JOC The Journal of Organic Chemistry

pubs.acs.org/joc Featured Article

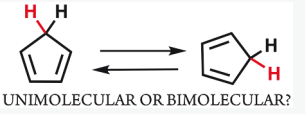
Probative Evidence and Quantitative Energetics for the Unimolecular Mechanism of the 1,5-Sigmatropic Hydrogen Shift of Cyclopentadiene

Quan Tran, Arkajyoti Sengupta, and K. N. Houk*

Cite This: J. Org. Chem. 2022, 87, 14995−15000 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: While the 1,5-sigmatropic hydrogen shift in cyclopentadiene is generally thought to be a unimolecular pericyclic reaction, Yamabe proposed a more complex bimolecular mechanism proceeding through the *exo* dimer of cyclopentadiene. DFT computations by Yamabe were claimed to show that the bimolecular mechanism was kinetically more favorable than the unimolecular mechanism. Reinvestigation of the unimolecular concerted mechanism and Yamabe's bimolecular mechanism with ωB97X-D and DLPNO-CCSD(T) calculations demonstrates a 25 kcal/mol preference for the unimolecular mechanism relative to the bimolecular mechanism. While Yamabe's calculations were performed with the less accurate B3LYP functional, the incorrect conclusion was the result of a different error discovered here. We have also computed corrections for tunneling that result in computed activation barriers within 1.5 kcal/mol of the experimental values.



INTRODUCTION

The unexpected discovery of 1,4-diphenylcyclopentadiene from the decarboxylation of 2,4-diphenylcyclopentadiene-1-carboxylate resulted the first report of [1,5]-hydrogen shift in 1939 by Drake and Adams.[1] Figure 1a shows the decarboxylation leading to a rearranged product of the assumed 1,3-diphenylcyclopentadiene. The final product has a continuous chain of conjugated double-bond linkages. In the subsequent years, similar [1,5]-hydrogen shifts were found in other substituted cyclopentadienes.[2−5]

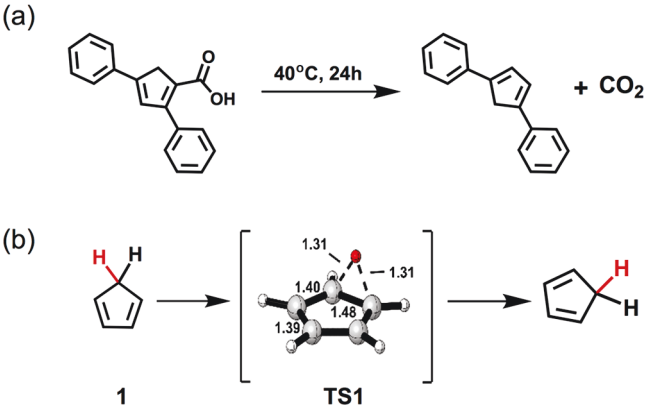


Figure 1. (a). First report of 1,5-[H] shift by Drake and Adams (in 1939, ref 1) observed in decarboxylation of 2,4-diphenylcyclopentadiene-1-carboxylate. (b) DFT-optimized transition state **TS1** for the direct 1,5-hydrogen shift in cyclopentadiene (**1**) calculated at ωB97X-D/def2-TZVP level of theory.

The experiments of Csicsery (in 1960) reported the existence of methylcyclopentadiene as a mixture of 5-methyl, 1-methyl, and 2-methyl isomers in a 3:45:52 ratio at thermodynamic equilibrium.[6] The isomerization of methylcyclopentadiene was elucidated as 1,5-hydrogen shifts by Mironov and Elizarova in 1963.[7,8] Kinetic studies by McLean showed that the rearrangement of 5-methylcyclopentadiene to 1-methylcyclopentadiene occurs with a rate constant of 1.8×10^{-4} s^{-1} at 25 °C.[9] Similar kinetic studies with primary H/D kinetic isotope effect (KIE) on [1,5]-hydrogen shifts in the acyclic Z-1,3-pentadiene provided detailed mechanistic insights in such isomerizations.[10]

