for 14, *trans*-13/14, and *cis*-13/14.

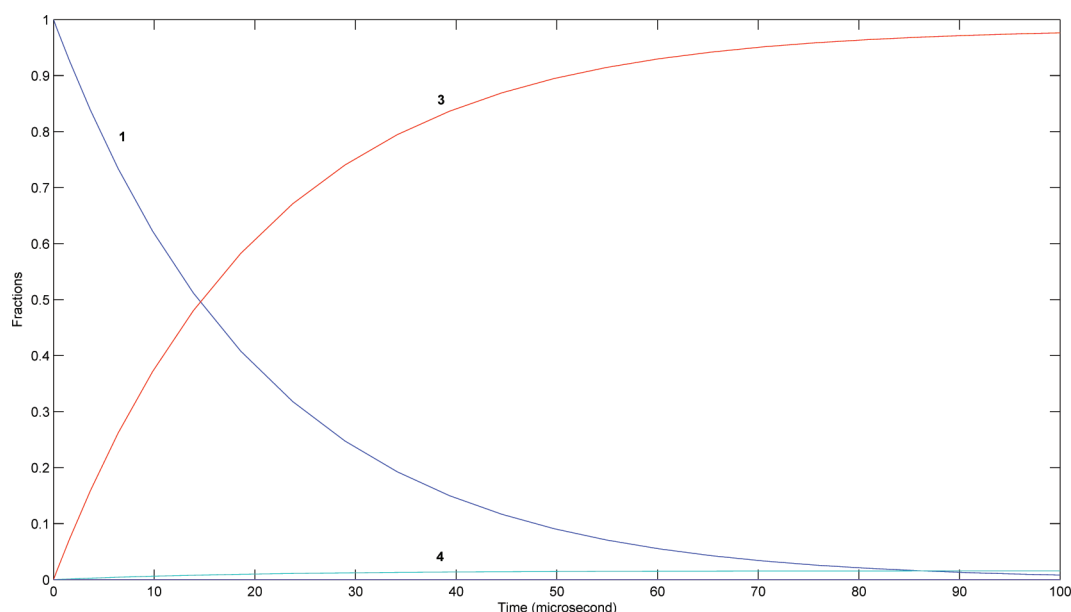


Figure 7. Time-dependent fractions for rearrangements of 2-vinylmethylenecyclopropane at 500 °C (initial molecule is 1).

