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Transition Structures, Energetics, and Nucleus-Independent Chemical Shifts for 6π Electrocyclizations of Dienylketenes to Cyclohexadienones: A DFT Study

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6π electrocyclizations of dienylketenes to 2,4-cyclohexadienones have been investigated at the (U)B3LYP/6-31G* level and found to be a favored and exothermic process for most dienylketenes. As evidenced by calculations, dienylketene cyclizations proceed via a pseudopericyclic process. If the terminal double bond of dienylketenes is embedded into a benzenoid-type aryl moiety, the partial or complete loss of aromaticity, as indicated by NICS values, increases the activation barrier and makes the reaction less exothermic or even endothermic. The effect of aromaticity is slightly less pronounced for dienylketenes carrying five-membered heterocyclic aromatic substituents. Slightly distorted planar transition structures have been located for these types of cyclizations. Forming bond lengths in transition structures range from 1.950 to 2.339 Å.

Introduction

The appearance of ketenes in organic synthesis has gained enhanced frequency over the past few decades.[1] Ketenes are known as reactive intermediates and are arguably one of the most versatile organic synthetic intermediates. Ketenes, which are more commonly presented as the "neutral" cumulenic form ($H_2C_\beta{=}C_\alpha{=}O$), are in resonance with the "zwitterionic" form ($H_2C_\beta{}^-{-}C_\alpha{\equiv}O^+$) in which the O atom is partially positively charged and the C_β atom is partially negatively charged.[1e,f] The formation of the zwitterionic form is effected by both the importance of a C≡O triple bond and the influence of the O atom on the charge separation. Because of the fascinating electronic structure of ketenes, these species have frequently been the subject of intense investigations.[1,2] Many substituted ketenes have been generated and their properties and reactions examined. Tidwell and co-workers have theoretically investigated the substituent effects on ketene stability.[3] Calculated structures and energies indicate major stabilization of ketenes by electropositive groups and destabilization by electronegative substituents. There is also evidence that π-acceptor substituents stabilize and π-donor substituents destabilize ketenes. Wong has reported a theoretical study of properties and reactivities of ketenes, thioketenes, and selenoketenes.[4] Thioketenes and selenoketenes, which are best represented by neutral cumulenic forms, have been found to be more reactive than ketenes. Bernasconi has recently reported a high-level ab initio study of gas-phase acidities, barriers for the identity proton transfers, and charge distributions for ketenes and related molecules.[5] The results have shown that the acidities for $H_2C{=}C{=}X$, where X = O, S, NH, and CH_2, are all higher while the barriers are lower than the corresponding $CH_3CH{=}X$ series.

Recently, investigations of new methods for the in situ generation and reaction of ketene systems have received significant attention.[1,2] In particular, cyclobutenones bearing an unsaturated substituent at the 4-position, such as **1**, have emerged as valuable reagents in organic synthesis since such cyclobutenones have been found to sustain facile electrocyclic ring opening to the respective dienylketenes, **2**, which, in turn, undergo ring closure to afford cyclohexadienones **3** and thus lead to a variety of aromatic compounds, **4** (Scheme 1).[6] Within the last 15 years, the ready availability of numerous cyclobutenones

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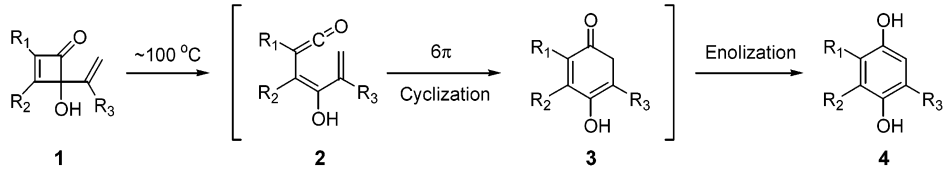
SCHEME 1