The [1,5]-hydrogen shift observed in 1,3-cyclopentadiene is thought to be the prototypical sigmatropic shift (Figure 1b). Compared to the corresponding isomerization in 1,3-pentadiene, the hydrogen shift in cyclopentadiene is more favorable because the carbons that are the origin and terminus of the shifting hydrogen are bonded to each other.[11] The best experimental value for the activation barrier of this reaction is 24.3 ± 0.5 kcal/mol.[12]

Tunneling also contributes to the observed reaction rate, allowing reactions with insufficient energy to proceed by passage of the molecule through the barrier. Tunneling is most prevalent with hydrogen, but heavy atoms such as carbon and nitrogen have been observed to tunnel.[13−16] Tunneling from the ground state is rare, but generally occurs from higher energy vibrational states.[17−19] This is sometimes referred to as

Received: September 6, 2022
Published: November 1, 2022

https://doi.org/10.1021/acs.joc.2c02145
J. Org. Chem. 2022, 87, 14995−15000

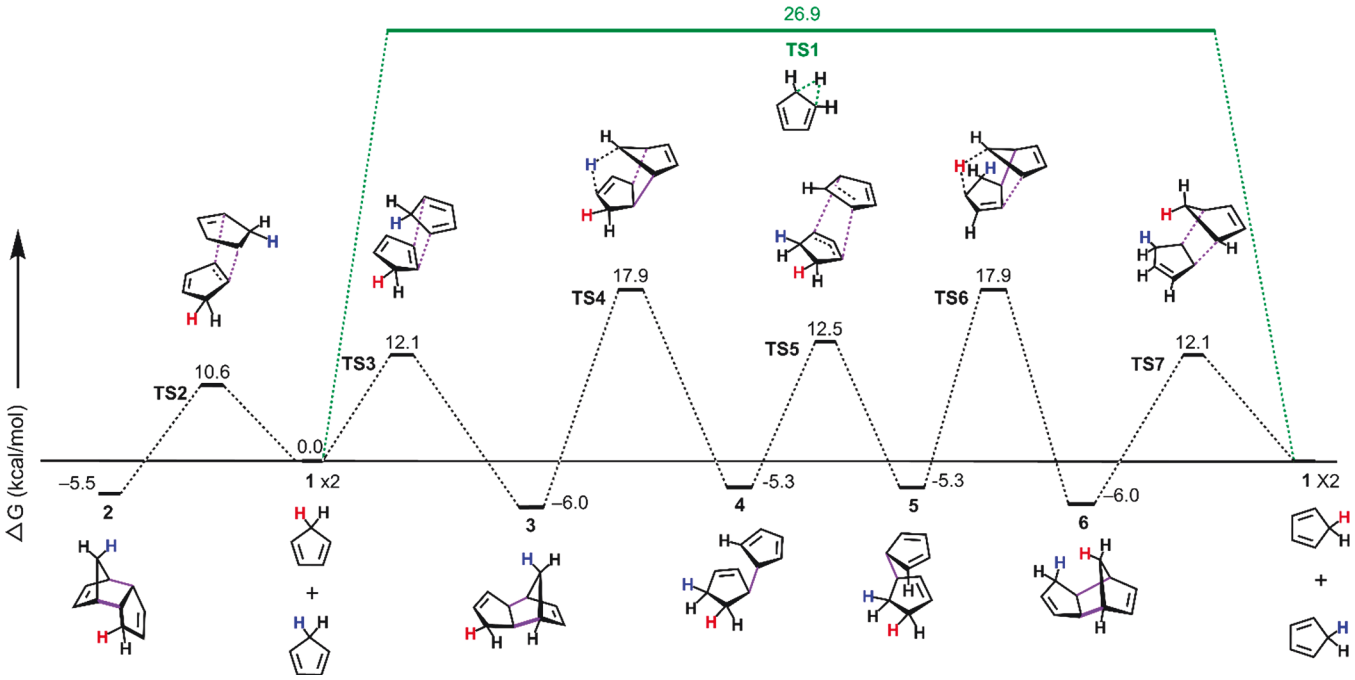


Figure 2. Yamabe's calculated Gibbs free energies (kcal/mol) (298.15 K, 1 M) for two mechanisms for the [1,5]-H-sigmatropic shift in cyclopentadiene with B3LYP/6-31G*.

vibrationally assisted tunneling (VAT) and has been proposed to have a large contribution to sigmatropic shift barriers.[20−22]

Despite the general acceptance of tunneling in this mechanism, a different mechanism for this hydrogen shift was proposed by Yamabe and co-workers involving a bimolecular, multistep process.[23] Their calculated barriers with B3LYP/6-31G* indicate a preference for their proposed pathway.