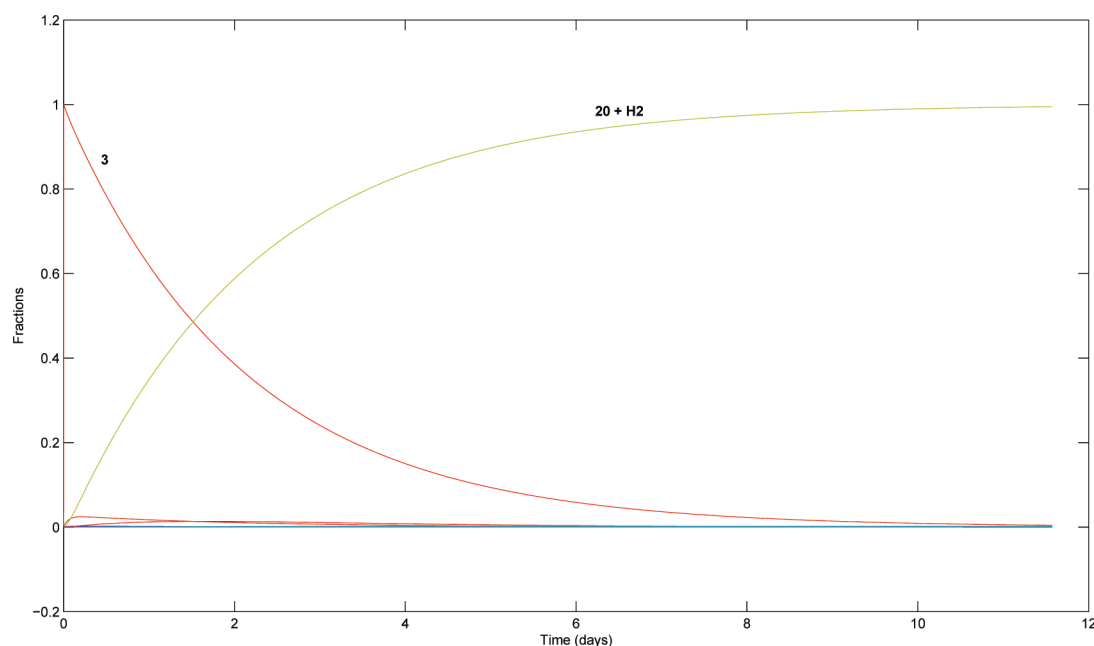


Figure 8. Time-dependent fractions for rearrangements of 2-vinylmethylenecyclopropane at 600 °C (initial molecule is 1).

the $6 \rightarrow 10$ reaction. Hence, the bottleneck for the aromatization of 2-vinylmethylenecyclopropane is the TS $6/10$. The relative energy of the barrier for the $1 \rightarrow 3$ conversion is only $64.2 \text{ kcal mol}^{-1}$, being 8 kcal mol^{-1} lower than that of TS $6/10$ over the aromatization route. Thus, our results clearly explain why only 3 was observed kinetically in the thermal reactions of 1 at low temperatures.¹

For the *trans*-to-*cis* geometrical isomerization of 13, our activation barrier of $45.0 \text{ kcal mol}^{-1}$ ($58.8 - 13.8 = 45.0$) is in agreement with the experimental results of $44.3 \pm 1.2 \text{ kcal mol}^{-1}$ (Doering and Beasley⁷²) and $43.4 \pm 0.5 \text{ kcal mol}^{-1}$ (Orchard and Thrush⁷³). For *cis*-13 \rightarrow 15 conversion, the computed reaction energy and activation barrier of -16.3 and $30.8 \text{ kcal mol}^{-1}$ ($46.3 - 15.5 = 30.8$) are in harmony with the experimental values of -14.5 (ΔH) and $29.9 \text{ kcal mol}^{-1}$,^{19,74}

respectively, and also consistent with an activation barrier of $29.4 \text{ kcal mol}^{-1}$ for the cyclization of a dimethyl-substituted analogue of 13.^{19,75,76} For $19 \rightarrow 20 + \text{H}_2$ reaction, the computed reaction barrier, $46.4 \text{ kcal mol}^{-1}$, is in reasonable agreement with the experimental values of 42.7 (Ellis and Frey⁷⁷) and $43.3 \text{ kcal mol}^{-1}$ (Orchard and Thrush⁷³). Molecule 15 aromatizes by reverting to 12 followed by reopening to 19, as suggested by Orchard and Thrush.⁷³ For $15 \rightarrow 20 + \text{H}_2$ reaction, our activation barrier, $63.8 \text{ kcal mol}^{-1}$ [$63.0 - (-0.8) = 63.8$] conforms with the experimental value of $61.7 \text{ kcal mol}^{-1}$.⁷³ Geometries of *trans*-13 and *cis*-13 are shown in Figure 5.

3-Vinylcyclobutene (14) rearranges to *trans*-13 via an outward rotation of the vinyl substituent connected to the C_3 carbon atom, the corresponding reaction energy and barrier