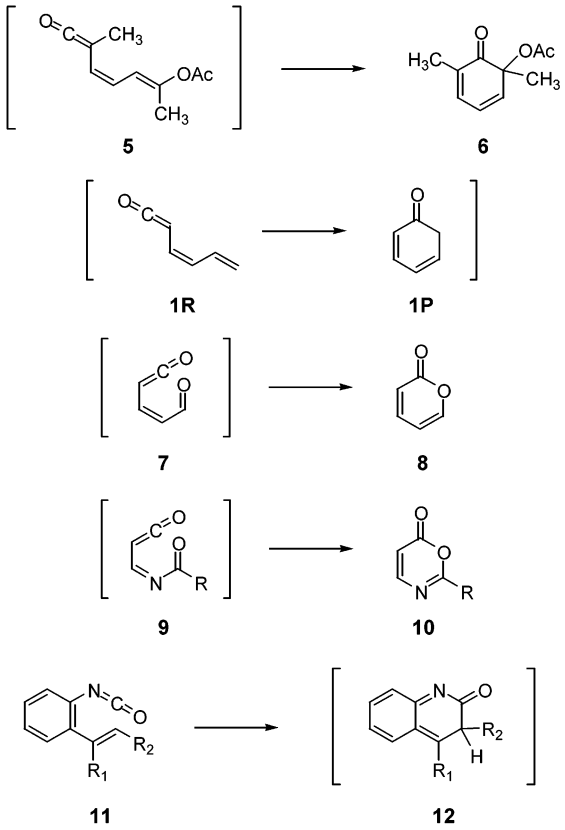


from commercially available squaric acid has opened the way to development of the syntheses of highly functionalized ring systems.[7] Since the starting cyclobutenones are now available with a variety of substitution patterns and the yields of the rearrangements are generally high, these ring expansions constitute one of the most versatile regiospecific routes to highly substituted aromatic compounds. By using this technology many medicinally important natural and unnatural products have been synthesized.[6,8]

Cyclobutenones provide, upon thermolysis, the conjugated ketenes via conrotatory electrocyclic ring opening.[6] There have been many experimental and theoretical studies of stereochemistry and activation parameters for the electrocyclic ring opening of cyclobutenones. Nguyen, Ha, and More O'Ferrall carried out a theoretical study of the electrocyclic reactions of cyclobutenones and showed that the unsubstituted cyclobutenone ring opening is nearly thermoneutral, consistent with its reversibility.[9] Tidwell and co-workers performed ab initio molecular orbital calculations on the ring opening of cyclobutene, cyclobutenone, and cyclobutenedione and found that the ring opening of cyclobutenone has the lowest activation energy (26.2 kcal/mol) in this series.[10] Houk and co-workers theoretically investigated the substituent effects on the ring opening of cyclobutenones.[11] Donor substituents on C4 of cyclobutenones prefer outward rotation while strong acceptors prefer inward rotation. The effects of substituents on the direction of cyclobutenone ring opening are the same as in cyclobutenes,[12] but the substituent effects are smaller in the cyclobutenone case due to the larger energy difference between the frontier molecular orbitals.[11]

Although thermal cyclizations of dienylketenes to cyclohexadienones have been extensively utilized in the synthesis of complex polycyclic aromatic compounds,[6] there are only few studies concerning the kinetic and

SCHEME 2



theoretical aspects of these conversions. The experimental barrier in solution for ring closure of **5** has been measured as 13.5 kcal/mol (Scheme 2).[13] The activation barrier for the cyclization of (*Z*)-1,3,5-hexatrienone (**1R**) to 2,4-cyclohexadienone (**1P**) has been calculated to be 12.8, 14.5, and 18.2 kcal/mol at the B3LYP/6-31G*, B3LYP/6-311G**, and semiempirical AM1 levels, respectively (Scheme 2).[14,15] In a study carried out by Birney,[16] ab initio (MP4(full,SDQ)/D95**//MP2/6-31G*+ZPE) calculations have shown that 5-oxo-2,4-pentadienal (**7**), a vinylog of formylketene, cyclizes to pyran-2-one (**8**) without a barrier via a pseudopericyclic pathway (Scheme 2). Rodriguez-Otero and Cabaleiro-Lago[17] have reinves-

