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Transition Structures, Energetics, and Nucleus-Independent Chemical Shifts for Divinylcyclobutene-to-Cyclooctatriene Rearrangement: A DFT Study

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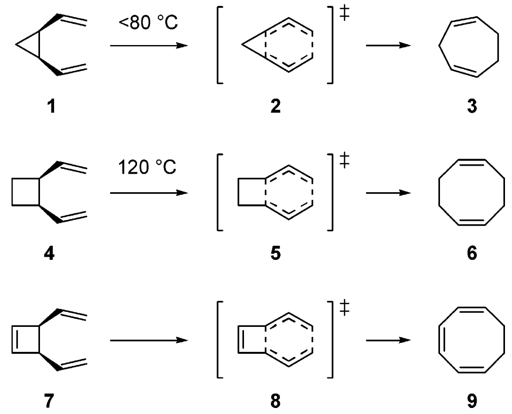
The minimum energy reaction paths and nucleus-independent chemical shifts (NICS) for the Cope rearrangement of *cis*-3,4-divinylcyclobutene, obtained by (U)B3LYP/6-31G* calculations, are reported. Three transition structures (endo-boatlike, chairlike, and exo-boatlike) have been located, giving rise to formation of *cis*,*cis*,*cis*-, *cis*,*cis*,*trans*-, and *trans*,*cis*,*trans*-1,3,5-cyclooctatrienes, respectively. The minimum energy path proceeds through an endo-boatlike, aromatic transition structure. The reaction path of the rearrangement is intervened by enantiomerization saddle point of the product. NICS values calculated for transition structures agree qualitatively with their activation energy and reaction exothermicity orders. Cope rearrangement and electrocyclic ring-opening processes of *cis*-3,4-divinylcyclobutene are competitive, but the former is relatively more favored and exothermic than the latter.

Introduction

Cope rearrangement of *cis*-1,2-alkenylcycloalkanes represents a very rapid entry into cycloalkadienes. Divinylcyclopropane-to-cycloheptadiene (**1** to **3**) and divinylcyclobutane-to-cyclooctadiene (**4** to **6**) rearrangements are the most known and studied examples of these types of reactions (Scheme 1).[1] Vogel[2] first reported these rearrangements in the late 1950s, and since then they have been studied quite extensively from a mechanistic point of view. It appears to be well accepted that both rearrangements proceed in a concerted fashion via a boatlike transition structure (TS),[1,2] although for the parent [3,3]-sigmatropic rearrangement of 1,5-hexadiene, the chairlike TS is favored over a competing boatlike alternative.[3] Apparently, depending on the substituents, the minimum energy path for the rearrangement switches between two reaction channels (chairlike vs boatlike rearrangement). Particularly since 1980, synthetic applications of these reactions have also been explored and these rearrangements have proved to be a versatile, effective method for the construction of functionalized cyclic compounds.[1]

SCHEME 1



In contrast, divinylcyclobutene-to-cyclooctatriene rearrangement (**7** to **9**), a prototype reaction in this area, is not known, although in recent years, its anionic and doubly anionic oxy-Cope versions have been extensively utilized in the synthesis of highly substituted polyquinanes[4] and eight-membered ring carbocycles.[5] The mechanisms and activation barriers of pericyclic reactions are a subject of long-standing and continuing interest.[6] In particular, the [3,3]-sigmatropic shifts of divinylcyclobutene systems present a challenge to understand the rate effects caused by substituents and ring strain. By elementary considerations, it is expected that Cope rearrangement of divinylcyclobutene **7** should be faster than those of divinylcyclopropane **1** and divinylcyclobu-

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tane **4** since strain energy in cyclobutene (28.4 kcal/mol) is higher than those in cyclopropane (27.5 kcal/mol) and cyclobutane (26.5 kcal/mol).[7] The aim of this study is to contribute to a better understanding of such processes. We report herein a detailed study of this rearrangement at the density functional theory (DFT) level and explore properties of the TSs involved, particularly via nucleus-independent chemical shift (NICS) values.[8]