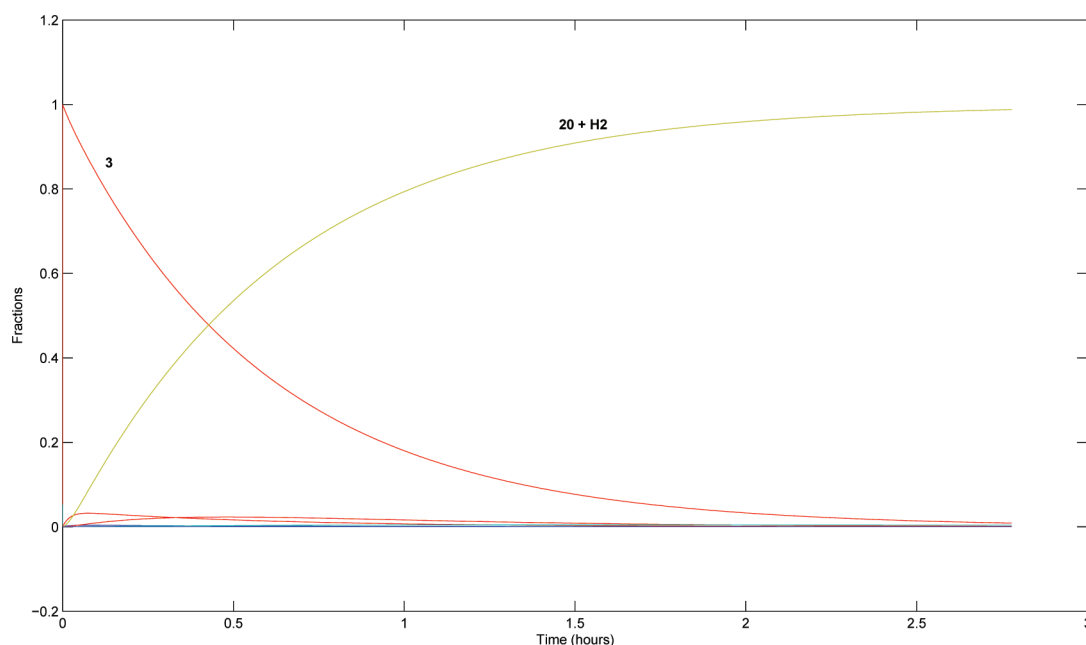


Figure 9. Time-dependent fractions for rearrangements of 2-vinylmethylenecyclopropane at 700 °C (initial molecule is **1**).

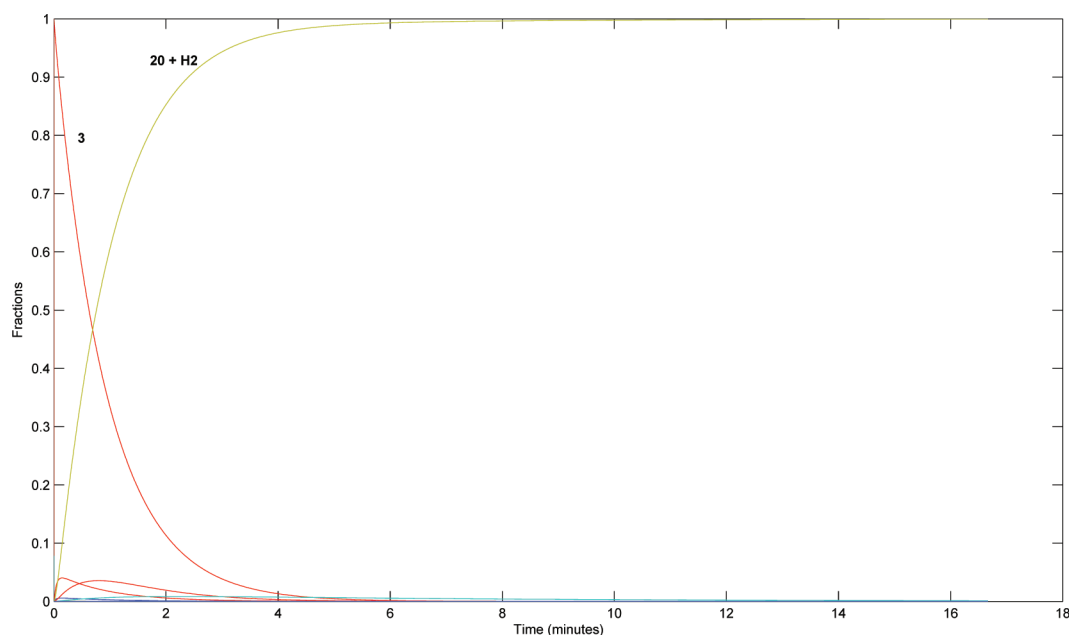


Figure 10. Time-dependent fractions for rearrangements of 2-vinylmethylenecyclopropane at 800 °C (initial molecule is **1**).