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tigated this reaction, and indicated that conversion of **7** to **8** has no barrier at the B3LYP/6-31G** level, there is a barrier of 1.52 kcal/mol at the HF/6-31G** level, consistent with Birney's result.[16] Alajarin and co-workers[18] have recently described a similar pseudopericyclic process in which the in situ generated *N*-acylimidoylketenes **9** convert to 2-substituted 1,3-oxazin-6-ones **10** (Scheme 2). Computational studies have shown that the cyclization of **9** to **10**, where R = H, has no activation barrier at the B3LYP/6-311++G** and MP2/6-311++G** levels but does have an activation barrier of only 0.06 kcal/mol at the RHF/6-31G* level.[19] Interestingly, in the pseudopericyclic electrocyclization of *o*-vinylphenyl isocyanate (**11**) to 3*H*-quinolin-2-one (**12**) (Scheme 2), reported by Dolbier,[20] a torquoselectivity[12a−c,21] has been observed depending on the identity of *E* versus *Z* R_2 substituents. Moreover, the calculated activation barrier (29.8 kcal/mol) at the MP2/6-31G*//RHF/6-31G*+ZPE level for this cyclization, where $R_1 = R_2 = H$, is in very good agreement with the experimental value. In fact, pseudopericyclic reactions have been originally defined by Lemal[22] as pericyclic reactions in which there is a disconnection in the cyclic array of overlapping orbitals due to the presence of orthogonal orbital systems, making the otherwise forbidden processes allowed.[23] Pseudopericyclic reactions have been ignored for about 20 years but they have been placed on a solid foundation due to the recent works of Birney[2d,16,24] and others.[20,25] As concluded by Birney,[2d,24] pseudopericyclic reactions are typically characterized by planar (or almost planar) transition states and low (or nonexistent) activation barriers. Moreover, a pseudopericyclic reaction is orbital symmetry allowed regardless of the number of participating electrons since there is no closed loop of interacting orbitals, thus causing the orbital disconnections.

In contrast, little is known about the transition structures and energetics of the processes in which the terminal vinyl group of the parent dienylketene system is embedded into a cyclic olefin or an aromatic moiety, or is replaced with an allene or imine moiety, as in the ketene structures listed in Table 1.[14] The mechanisms and activation barriers of potentially pericyclic reactions are subjects of long-standing and continuing interest for the chemical community.[26] The aim of this study is to contribute a better understanding of such processes. Reported herein is a detailed study of 6π electrocyclization of dienylketenes at the Density Functional Theory level and an exploration of the properties of the transition structures involved, particularly via nucleus-independent chemical shift (NICS)[27] values.

Computational Methods

All calculations were performed at the Density Functional Theory (DFT) level by using the Gaussian 98 program suite.[28] Becke's three-parameter exchange functional (B3)[29] was employed in conjunction with the Lee−Yang−Parr correlation functional (LYP),[30] as implemented in Gaussian 98.[28] In geometry optimizations, Pople's 6-31G* split valence basis set was used.[31] 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 the "guess=(mix,always)" option). Geometries were optimized without constraint, and vibrational frequencies were then computed to characterize each structure as a minimum or transition structure (TS), via the number of imaginary frequencies (zero for minima and one for saddle points, respectively). After locating a TS, an intrinsic reaction coordinate (IRC)[32] calculation 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. The electronic energies, zero point vibrational energies (ZPVE), and imaginary vibrational frequencies (IMF) of the reactants, TSs, and products are provided in the Supporting Information. The reported energies in Table 1 and throughout the text are the activation ($\Delta H^{\ddagger}$) and reaction (ΔH) enthalpies at 298.15 K and 1 atm, including unscaled ZPVEs.

It should be noted that Houk and co-workers have explored in detail the advantages and disadvantages of the (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

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such reactions.[26c,33] Recently, (U)B3LYP calculations with similar basis sets have been successfully used in the calculation of TSs and reaction parameters for 6π electrocyclizations of (*Z*)-1,2,4,6-heptatetraene, (2*Z*)-2,4,5-hexatrienal, (2*Z*)-2,4,5-hexatrien-1-imine, and (*Z*)-5-oxo-2,4-pentadienal.[17,34]

Absolute NMR shielding values[35] were calculated by using the Gauge-Independent Atomic Orbital (GIAO) method[36] in the restricted Hartree−Fock (RHF) formalism employing the 6-31+G* basis set[31] at the B3LYP/6-31G* optimized geometries. NICS(0) values were obtained by calculating absolute NMR shielding at ring centers (nonweighted mean of the heavy atom coordinates). NICS values, pioneered by Schleyer,[27] are effective probes of aromaticity in transition states of pericyclic reactions.[37] Note that negative NICS values denote aromaticity (−11.5 for benzene, −11.4 for naphthalene) and positive NICS values show antiaromaticity (28.8 for cyclobutadiene, 21.7 for heptalene) while small NICS values indicate nonaromaticity (−2.1 for cyclohexane, −1.1 for adamantane).[27a]