Computational Methods

All calculations were performed at the density functional theory (DFT) level by using the Gaussian 98 program package.[9] Becke's three-parameter exchange functional (B3)[10] in conjunction with the Lee−Yang−Parr correlation functional (LYP)[11] was employed as implemented in Gaussian 98.[9] In all geometry optimizations, Pople's 6-31G* split valence basis set was used.[12] In all regions of the potential energy surfaces explored in this study, the spin-restricted DFT was stable with respect to spin-symmetry breaking (i.e., $\langle S^2 \rangle = 0$ with UB3LYP using "guess = (mix,always)" option). Geometries were optimized without constraint. Vibrational frequencies were computed to characterize each stationary structure as a minimum or TS, via the number of imaginary frequencies (zero for minima and one for saddle points, respectively). After locating a TS, intrinsic reaction coordinate (IRC) calculation[13] was carried out to identify its respective reactant and product. All results reported in this work refer to such completely verified reactant-TS-product triples. Table 1 summarizes the electronic energies, zero-point vibrational energies (ZPVE), and imaginary vibrational frequencies (IMF) of the reactants, TSs, and products for Cope rearrangement of divinylcyclobutene **7** as well as those for competing processes.

TABLE 1. Electronic Energies, Zero-Point Vibrational Energies (ZPVE), and Imaginary Vibrational Frequencies (IMF) of Reactants, Transition Structures, and Products for Cope Rearrangement of *cis*-3,4-Divinylcyclobutene (7) and for Competing Reactions

structure	RB3LYP/6-31G* (au)	ZPVE (kcal/mol)	IMF (cm^{-1})
7nn (C_s)	−310.757 272 5	96.1	
7nx (C_1)	−310.759 551 5	96.2	
7xx (C_s)	−310.759 548 5	96.2	
8nn (C_s)	−310.726 392 7	95.4	−431.7
8nx (C_1)	−310.711 583 7	95.5	−517.9
8xx (C_s)	−310.709 681 7	95.0	−443.2
9 ccc (C_1)	−310.811 850 1	98.8	
9 cct (C_1)	−310.778 953 2	98.6	
9tct (C_s)	−310.740 198 3	97.5	
TS7′ (C_1)	−310.755 302 6	95.9	−113.3
TS7″ (C_1)	−310.753 965 7	95.9	−123.8
TSe9 (C_s)	−310.799 394 9	98.3	−197.1
10xx (C_1)	−310.723 363 8	94.7	−499.0
11ct (C_s)	−310.802 614 1	96.1	
12x (C_1)	−233.367 433 9	75.4	
13x-*in* (C_1)	−233.315 480 1	73.8	−652.2
13x-*out* (C_1)	−233.322 184 5	73.8	−630.9
14c (C_{2v})	−233.395 506 7	74.9	
14t (C_{2h})	−233.398 547 2	74.8	
15x (C_1)	−310.749 447 8	95.9	−523.7
16x (C_1)	−310.810 246 5	97.7	

It should be noted that Houk and co-workers have explored in detail the advantages and disadvantages of (U)B3LYP/6-31G* method for potentially pericyclic reactions and concluded that the (U)B3LYP/6-31G* method is an effective and inexpensive way to compute the structures and energetics for such reactions.[6c,14] Very recently, (U)B3LYP/6-31G* calculations have been successfully used in the calculation of TSs and reaction parameters for the Cope rearrangements of divinylcyclopropanes,[15,16] divinylcyclobutanes,[16] and fickle hexadienes.[17] Notably, the calculated activation barriers of 19.7[15,16] and 25.0[16] kcal/mol for Cope rearrangements of **1** and **4** are in good agreement with their experimentally derived values of 19.0−20.0[18] and 24.0[19] kcal/mol, respectively.