being -15.4 and 28.0 kcal mol $^{-1}$, respectively. The computed activation energy of 28.0 kcal mol $^{-1}$ agrees well with the experimental value of 26.8 kcal mol $^{-1}$.¹⁹ Further, **14** can also rearrange to *cis*-**13** via an inward rotation of the vinyl substituent, the corresponding reaction energy and barrier being -13.7 and 32.1 kcal mol $^{-1}$, respectively. The MEP for the formation of *cis*-**13** from **14** passes through *trans*-**13**. The barrier between *trans*-**13** and *cis*-**13** is 1.6 kcal mol $^{-1}$ higher than that between **14** and *trans*-**13**. Our results thus explain why, kinetically, the formation of *cis*-**13** is slow while *trans*-**13** is rapidly formed, as experimentally observed.¹⁹ The aromatization of **14** can be rationalized via a reaction path passing through **14** \rightarrow *trans*-**13** \rightarrow *cis*-**13** \rightarrow **12** \rightarrow **19** \rightarrow **20** + H $_2$. Considering the MEP for the **14** \rightarrow **20** + H $_2$ conversion, the

highest barrier (63.0 kcal mol $^{-1}$) belongs to the *cis*-**13** \rightarrow **12** reaction. Hence, aromatization of 3-vinylcyclobutene requires an activation energy of $63.0 - 29.2 = 33.8$ kcal mol $^{-1}$. On the other hand, the highest barrier on the MEP for aromatization of 2-vinylmethylenecyclopropane (**1**) is 72.5 kcal mol $^{-1}$, requiring an activation energy of $72.5 - 36.1 = 36.4$ kcal mol $^{-1}$. It may be concluded that the aromatization of **14** is more facile than that of **1**. Therefore, **14** may yield benzene at lower temperatures than that required for **1**. Geometries of **14**, *trans*-**13**/**14**, and *cis*-**13**/**14** are depicted in Figure 6.

In a 2002 study, Lovchik and Pinhas⁷⁸ investigated rearrangements of a 3-vinylcyclobutene derivative in the presence of metallic Lewis acids, such as WCl $_6$ and AlCl $_3$, and they obtained an analogue of **17**. However, in the absence

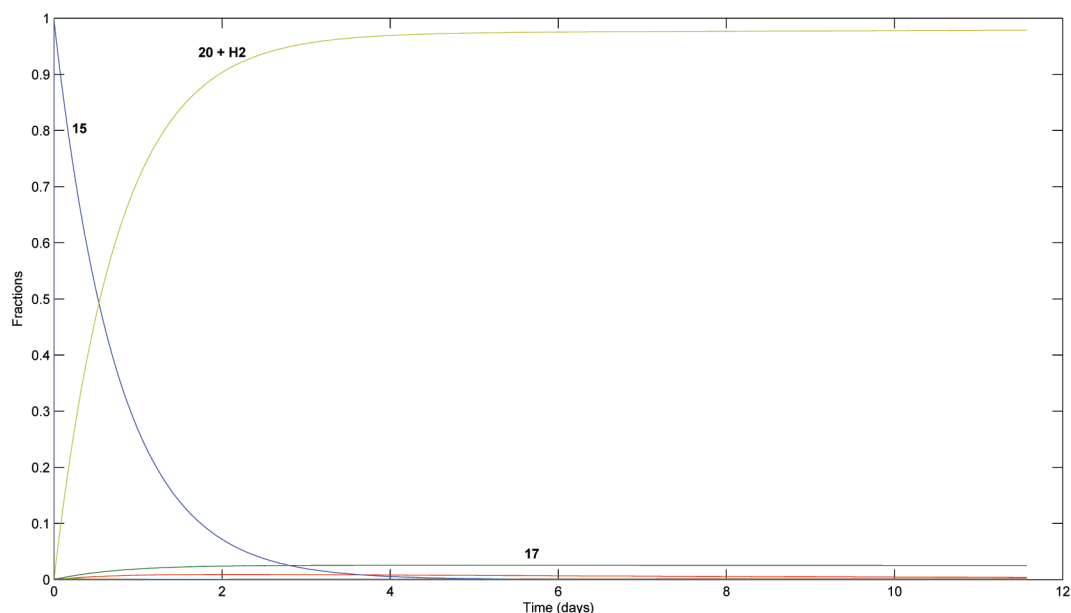


Figure 11. Time-dependent fractions for rearrangements of 3-vinylcyclobutene at 500 °C (initial molecule is 14).