Results and Discussion

Table 1 summarizes the activation and reaction enthalpies for 6π electrocyclizations of dienylketenes (entries 1−14) and related systems (entries 15 and 16). Reactants are denoted as **NR**, TSs as **NT**, and products as **NP**, where **N** is the entry number in Table 1. The numbering of the atoms (non IUPAC numbering) in reactants and products is provided in Table 1. The numbering system for TSs is the same as those for products and is provided in Figure 1. For comparison purposes, 6π cyclizations of (*Z*)-1,3,5-hexatriene (**15R**)[38,39] and (*Z*)-1,2,4,6-heptatetraene (**16R**)[40] at the same level of theory (entries 15 and 16, respectively) were also investigated. The closure of **15R** has been studied previously at many levels of theory[21] but, to the best of our knowledge, not at the B3LYP/6-31G* level. This level of theory predicts an activation enthalpy of 29.5 kcal/mol, which agrees well with the experimentally determined barrier of 29.0 kcal/mol.[38] The cyclization of **16R** has been previously investigated at the B3LYP level, but using 6-31G** and 6-31+G* basis sets.[34a,b] The B3LYP/6-31G* calculated activation barrier (19.2 kcal/mol) for this cyclization is in good agreement with those calculated with relatively larger basis sets (20.0 and 20.6 kcal/mol, respectively).[34a,b]

Several conformations have been located for each ketene, the most stable of which is generically depicted in Table 1. It should be noted that conformers of a particular ketene readily convert into each other due to the low activation barriers. Only the conformer with all the C−C single bonds in the s-cis conformation, however, has directly cyclized to a cyclohexadienone product, as proved by an IRC analysis.[32] For most ketenes the C1−C2−C3−C4 subsystem adopts a transoid conformation but it adopts a cisoid conformation for the ketene **5R**, presumably due to the stabilizing interaction between nitrogen and the ketene carbon. The C1−C5 subunit in all ketenes is essentially planar. In ketenes **1R**, **4R**, **5R**, **9R**, **11R**, **12R**, and **14R**, the C6 carbon is coplanar with the C1−C5 subsystem but in other ketenes studied it deviates from coplanarity since the C3−C4−C5−C6 subsystem is twisted to minimize the steric interactions. This deviation ranges from approximately 20.4° to 46.3° and reaches its maximum value for the α-naphthyl group in **7R**.

Figure 1 illustrates the TSs located for dienylketene cyclizations, which exist in a slightly distorted planar (or a slightly nonplanar) conformation. Notably, TSs do not seem to be of a typical, disrotatory, 6π pericyclic process. In all TSs, the C1−C5 subunit is essentially planar and the terminal vinyl group twists in the range of 23.5−34.2°, which channels its terminal p-orbital on the C6 atom for suitable overlap with the orthogonal p-orbital of the C1 atom in the ketene function (see **1X** in Figure 1), rather than with that of the C1=C2 π-bond, which would have happened in a typical, disrotatory pericyclic process. The formation of the σ-bond between C1 and C6 atoms leads to a disconnection in the cyclic array of overlapping orbitals since the atomic orbitals that are interchanging roles are mutually orthogonal. Since a single disconnection in the orbital overlap would be sufficient to make a reaction pseudopericyclic,[24a] the dienylketene cyclizations were classified as a pseudopericyclic process, consistent with the finding of Dolbier on a very similar system (**11** → **12**, Scheme 2).[20] Lower activation barriers and slightly aromatic TSs also support the pseudopericyclic nature of dienylketene cyclizations. Table 2 collects the NICS(0) values for TSs studied and reference compounds. Differences in NICS(0) values relative to those in reference compounds, i.e., ΔNICS(0) values, are also given in Table 2. Note that negative differences indicate an enhancement of aromaticity but positive differences indicate a reduction of aromaticity. In TSs **1T**−**14T**, NICS(0) values for the forming six-membered rings vary between −0.8 and −6.3 ppm, which indicates the nonaromatic or slightly aromatic nature of TSs, as compared to −15.2 and −11.1 ppm for those in **15T** and **16T**, respectively. It should be noted that the cyclization of **16R** via **16T** has recently been studied and termed not a pseudopericyclic process but rather a