Absolute NMR shielding values were calculated using the gauge-independent atomic orbital (GIAO) method[20] in the restricted Hartree−Fock (RHF) formalism employing the 6-31+G* basis set[12] at the B3LYP/6-31G*-optimized geometries. NICS values were obtained by calculating absolute NMR shielding at ring centers (nonweighted mean of the heavy atom coordinates) (NICS(0)). NICS values, pioneered by Schleyer,[8] are effective probes of aromaticity in transition states of pericyclic reactions.[21] Note that negative NICS values denote aromaticity (−11.5 for benzene, −11.4 for naphthalene) and positive NICS values show antiaromaticity (28.8 for

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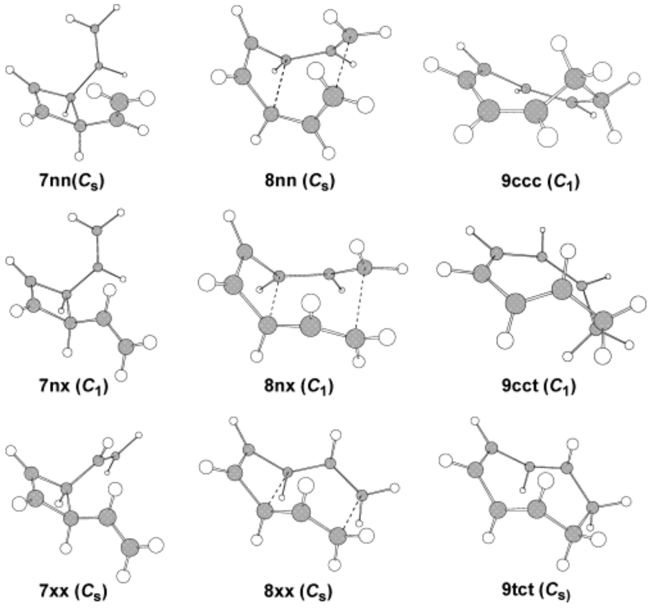
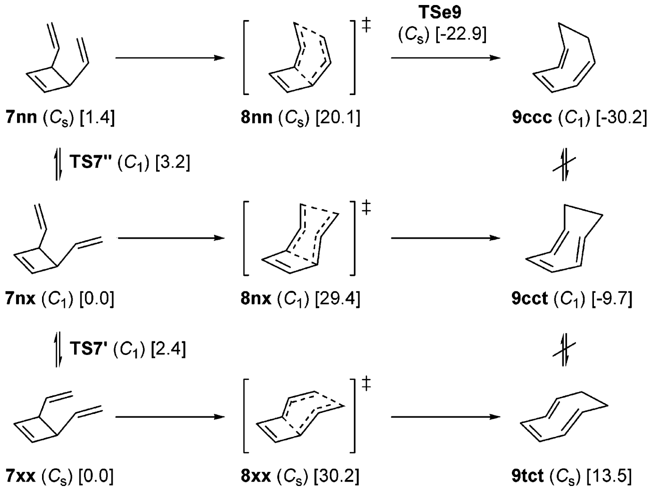


FIGURE 1. B3LYP/6-31G*-optimized geometries for species shown in Scheme 2.

SCHEME 2[a]



[a] Key: energies including ZPVE (kcal/mol) are in brackets and relative to that of **7xx**.

cyclobutadiene, 21.7 for heptalene) while small NICS values indicate nonaromaticity (−2.1 for cyclohexane, −1.1 for adamantane).[8]

Results and Discussion

The computed geometries of reactants, TSs, and products are depicted in Figure 1 (see the Supporting Information for a table of selected structural parameters). Relative energies for these species are illustrated in Scheme 2. Note that **n** denotes a vinyl group in the endo orientation while **x** shows that in the exo orientation. In addition, **c** indicates a cis double bond while **t** denotes a trans one. Depending upon the orientation of vinyl groups, three distinct conformations of **7** were located. These conformers are easily interconvertible isomers due to low activation barriers. The conformational barrier from **7xx** to **7nx** is 2.4 kcal/mol and that from **7nx** to **7nn** is 3.2 kcal/mol. No direct pathway between **7xx** and **7nn** could be located. In all conformers, the four-membered ring is almost planar.