Although faster and less computationally expensive, B3LYP is now well-known for its significant errors in reaction energetics,[24] and to underestimate barrier heights for cycloadditions.[25] Nevertheless, useful results often occur with B3LYP due to error cancellation. While the functional underestimates protobranching[26] and long-range dispersion interactions[27] overestimation of energies for the conversion of π bonds into σ bonds gives 5 kcal/mol errors in barrier energies and 10 kcal/mol errors in reaction energies.[28] Criticisms of B3LYP have led computational chemists to move away from the use of the venerable functional.[24,29]

Recent advances in both computational hardware and improved algorithms now enable more accurate density functionals as well as wave function based ab initio CCSD(T) on medium to large systems.[30] Neese's domain-based local pair natural orbital (DLPNO) implementation of CCSD(T) abbreviated as DLPNO-CCSD(T)[31,32] closely approximates the "gold-standard" CCSD(T) energies for medium-sized organic molecules with errors <0.5 kcal/mol. ORCA[33] is a general package purpose program for electronic-structure calculations that provides routine single point DLPNO-CCSD(T) calculations on DFT optimized geometries obtained with ORCA, Gaussian, or other programs.[34,35] We have reinvestigated both unimolecular and bimolecular mechanisms of the hydrogen shift using a modern density functional that incorporates dispersion for accurate geometry and energies,[29,36] and DLPNO-CCSD(T) energies.

COMPUTATIONAL METHODS

Geometry optimizations were performed with the Head-Gordon functional, ωB97X-D,[37] and the def2-TZVP[38] basis, as well as the Yamabe-employed B3LYP[39] and the 6-31G*[40] basis set using Gaussian 16.[41] All the transition states were characterized as possessing one and only one imaginary frequency characteristic of a true first order saddle point. The identity of these transition states was further confirmed as representing the desired reaction coordinate by using intrinsic reaction coordinate (IRC) analysis. Single point energy calculations were performed in ORCA at the DLPNO-CCSD(T)/cc-pVQZ level on the optimized structures. Frequency analysis of these structures was done using the GoodVibes program.[42] Structures are represented with CYLview.[43]

RESULTS AND DISCUSSION

Unimolecular vs Bimolecular. Yamabe and co-workers proposed the bimolecular mechanism shown in Figure 2. Their reported energetics at the B3LYP/6-31G* level are shown. The Yamabe mechanism begins with an unfavorable *exo* [4 + 2] cycloaddition of two cyclopentadienes. The *endo* dimerization, via a bis-pericyclic transition state[44] (redefined as ambimodal by Houk and co-workers) is favored by 1.6 kcal/mol (Figure 2).

The hydrogen shift from one cyclopentadiene moiety to the other occurs in a retro-ene step (the rate-limiting step) in the *exo* dimer. Subsequently, a Cope rearrangement positions the cycloadduct for yet another hydrogen shift— this time in the reverse direction. Finally, a retro-Diels−Alder reaction releases two isomerized cyclopentadienes that have apparently undergone a [1,5]-hydrogen shift. This remarkable mechanism involves five pericyclic reactions.

The Yamabe calculations predicted a preference of 3.0 kcal/mol for this retro-ene rate limiting step (23.9 kcal/mol) as compared to the direct 1,5-sigmatropic hydrogen shift in