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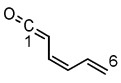
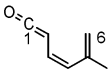
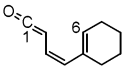
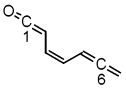
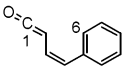
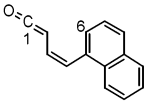
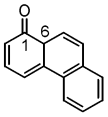
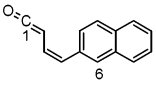
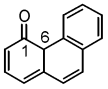
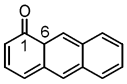
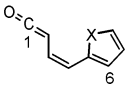
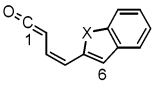
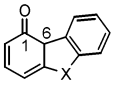
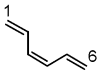
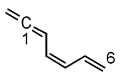
TABLE 1. B3LYP/6-31G* Calculated Activation and Reaction Enthalpies (kcal/mol) for 6π Electrocyclizations of Dienylketenes and Related Molecules

Entry	Reactants (**R**)	Products (**P**)		$\Delta H^{\neq}$	ΔH
1				11.9[a,b]	-23.4
2				8.1	-28.3
3				7.5	-26.4
4				10.5	-39.9
5				16.7	-19.1
6				16.1	1.6
7				13.4	-5.6
8a				12.2	-4.8
8b	**8aR**			19.6	10.4
9			X = O	15.3	-2.8
10			X = N	11.3	-5.3
11			X = S	13.7	-5.5
12			X = O	13.4	-7.9
13			X = N	8.4	-12.3
14			X = S	11.3	-10.4
15				29.5 (29.0)[c]	-13.5 (-15.2)[d]
16				19.2[e,f]	-28.7[g,h]

[a] 12.8 kcal/mol at 0 K (ref 14). [b] 14.5 kcal/mol at the B3LYP/6-311G*//B3LYP/6-311G** level (ref 15). [c] Experimental activation enthalpy (ref 38). [d] Experimental reaction enthalpy (ref 39). [e] 20.0 and 17.2 kcal/mol at the B3LYP/6-31G** and MP4SDTQ/6-31+G** levels, respectively (ref 34b). [f] $\Delta E_a(\epsilon=1.00)$ = 17.4 kcal/mol at B3LYP/6-31+G* level (ref 34a). [g] −27.0 and −31.4 kcal/mol at the B3LYP/6-31G** and MP4SDTQ/6-31+G** levels, respectively (ref 34b). [h] $\Delta E_{rxn}(\epsilon=1.00)$ = −29.1 kcal/mol at the B3LYP/6-31+G* level (ref 34a).

pericyclic reaction by the research groups of both Cossio[34a,c] and Rodriguez-Otero.[17,34b]

Compared with those in ketenes, C1−C2 and C3−C4 bonds in TSs **1T**−**14T** change from double to single bonds while C2−C3 and C4−C5 bonds change from single to double bonds. O−C1 bonds slightly weaken as well. Furthermore, the ketene moiety is no longer linear and the O−C1−C2 bond angle switches from 140.8° to 151.3°. The forming bond length (C1−C6) in TSs ranges from 1.950 to 2.339 Å, which, for most ketenes, resembles