In principle, each conformer of **7** might give rise to a different isomer of cyclooctatriene **9** through an initial-conformer-specific TS (Scheme 2, Figure 1). As anticipated, we located three TSs: two of them (**8nn** and **8xx**) are boatlike and one (**8nx**) is chairlike. The boatlike TSs can also be classified as endo- (**8nn**) and exo-boatlike (**8xx**) TSs due to the position of vinyl groups relative to four-membered ring. In all TSs, four-membered ring adopts a planar structure. Forming and breaking bonds in boatlike TSs are eclipsed. Thus, boatlike TSs appear to suffer from the slightly worse eclipsing interactions. On the other hand, the forming and breaking bonds in the chairlike TS are staggered in the angles of 69.1 and 24.3°, respectively, which partially reduces the eclipsing of bonds. However, it is notable that overall endo- and exo-boatlike TSs **8nn** and **8xx** are looser than chairlike TS **8nx** since the forming (2.453 and 2.334 Å) and breaking (2.179 and 2.208 Å) bonds in the boatlike TSs are slightly longer than the forming (2.264 Å) and breaking (2.109 Å) bonds in the chairlike TS. Moreover, we have predicted activation barriers of 20.1, 29.4, and 30.2 kcal/mol for three possible Cope rearrangements illustrated in Scheme 2. Clearly, the lowest energy path goes through an endo-boatlike TS, **8nn**, as has been the case in the Cope rearrangements of divinylcyclopropane **1** and divinylcyclobutane **4**. Compared to the Cope rearrangement of parent 1,5-hexadiene (barriers of 34.0 kcal/mol for chairlike rearrangement and 42.0 kcal/mol for boatlike rearrangement at the same level of theory),[22] the barriers for the rearrangement of divinylcyclobutene **7** are decreased by 21.9, 4.6 and 11.8 kcal/mol for the endo-boatlike, chairlike, and exo-boatlike rearrangements, respectively. This rate acceleration is no doubt due to four-membered ring's strain. Interestingly, the activation barrier for Cope rearrangement of divinylcyclobutene **7** is 0.4 kcal/mol higher than that for divinylcyclopropane **1**[15,16] but it is 4.9 kcal/mol lower than that for divinylcyclobutane **4**,[16] at the same level of theory. The slightly lower barrier for divinylcyclopropane **1** relative to divinylcyclobutene **7** cannot be explained only by ring strain since cyclopropane has less ring strain than cyclobutene by 0.9 kcal/mol.[7] In fact, as shown by Houk and co-workers using similar systems,[23] activation barriers are not strictly dependent on the ring strain. Houk and co-workers have explained the relative facilities of ring opening by orbital interactions through bonds (OITB),[23,24] i.e., by examining the interactions between

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the orbitals of the breaking bond and the σ framework of the small rings.

It should be noted that the C_s symmetry of TS **8nn** is broken before reaching the cyclooctatriene **9ccc**, which has C_1 symmetry. IRC calculations initiated from **8nn** to **9ccc** have shown that the reaction path directly reaches the C_s-symmetric saddle point labeled as **TSe9**, which is the TS for enantiomerization of **9ccc**, and the reaction path turns into a ridge near **TSe9**. Upon reaching the ridge of **TSe9**, it bifurcates and ends up with an enantiomer of **9ccc**. Note that, during the enantiomerization process, the symmetry of **9ccc** converts to C_1 symmetry. The barrier for the passage of chiral **9ccc** to its enantiomer through **TSe9** is about 7.3 kcal/mol. There is no such enantiomerization saddle point on the other side as the C_s-symmetric **7nn** is stable. Examples of such sequential TSs without intervening intermediates are known.[25]

The formation of cyclooctatriene **9ccc** is highly exothermic as compared to those of cyclooctatrienes **9cct** and **9tct** (Scheme 2). Cyclooctatriene **9ccc** is twisted in the angle of 71.5°, which brings methylene carbons into staggered conformation, and the point group changes from C_s to C_1 as noted previously (Figure 1). This relieves the eclipsing strains and improves the conjugation between the double bonds. As stated before, cyclooctatriene with the point group of C_s is the TS for enantiomerization of the chiral **9ccc** conformations with the barrier of 7.3 kcal/mol. Anet has found this enantiomerization barrier previously to be 4.8 kcal/mol by using force-field calculations.[26] Moreover, it has been shown that cyclooctatriene moiety in η^6-1,3,5-cyclooctatrienechromium tricarbonyl complex adopts such a twisted conformation.[27] The formation of cyclooctatriene **9cct** is also exothermic. However, **9cct** is less stable than **9ccc** by 20.5 kcal/mol. This may be taken as the amount of the ring strain caused by the change of one cis double bond in **9ccc** with a trans one. Methylene carbons in **9cct** are staggered in the angle of 42.3°.