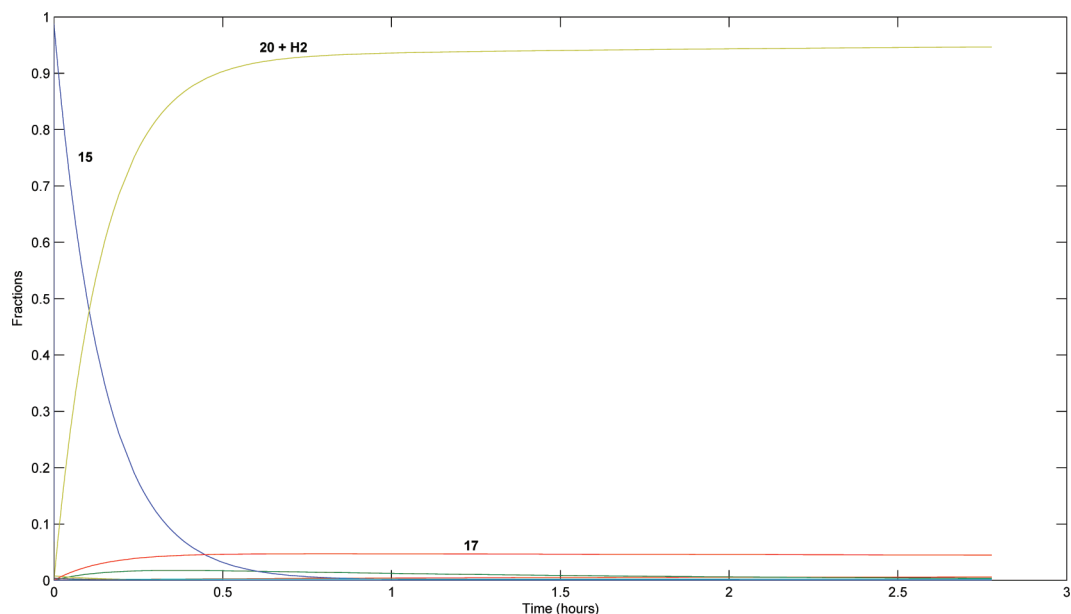


Figure 12. Time-dependent fractions for rearrangements of 3-vinylcyclobutene at 600 °C (initial molecule is 14).

of metallic catalysis, they observed analogues of 13 and 15. Considering 3-vinylcyclobutene (14), the relative energies of TSs on the MEPs for formations of 13 (and 15) and 17 are 61.3 and 69.7 kcal mol⁻¹, respectively. Hence, there is a considerable energy difference (by 8.4 kcal mol⁻¹) between the 14 → 13 and 14 → 17 reaction paths. Thus, our results clearly explain why the analogue of 17 was not observed in absence of metallic Lewis acids.⁷⁸

4.2. Kinetic Simulations. The entire mechanism given in Scheme 3 was considered in the kinetic simulations. The results of kinetic simulations at several temperatures (500–800 °C) for rearrangements of 2-vinylmethylenecyclopropane and 3-vinylcyclobutene are provided in Figures 9–14. Dalacker and Hopf^{24,30} observed the benzene molecule at 530 °C as a minor product (starting compound was 1-ethynyl-2-methylcyclopropane), and they did not observe benzene at lower temperatures.

Further, Berson et al.⁷⁹ carried out thermal rearrangements of a dimethyl-substituted analogue of 8, and they observed the aromatization product (toluene) as a major product at 700 °C. Hence, we do not expect the aromatization product at temperatures lower than 500 °C, and for this reason, we present kinetic simulations at 500, 600, 700, and 800 °C.