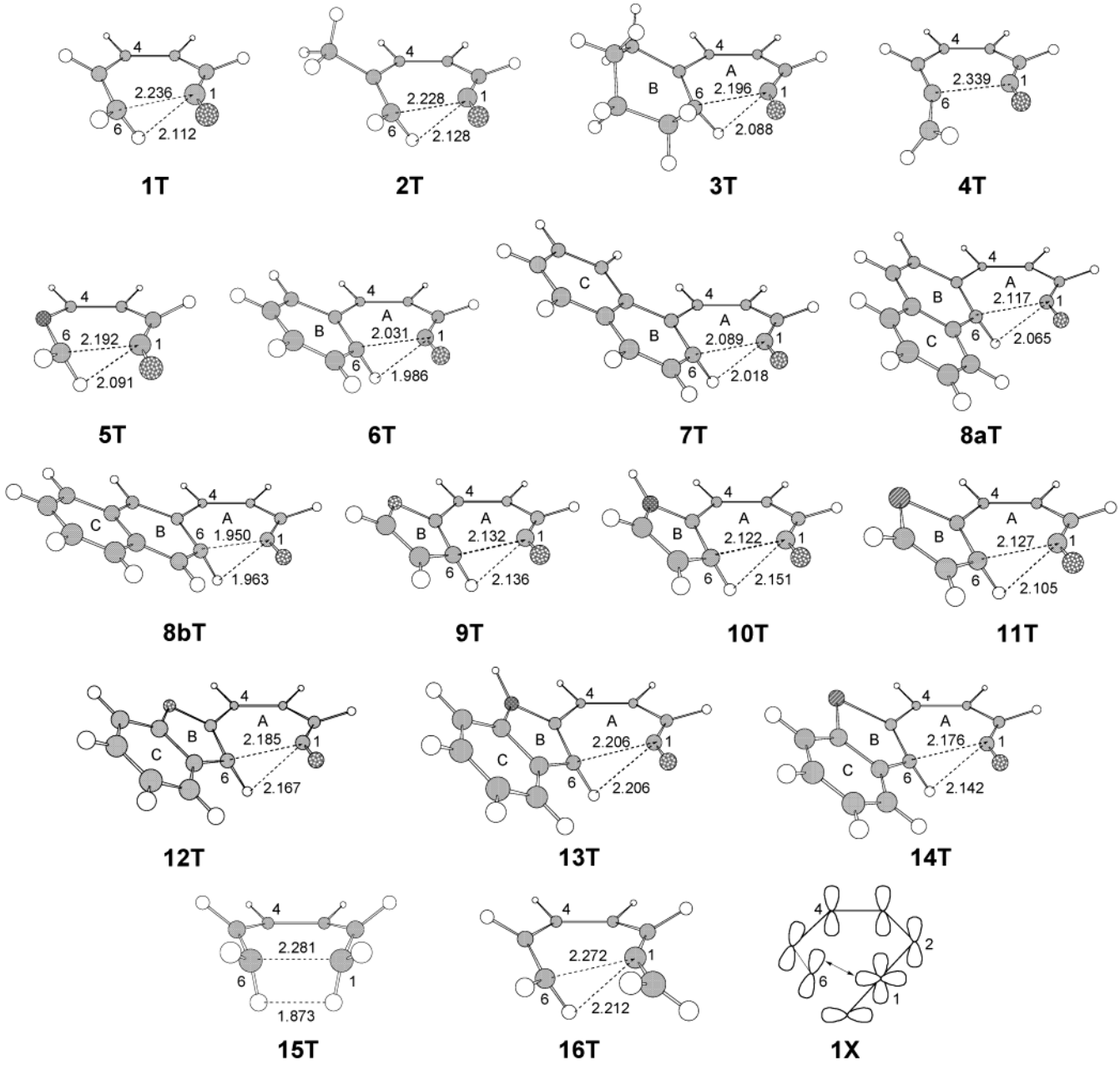


FIGURE 1. Transition structures and an orbital diagram for 6π electrocyclizations of dienylketenes and related molecules as well as atom numbering and selected bond distances in angstroms.

those observed for pericyclic reactions (2.1−2.3 Å).[26a] An interesting feature for most TSs is the close interaction distance (1.986−2.167 Å) between the C1 atom and the inward hydrogen of the C6 atom (Figure 1), which is 0.018−0.124 Å shorter than the corresponding C1−C6 forming bond distance. If this interaction were a serious steric interference to cyclization, then the relatively longer C1−C6 bond lengths necessary to decrease the repulsive interactions and/or higher activation energies necessary to overcome such interactions would be expected. This is not the case here since the C1−C6 bond distances are very similar to those for pericyclic reactions and activation energies are less than half of the typical activation barrier for pericyclic reactions (32 ± 3 kcal/mol).[26a] As shown previously by Houk,[21a,b] a close interaction distance is also observed between the two inward hydrogens of the terminal carbons of **15T**.

In TS **4T**, two orthogonal p-orbitals, i.e., those of ketene and allene functions, interact with each other, and thus the C5−C6 bond of **4T** is the least twisted (−23.5° out of plane) as compared to those in other TSs. It should be noted that TSs for dienylketene cyclizations are significantly different than that for 6π cyclization of hexatriene **15R** to cyclohexadiene **15P** since the latter operates through a boat-like TS, **15T** (Figure 1).[21a,b] The TSs roughly close to planar for the formers are presumably due to the orthogonal orbital of the ketene moiety since they easily react with the terminal olefin function without much disturbance of the planarity of TS. However, TSs for dienylketene cyclizations are very similar to that