Formation of cyclooctatriene **9tct** is not energetically favorable since the presence of two trans double bonds as well as eclipsing interactions between methylene carbons increase the strain by 23.2 and 43.7 kcal/mol in comparison to its cis,cis,trans (**9cct**) and cis,cis,cis (**9ccc**) analogues, respectively. Hence, it is unlikely to be stable under the experimental conditions. Moreover, the bond distance between methylene carbons is slightly longer (1.630 Å) for a C−C single bond,[28] most likely as a result of the strain present in this compound. The ring strains and eclipsing interactions associated with 1,3,5-cyclooctatrienes seem to be reflected inversely in the exothermicities of the rearrangements to some extent. The direct interconversion of cyclooctatrienes **9ccc**, **9cct**, and **9tct** is most unlikely since a formal cis/trans alkene isomerization of this type could occur only by a stepwise mechanism.[17] To the best of our knowledge, cyclooctatrienes **9cct** and **9tct** are unknown compounds. Notably, the rearrangement of divinylcyclobutene **7** is more exothermic than those of divinylcyclopropane **1**[15,16] and divinylcyclobutane **4**[16] by 10.1 and 12.9 kcal/mol, respectively, at the same level of theory, which might be attributed to higher ring strain in **7**. It is not clear to exactly what the ring strain affects the reaction exothermicity but the ring strain influences the exothermicity of a reaction more than its activation barrier, as seen in the rearrangements of **1**, **4**, and **7**.

TABLE 2. **GIAO-HF/6-31+G*//B3LYP/6-31G* Calculated NICS(0) (ppm) and ΣNICS(0)[a] (ppm) Values for Transition Structures of Cope Rearrangement of *cis*-3,4-Divinylcyclobutene (7)[b]**

	NICS(0)		
	4MR	6MR	ΣNICS(0)
8nn (C_s)	−8.2	−22.4	−30.6
8nx (C_1)	−1.8	−22.7	−24.5
8xx (C_s)	2.6	−19.5	−17.1
cyclobutene (C_{2v})	0.6		

[a] Sum of NICS values of rings in compound. [b] 4MR and 6MR denote four- and six-membered rings, respectively.

Some evidence for aromaticity of TSs comes from NICS values. Table 2 shows NICS(0) and ΣNICS(0) values for TSs in Scheme 2, as well as for the reference compound, cyclobutene. On the basis of their NICS(0) values, six-membered rings in all TSs show considerable aromaticity but their aromaticity indicates a decreasing trend in the order of **8nx**, **8nn**, and **8xx**. On the other hand, the four-membered ring is aromatic in **8nn**, slightly aromatic (or nonaromatic) in **8nx**, and weakly antiaromatic in **8xx** compared to its nonaromatic character in cyclobutene. Note that the overall aromaticity of a TS is better indicated by the ΣNICS(0) value. As expected, ΣNICS(0) values for TSs indicate a negatively decreasing trend in the order of **8nn**, **8nx**, and **8xx**, which agree qualitatively with both their activation energy and reaction exothermicity orders. Apparently, aromatic stabilization of TS is responsible for faster reaction.

Alternatively, divinylcyclobutene can undergo a conrotatory, electrocyclic ring opening to produce an octatetraene derivative, as shown in Scheme 3. Although we have located few TSs for this process, the lowest energy TS (**10xx**) is obtained from the ring opening of **7xx**, producing (E,Z)-1,3,5,7-octatetraene, **11ct**.[29] For this concerted reaction, we have calculated the activation barrier to be 21.2 kcal/mol. Importantly, the activation barrier for this opening is lowered by 12.6 kcal/mol as compared to that for cyclobutene ring opening, which has an activation barrier of 33.8 kcal/mol at the same level