Our results show that at 500 °C and lower temperatures 2-vinylmethylenecyclopropane (1) kinetically yields methylenecyclopentene 3 as a unique product, and the formation of benzene is not favorable (Figure 7). At higher temperatures, 1 rearranges to 3 at first ($\sim 10^{-8}$ – 10^{-5} s), then 3 decomposes to benzene + H₂. At 600 °C (Figure 8), 1 can yield benzene in several days (2–10 days) with a yield of $\geq 80\%$. In reaction times shorter than 1 day, the benzene molecule might be observed as a minor product in addition to 3. At 700 °C (Figure 9), in a few hours, the benzene molecule can be

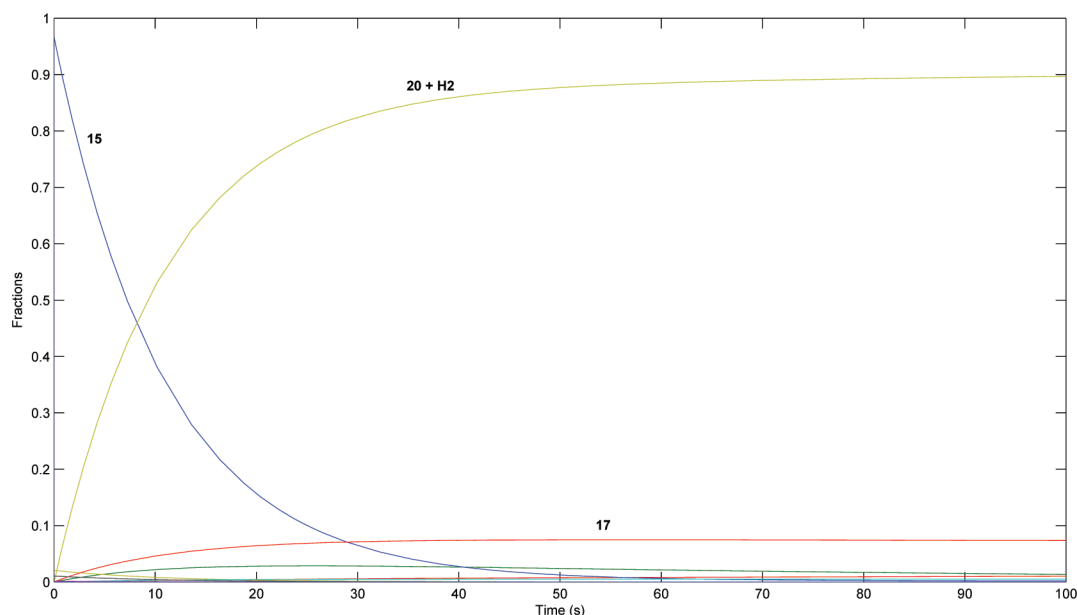


Figure 13. Time-dependent fractions for rearrangements of 3-vinylcyclobutene at 700 °C (initial molecule is **14**).