https://doi.org/10.1021/acs.joc.2c02145
J. Org. Chem. 2022, 87, 14995−15000

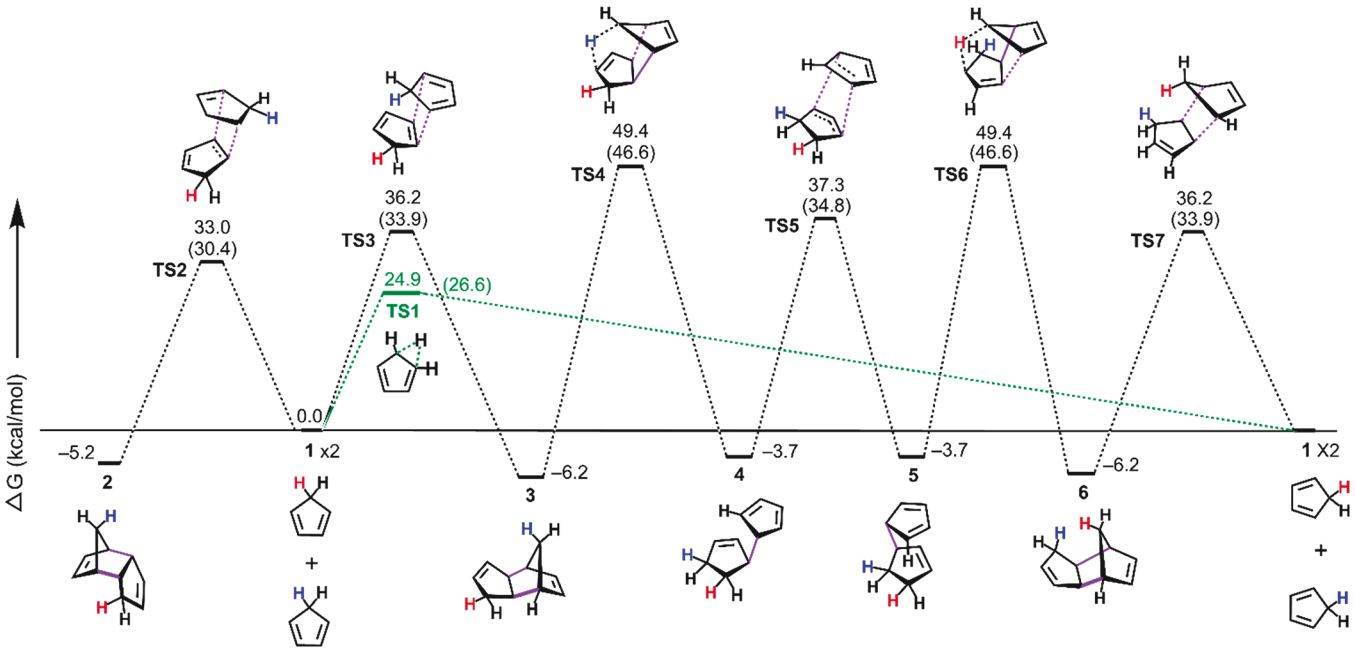


Figure 3. Calculated Gibbs free energies (kcal/mol) (298.15 K, 1 M) from this work for two mechanisms of the [1,5]-H-sigmatropic shift in cyclopentadiene with ωB97X-D/def2-TZVP. Values in parentheses are DLPNO-CCSD(T)/cc-pVQZ single point energies.