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(25) For examples and theoretical studies of such sequential TSs, see: (a) Taketsugu, T.; Hirano, T. *J. Chem. Phys.* **1993**, *99*, 9806. (b) Taketsugu, T.; Hirano, T. *THEOCHEM* **1994**, *116*, 169. (c) Yanai, T.; Taketsugu, T.; Hirao, K. *J. Chem. Phys.* **1997**, *107*, 1137. (d) Kumeda, Y.; Taketsugu, T. *J. Chem. Phys.* **2000**, *113*, 477. (e) Castano, O.; Frutos, L. M.; Palmeiro, R.; Notario, R.; Andres, J. L.; Gomperts, R.; Blancafort, L.; Robb, M. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2095. (f) Taketsugu, T.; Kumeda, Y. *J. Chem. Phys.* **2001**, *114*, 6973. (g) Bartsch, R. A.; Chae, Y. M.; Ham, S.; Birney, D. M. *J. Am. Chem. Soc.* **2001**, *123*, 7479. (h) Castano, O.; Palmeiro, R.; Frutos, L. M.; Luisandres, J. *J. Comput. Chem.* **2002**, *23*, 732. (i) Caramella, P.; Quadrelli, P.; Toma, L. *J. Am. Chem. Soc.* **2002**, *124*, 1130. (j) Singleton, D. A.; Hang, C.; Szymanski, M. J.; Meyer, M. P.; Leach, A. G.; Kuwata, K. T.; Chen, J. S.; Greer, A.; Foote, C. S.; Houk, K. N. *J. Am. Chem. Soc.* **2003**, *125*, 1319. (k) Lasome, B.; Dive, G.; Lauvergnat, D.; Desouter-Lecomte, M. *J. Chem. Phys.* **2003**, *118*, 5831. (l) See also ref 16.

(26) (a) Anet, F. A. L.; Yavari, I. *Tetrahedron Lett.* **1975**, *16*, 4221. (b) Anet, F. A. L.; Yavari, I. *Tetrahedron* **1978**, *34*, 2879.

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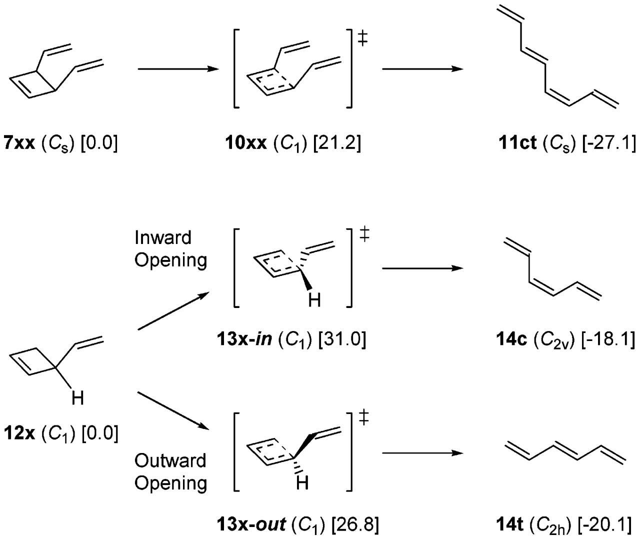
(28) For a study of C−C bond lengths, see: Zavitsas, A. A. *J. Phys. Chem. A.* **2003**, *107*, 897.

(29) For synthesis of E,Z-1,3,5,7-octatetraene, see: Ziegenbein, W.; Peitscher, G. *Chem. Ber.* **1965**, *98*, 1427 and references therein.

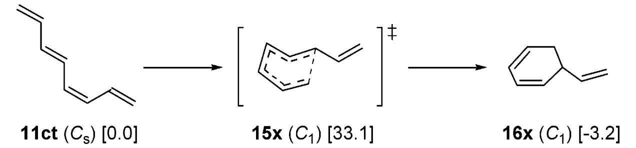
SCHEME 3[a]



[a] Key: energies including ZPVE (kcal/mol) are in brackets and relative to those of **7xx** and **12x**.