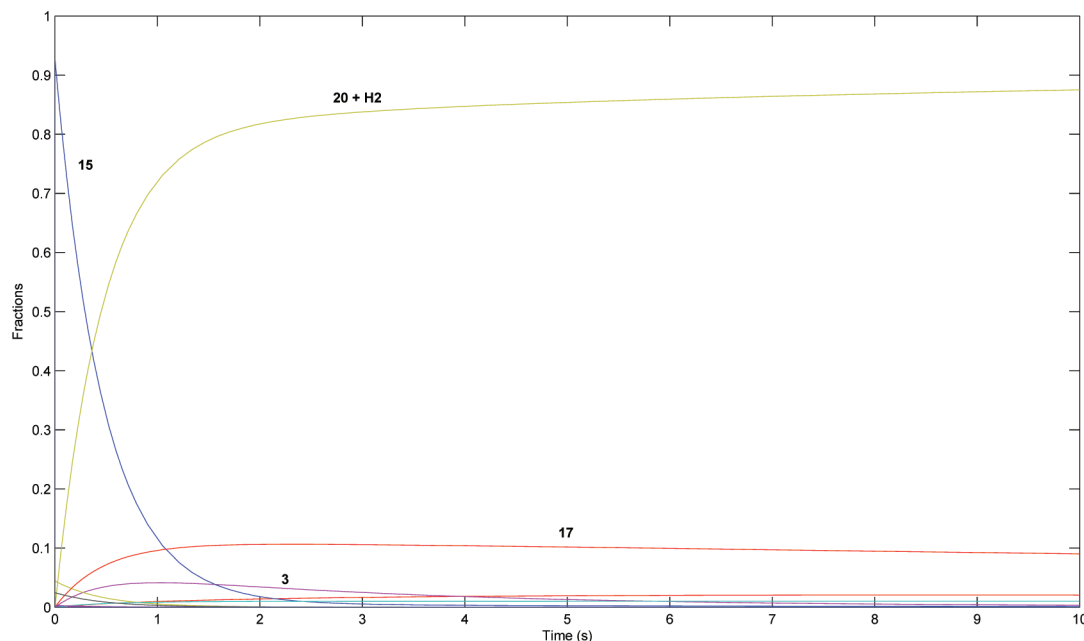


Figure 14. Time-dependent fractions for rearrangements of 3-vinylcyclobutene at 800 °C (initial molecule is **14**).

obtained in a considerable amount (yield $\geq 80\%$). At reaction times shorter than 30 min, **1** may yield benzene as a minor product in addition to **3** (major product). At a higher temperature, 800 °C (Figure 10), **1** can be completely converted to benzene in just 6 min. At reaction times shorter than 1 min, benzene might also be observed as a minor product in addition to **3**. Hence, in an experimental flow system at 800 °C and higher temperatures, one should readily obtain the aromatization product (benzene) in excessive amounts from **1**. Thus, our computations demonstrated that at high temperatures (at 700 °C and higher) the thermal aromatization of 2-vinylmethylenecyclopropane is feasible under appropriate experimental conditions.

Our simulations show that at 300 °C and lower temperatures 3-vinylcyclobutene (**14**) can kinetically yield only *trans*-**13**

(major) and *cis*-**13** (minor). At $300 < T < 500$ °C, **14** is almost completely converted to cyclohexadiene **15**. At higher temperatures, **14** mostly rearranges to *trans*-**13** at first ($\sim 10^{-8}$ – 10^{-4} s), then **13** rearranges to **15**, and finally **15** decomposes to benzene + H₂. At 500 °C (Figure 11), **14** yields benzene in a few days; however, in reaction times shorter than 1 day, benzene might be expected as a minor product in addition to **15** (major product). At 600 °C (Figure 12), **14** can be completely converted to benzene in 1 h, while at times less than 15 min, the major product will be **15**. At 700 °C (Figure 13), with a reaction time of ≥ 10 s, benzene will be formed in considerable amounts. Finally, at 800 °C (Figure 14), 3-vinylcyclobutene can yield the aromatization product just in a few seconds. Compared to 2-vinylmethylenecyclopropane (**1**), the aromatization of 3-vinylcyclobutene (**14**) is easier as

discussed in Energetics subsection, due to the fact that the aromatization path passes through lower barriers in the case of **14**. Hence, our kinetic simulations demonstrated that, at high temperatures (at 500 °C and higher), the thermal aromatization of 3-vinylcyclobutene is feasible under appropriate experimental conditions.

5. CONCLUSIONS

In this research, thermal rearrangements of 2-vinylmethylenecyclopropane, 3-vinylcyclobutene, 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 C₆H₈ chemical system have been explored in order to provide theoretical insights for the thermal aromatization of the title molecules.

Our results demonstrated that at high temperatures thermal aromatizations of 2-vinylmethylenecyclopropane (at 700 °C and higher) and 3-vinylcyclobutene (at 500 °C and higher) are feasible under appropriate experimental conditions. However, at low temperatures (at 500 °C and lower), 2-vinylmethylenecyclopropane kinetically yields 3-methylenecyclopentene as a unique product, and the formation of benzene is not favorable. Similarly, at 300 °C and lower temperatures, 3-vinylcyclobutene can only yield *trans*-1,3,5-hexatriene (major) and *cis*-1,3,5-hexatriene (minor). At 300 < *T* < 500 °C, 3-vinylcyclobutene almost completely rearranges to 1,3-cyclohexadiene. Hence, our computations provide a useful insight for the synthesis of substituted aromatic compounds. Further, calculated energy values (reaction energies and activation parameters) are in accord with the available experimental results.

■ ASSOCIATED CONTENT

■ Supporting Information

Cartesian coordinates, total energies, ZPVEs, and free energies for all stationary structures are reported in the Supporting Information. 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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