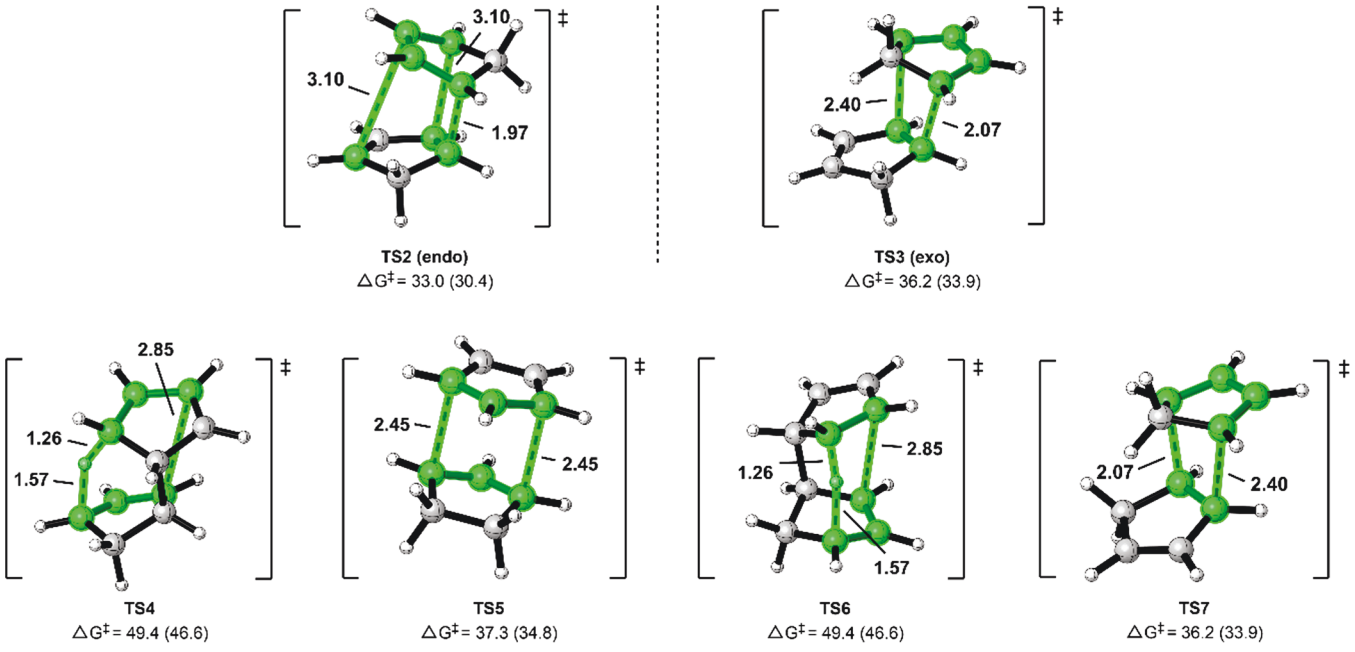


Figure 4. Calculated Gibbs free energies (kcal/mol) and transition structures for different reactions involved in [1,5]-H-sigmatropic shifts. Selected bond lengths are given in Å. Single point energies and geometry optimizations are calculated at DLPNO-CCSD(T)/cc-pVQZ (shown in parentheses) and ωB97X-D/def2-TZVP levels of theory, respectively.

cyclopentadiene (26.9 kcal/mol).[45] Yamabe and co-workers' proposal, while novel, erroneously presents free energies for bimolecular reactions that are one-half of the actual values. This is presumably because they had divided reaction and activation energies by two, perhaps believing they should compute the reaction of one cyclopentadiene proceeding to one-half dimer. Otherwise, they would have correctly predicted the unimolecular mechanism.

Computed and Experimental Values for Various Reactions of Cyclopentadiene. Our calculations with ωB97X-D/def2-TZVP on this scheme (Figure 3) show that the direct [1,5]-H shift barrier (24.9 kcal/mol) is 30.7 kcal/mol below the rate-determining retro-ene step. We instead calculated a staggering 55.6 kcal/mol free energy of activation with ωB97X-D beginning from the *exo* dimer, **3**. Figure 4 provides structures of the transition states figures modeled in their reactions.

The calculations show definitively that the unimolecular mechanism is the correct mechanism, as has been generally accepted in the literature. Table 1 contains values of computed and experimental energies of activation for the *endo* dimerization of cyclopentadiene. The best experimental given

https://doi.org/10.1021/acs.joc.2c02145
J. Org. Chem. 2022, 87, 14995−15000

Table 1. Computed and Experimental Activation Energies of the Cyclopentadiene Dimerization (kcal/mol)[a]

	exptl[45−48]	L1	L2	L3	L4	L5
E_a	16.7				17.7*	
$\Delta H^{\ddagger}$	15.2	17.02	19.9	11.6	17.8, 19.0*	
$\Delta G^{\ddagger}$	27.4	31.05	33.8	24.9	27.3, 33.0*	30.4*

[a]L1 = MPW1PW91/6-31+G(d) in ref 49; L2 = MP3/6-31G*//6-31G* in ref 50; L3 = CBS-QB3 in ref 46; L4 = ωB97X-D/6-31G* in ref 51 and ωB97X-D/def2-TZVP; L5 = DLPNO-CCSD(T)/cc-pQVZ//L4. *This work.

is 27.4 kcal/mol, while computation gives values from roughly 25−33 kcal/mol. The best value for this reaction computed by this work is 30.4 kcal/mol using the DLPNO-CCSD(T)/cc-pQVZ functional and basis set. However, these values tend to be somewhat higher than experiment.