of theory,[30] comparable to 32.5 kcal/mol obtained by the experiment.[31] For comparison purposes, we have also studied the electrocyclic ring opening of 3-vinylcyclobutene (**12x**), which was previously studied at several levels,[32] but not at the B3LYP/6-31G* level. We have found that the ring opening of **12x** with inward rotation of the vinyl group via TS **13x-*in*** (inward opening) has a barrier of 31.0 kcal/mol while the opening with outward rotation of the vinyl group via TS **13x-*out*** (outward opening) has a barrier of 26.8 kcal/mol. For substituted cyclobutenes, torquoselectivity (the preference for one of two opening modes) has been described in detail by Houk and co-workers.[32,33] These researchers have found that donor substituents rotate away from the breaking bond preferentially, while strong acceptor substituents rotate inward. Although both opening modes of vinylcyclobutene **12x** are more facile than cyclobutene ring opening, the outward opening is favored by 4.2 kcal/mol over the inward opening. In general, a vinyl group behaves as a weak donor (Taft $\sigma_R{}^0$ value $= -0.03$),[32] and thus it has less effect on the inward TS **13x-*in*** than the outward TS **13x-*out***, consistent with the earlier finding of Houk.[32] It should be noted that, as compared to the cyclobutene ring opening, the decrease in activation barrier for the ring opening of divinylcyclobutene **7xx** via TS **10xx** is 2.8 kcal/mol more than the sum of those for inward and outward opening of vinylcyclobutene **12x** via TSs **13x-*in*** and **13x-*out***. Although it has not been studied in detail, disubstitution seems to be more effective on the ring opening of cyclobutene than the corresponding cumulative mono substitutions. In the calculated TSs **10xx**, **13x-*in***, and **13x-*out***, the four-membered ring skeleton is considerably twisted, as in cyclobutene ring opening TS,[30] and vinyl group in all is anti to the ring. The breaking bond for TSs **10xx**, **13x-*in***, and **13x-*out*** is 2.179, 2.182, and 2.137 Å, respectively, which is comparable to 2.144 Å for cyclobutene ring opening TS.[30] It should be noted that the electrocyclic ring opening of divinylcyclobutene **7xx** is overall 1.1 kcal/mol less favored and 3.1 kcal/mol less exothermic than its Cope rearrangement (i.e., **7xx** to **9ccc**), but the ring opening process of **7xx** is expected to be operative to some extent to yield an octatetraene derivative.

SCHEME 4[a]



[a] Key: energies including ZPVE (kcal/mol) are in brackets and relative to that of **11ct**.

As anticipated, if an octatetraene derivative is produced, it can cyclize to a vinyl substituted cyclohexadiene derivative. We have also investigated 6π disrotatory electrocyclization of octatetraene **11ct** to 5-vinyl-1,3-cyclohexadiene (**16x**), as illustrated in Scheme 4. Note that, due to the presence of a trans double bond, **11ct** cannot give rise to formation of 1,3,5-cyclooctatriene. The concerted closure of **11ct** to **16x** proceeds with a barrier of 33.1 kcal/mol and is exothermic by 3.2 kcal/mol, which is compared to a barrier of 30.3 kcal/mol and overall exothermicity of 12.6 kcal/mol for the closure of 1,3,5-hexatriene,[34] consistent with the experimental values of 29.0[35] and 15.2[36] kcal/mol, respectively. The cyclization of **11ct** proceeds via a boatlike TS, **15x**, with a forming bond length of 2.253 Å and a close interaction distance (1.882 Å) of two inward hydrogens of C1 and C6 carbons, similar to that of 1,3,5-hexatriene.[37] However, vinyl substitution increases the activation barrier and, more importantly, decreases the reaction exothermicity significantly as compared to that of 1,3,5-hexatriene.[34] More strikingly, the cyclization of **11ct** to **16x** is 13.0 kcal/mol less favored and 27.0 kcal/mol less exothermic than the divinylcyclobutene-to-cyclooctatriene rearrangement (**7xx** to **9ccc**).