TABLE 2. GIAO-HF/6-31+G*//B3LYP/6-31G* Calculated NICS(0) and ΔNICS(0) Values (ppm) for 6π Electrocyclizations of Dienylketenes and Related Molecules and for Reference Compounds

structure[a]		NICS(0) (ΔNICS(0))
1T	(6MR)	−3.1
2T	(6MR)	−2.8
3T	$(6MR)_A$	−2.9
	$(6MR)_B$	0.2
4T	(6MR)	−4.0
5T	(6MR)	−6.3
6T	$(6MR)_A$	−3.2
	$(6MR)_B$	−5.4 (4.3)
7T	$(6MR)_A$	−2.5
	$(6MR)_B$	−4.5 (5.4)
	$(6MR)_C$	−9.7 (0.2)
8aT	$(6MR)_A$	−2.0
	$(6MR)_B$	−4.5 (5.4)
	$(6MR)_C$	−10.1 (−0.2)
8bT	$(6MR)_A$	−2.9
	$(6MR)_B$	−6.9 (3.0)
	$(6MR)_C$	−5.8 (4.1)
9T	$(6MR)_A$	−2.0
	$(5MR)_B$	−7.6 (4.7)
10T	$(6MR)_A$	−1.4
	$(5MR)_B$	−9.4 (5.7)
11T	$(6MR)_A$	−1.9
	$(5MR)_B$	−8.2 (5.4)
12T	$(6MR)_A$	−1.6
	$(5MR)_B$	−5.7 (4.1)
	$(6MR)_C$	−11.5 (0.2)
13T	$(6MR)_A$	−0.8
	$(5MR)_B$	−7.9 (5.3)
	$(6MR)_C$	−11.2 (0.1)
14T	$(6MR)_A$	−1.6
	$(5MR)_B$	−6.2 (3.9)
	$(6MR)_C$	−10.6 (0.1)
15T	(6MR)	−15.2
16T	(6MR)	−11.1
benzene	(6MR)	−9.7[b]
naphthalene	(6MR)	−9.9[b]
furan	(5MR)	−12.3[b]
pyrrole	(5MR)	−15.1[b]
thiophene	(5MR)	−13.6[b]
benzofuran	(5MR)	−9.8[c]
	(6MR)	−11.7[c]
indole	(5MR)	−13.2[d]
	(6MR)	−11.3[d]
benzothiophene	(5MR)	−10.1[c]
	(6MR)	−10.7[c]

[a] 5MR and 6MR in parentheses indicate five- and six-membered rings, respectively. Subscripts A, B, or C show the place of the ring if there is more than one ring in the transition structure. See Figure 1. [b] From ref 27a. [c] From ref 27b. [d] From ref 41.

(**16T**) for the closure of heptatetraene **16R** to cyclohexadiene **16P** since **16T** bears similar orthogonal orbital characteristics as well.

The geometries of cyclohexadienones are qualitatively similar to those of the corresponding TSs. In all cyclohexadienones, ring skeleton carbons C1−C5 are almost in the same plane. The C6 carbon in cyclohexadienones **1P**−**5P** is almost coplanar with the C1−C5 subsystem. However, in other cyclohexadienones (**6P**−**14P**), it deviates from planarity in the range of 5.1−10.3°. As compared to those in ketenes and TSs, O−C1, C1−C2, C3−C4, and C5−C6 bonds become longer while C2−C3 and C4−C5 bonds become shorter. The newly formed C1−C6 single bond ranges from 1.339 to 1.555 Å, which is slightly longer than C1−C2, C3−C4, and C5−C6 single bonds.

The electrocyclization of hexatrienone **1R** to cyclohexadienone **1P** has been calculated to have an activation entalphy of 11.9 kcal/mol (Table 1). It is noteworthy that the activation energy for the 6π electrocyclization of **1R** is approximately 17.6 and 7.3 kcal/mol lower than those for the cyclizations of hexatriene **15R** and heptatetraene **16R**, respectively. This lowering is attributed to the reactivity of the ketene. For the cyclizations of ketenes **2R** and **3R**, relatively lower activation barriers (8.1 and 7.5 kcal/mol, respectively) have been predicted. Although it has not been studied in detail, electron-releasing groups at C5 appear to stabilize the TS, thus lowering the barrier. The closure of phenyl-substituted ketene **6R** proceeds with a barrier of 16.1 kcal/mol. As shown by the NICS(0) value (−9.7 → −5.4 ppm), the reduction in the aromaticity of the phenyl group increases the barrier. However, as compared to that for **6R**, the barriers calculated for the cyclizations of α- and β-naphthylketenes **7R** and **8aR** to cyclohexadienones **7P** and **8aP** have been lowered by 2.7 and 3.9 kcal/mol, respectively. Although NICS(0) values for the inner six-membered rings in TSs **7T** and **8aT** are negatively reduced to some extent, those for outer rings remain virtually the same, indicating that aromaticity in these TSs is preserved at least in one ring. As depicted in Table 1, ketene **8aR** can also cyclize to cyclohexadienone **8bP**, for which an activation barrier of 19.6 kcal/mol has been calculated, the highest barrier predicted in this study. Clearly, the loss of aromaticity in both rings of the naphthyl group increases the barrier (NICS(0) values for these rings are −6.9 and −5.8 ppm as compared to −9.9 ppm in naphthalene). Thus the cyclization of **8aR** to **8bP** is not feasible in comparison with that to **8aP**. The activation barriers for the closures of 2-furanyl- (**9R**), 2-pyrrolyl- (**10R**), and 2-thiophenyl-substituted (**11R**) ketenes show a decreasing trend in the order of **9R**, **11R**, and **10R**, which agrees qualitatively with the increasing aromaticity of their five-membered heterocyclic rings, as indicated by the NICS(0) values (−7.6, −8.2, and −9.4 ppm, respectively). A similar activation energy trend is observed for their benzo analogues **12R**, **14R**, and **13R**, but the barriers are relatively lower, presumably due to the retained aromaticity of their benzenoid rings, for which NICS(0) values remain virtually the same.