Figure 2 shows the reaction diagram for the conversion of divinylcyclobutene **7xx** to cyclooctatriene **9ccc** and to octatetraene **11ct** and vinylcyclohexadiene **16x**, which indicates that the two pathways are competitive. The formation of cyclooctatriene **9ccc** needs to overcome an overall activation barrier of 20.1 kcal/mol from **7xx** while that of octatetraene **11ct** needs to cover a slightly higher

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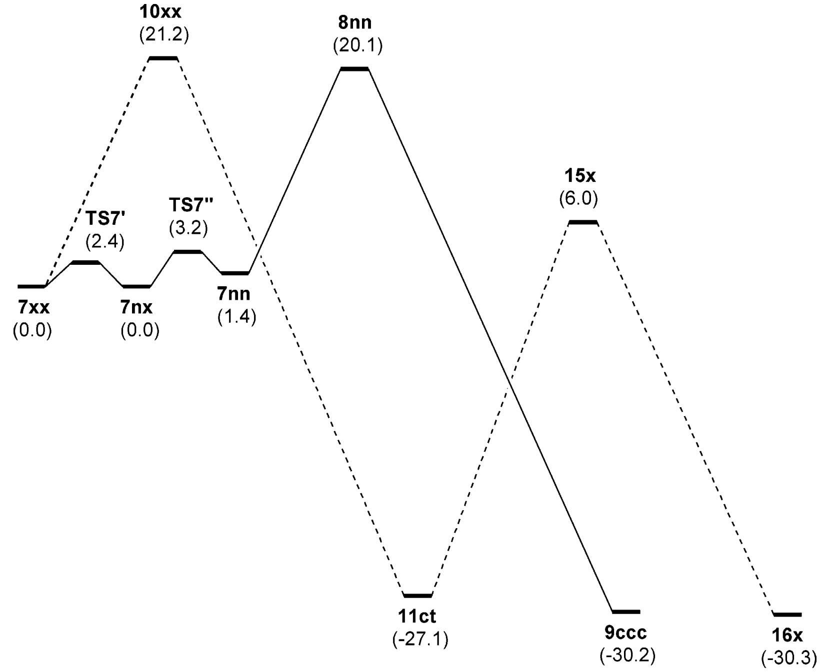

FIGURE 2. Reaction diagram for conversion of **7xx** to **9cc**, **11ct**, and **16x** (energies including ZPVE (kcal/mol) are in parentheses and relative to that of **7xx**).

activation barrier of 21.2 kcal/mol from **7xx**. However, if **9ccc** is produced, it is relatively more difficult for it to turn into **7xx** with a higher activation barrier being 50.3 kcal/mol, compared to an activation barrier of 48.3 kcal/mol for the turn of **11ct** to **7xx**. The comparatively higher activation barrier for the former reverse reaction provides to some extent an additional driving force for the formation of **9ccc** since the reaction pathway leading to **9ccc** bears relatively more irreversible character than that leading to **11ct**. The stabilities of cyclooctatriene **9ccc** and vinylcyclohexadiene **16x** are very similar, but the formation of the latter requires overcoming another activation barrier of 33.1 kcal/mol from **11ct**. Moreover, the activation barrier for the reverse reaction from **16x** to **11ct** is 36.3 kcal/mol, being more reversible as compared to those of **9ccc** and **11ct**. Finally, it is concluded that the reaction pathway leading to cyclooctatriene **9ccc** from **7xx** should take place somewhat more easily than both the electrocyclic ring opening of **7xx** and the subsequent cyclization of octatetraene **11ct** to vinylcyclohexadiene **16x**.

Conclusion

In summary, we have theoretically explored a previously unknown prototype reaction, divinylcyclobutene-to-cyclooctatriene rearrangement. Our DFT results reveal that divinylcyclobutene **7** rearranges via an endo-boat-like, aromatic TS, as in the case of Cope rearrangements of divinylcyclopropane **1** and divinylcyclobutane **4**. The reaction path of the rearrangement is intervened by enantiomerization saddle point of the product. NICS values predicted for TSs agree qualitatively with their activation energy and reaction exothermicity orders. Cope rearrangement and electrocyclic ring opening processes of divinylcyclobutene **7** are competitive but the former is relatively more favored and exothermic than the latter. Moreover, activation barrier for Cope rearrangement of **7** is slightly higher than (or comparable to) that of divinylcyclopropane **1**, but significantly lower than that of divinylcyclobutane **4**. However, Cope rearrangement of **7** is more exothermic than those of divinylcyclopropane **1** and divinylcyclobutane **4**. Furher study of this rearrangement as well as substituent effects is currently under investigation.

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Supporting Information Available: B3LYP/6-31G*-optimized Cartesian coordinates and energies for all structures as well as a table (Table S1) of selected structural parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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