For most of the ketenes considered, electrocyclization is a favored process, as illustrated in Table 1. The cyclization of hexatrienone **1R** has been calculated to be exothermic by 23.4 kcal/mol, which is 9.9 kcal/mol more exothermic than that for hexatriene **15R**. The cyclization of allenyl-substituted ketenes **4R** has been the most exothermic process studied (−39.9 kcal/mol). This result could be attributed to the stability of the resulting cyclohexadienone **4P** via extended conjugation. Most importantly, the interruption of aromaticity during cyclization affects the reaction exothermicity and makes the reaction less exothermic or even endothermic. For instance, formation of cyclohexadienone **6P** from phenyl-substituted ketene **6R** is endothermic by 1.6 kcal/mol. The cyclizations of α- and β-naphthylketenes **7R** and **8aR** to cyclohexadienones **7P** and **8aP** are exothermic by 5.6 and 4.8 kcal/mol, respectively, since in these cyclization aromaticities are retained at least in one ring, as mentioned before. For the closure of **8aR** to **8bP**, the complete destruction of aromaticity in both rings causes

a substantial decrease in the reaction enthalpy, and makes the process endothermic by 10.4 kcal/mol, which is the most endothermic process found in this study. The cyclizations of 2-furanyl- (**9R**), 2-pyrrolyl- (**10R**), and 2-thiophenyl-substituted (**11R**) ketenes to corresponding cyclohexadienones have been found to be exothermic by 2.8, 5.3, and 5.5 kcal/mol, respectively. However, the closures of their benzo analogues **12R**, **13R**, and **14R** have been relatively more exothermic, which is attributed to the increased stability of the products via the preserved aromaticity in the benzenoid ring. Interestingly, 6π cyclization of heptatetraene **16R** has been found to be a quite exothermic process (−28.7 kcal/mol), being 5.3 kcal/mol more exothermic than that for hexatrienone **1R**.

Conclusion

In summary, the present DFT study reveals that, for most dienylketenes, the electrocyclization to corresponding 2,4-cyclohexadienone is a quite favored and exothermic process as compared to the closure of (*Z*)-1,3,5-hexatriene to 1,3-cyclohexadiene. More importantly, as evidenced by calculations, the cyclization proceeds via a pseudopericyclic process. For dienylketenes in which the terminal double bond is embedded into the benzenoid-type aryl moiety, the activation barrier goes up and the reaction becomes less exothermic or even endothermic due to the partial or complete loss of aromaticity as indicated by NICS values. For dienylketenes bearing a five-membered heterocyclic aromatic substituent and for their benzo analogues, the interruption of the aromaticity is slightly less pronounced. Transition structures for dienylketene cyclizations adopt a slightly nonplanar conformation, in contrast to a boat-like conformation for the closure of (*Z*)-1,3,5-hexatriene to 1,3-cyclohexadiene. The forming bond length in transition structures ranges from 1.950 to 2.339 Å, which is typical of pericyclic reactions for most dienylketenes. Further study of dienylketene cyclizations including substituent effects is currently under investigation.

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Supporting Information Available: (U)B3LYP/6-31G*-optimized Cartesian coordinates and energies for all stationary points and tables of selected structural parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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