Tunneling through the Barrier of the [1,5]-Sigmatropic Hydrogen Shift. Tunneling contributes to the rate of the [1,5]-sigmatropic hydrogen shift.[52,53] Early calculations by Dewar and Merz for this reaction show a large KIE providing strong evidence for vibrationally assisted tunneling in the analogous penta-1,3-diene.[52] Borden and others, using Bell tunneling corrections and variational transition state theory (VTST), have computed the fraction of hydrogen shifting that occurs by tunneling.[53] Borden demonstrated that 88.9% of the shift occurs by tunneling at 300 K.

From this fraction, we may compute quantitatively the effect of tunneling on the activation free energy by taking the relative proportion of tunneling and nontunneling reactions as a rate ratio in $\Delta G^{\ddagger} = -RT \ln(k_{\text{tunnel}}/k_{\text{non-tunnel}})$. This result suggests a lowering of the activation barrier by approximately 1.2 kcal/mol. Consequently, the tunneling corrected DLPNO-CCSD-(T) free energy is 25.4 kcal/mol, which is only 1.1 kcal/mol higher than the experimental value.

Table 2 lists different barriers reported in literature via experiments and various computational studies for the direct hydrogen shift. The calculated values range from 25 to 27 kcal/mol.[54−59] Our calculations described in above paragraphs provide an enthalpic barrier of 24.6 kcal/mol and a free energy barrier of 24.9 and 26.9 kcal/mol at the two levels.

Table 2. Computed Activation Energies of the 1,5-Hydrogen Shift in Cyclopentadiene (kcal/mol)[a]

	exptl[2]	L1	L2	L3	L4	L5
E_a	24.3 ± 0.5		27.0			
$\Delta H^{\ddagger}$	23.7	25.8	21.0*	24.6*	26.3*	25.1*
		26.4	26.7*			
$\Delta G^{\ddagger}$	23.9		26.0*	24.9*	26.6*	25.4*
			27.0*			
			27.0*			

[a]L1 = MP2/6-31G* in refs 54 and55; L2 = B3LYP/6-31G* in refs 56−58; L3 = ωB97X-D/def2-TZVP; L4 = DLPNO-CCSD(T)/cc-pQVZ//L3; L5 = L4 plus tunneling corrections. *This work.

CONCLUSION

The calculations on the 1,5-shift in cyclopentadiene with dispersion corrected ωB97X-D functional and highly accurate DLPNO-CCSD(T) method confirm that the bimolecular mechanism proposed by Yamabe is highly unfavorable compared to the direct [1,5]-sigmatropic hydrogen shift. We describe an easy-to-use correction to incorporate tunneling in the [1,5]-H shift barrier using prior computations on the kinetics of the reaction with and without tunneling. Application of this correction factor and DLPNO−CCSD(T) calculations provide predicted barriers close to that measured by Roth experimentally.[10] The unimolecular [1,5]-sigmatropic hydrogen shift with tunneling is confirmed as the mechanism of cyclopentadiene isomerization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.2c02145.

Energies and coordinates of optimized geometries for computed species (PDF)

AUTHOR INFORMATION

Corresponding Author

K. N. Houk − *Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, United States;* orcid.org/0000-0002-8387-5261; Email: houk@chem.ucla.edu

Authors

Quan Tran − *Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, United States*

Arkajyoti Sengupta − *Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, United States;* orcid.org/0000-0002-9917-2472

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.2c02145

Author Contributions

All authors discussed the results, contributed to the manuscript and have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Dr. Jacob Sanders (UCLA) for fruitful discussions. We are grateful to the National Science Foundation (CHE-1764328) for financial support of this research.

REFERENCES

(1) Drake, N. L.; Adams, J. R. Some 1,4-Diaryl-1,3-Cyclopentadienes. *J. Am. Chem. Soc.* **1939**, *61*, 1326−1329.

(2) Alder, K.; Flock, F. H.; Hausweiler, A.; Reeber, R. Über Die KonstitutionDerCyclopentadien-CarbonsaüreAusCyclopentadien-Kalium. *Chem. Ber.* **1954**, *87*, 1752−1759.

(3) Peters, D. Cyclopentadienecarboxylic Acid. The Structure of the Monomer and the Dimers. *J. Chem. Soc.* **1959**, 1761−1765.

(4) Neureiter, N. Pyrolysis of 1,1-Dichloro-2-Vinylcyclopropane Synthesis of 2-Chlorocyclopentadiene. *J. Org. Chem.* **1959**, *24*, 2044−2046.

(5) Riemschneider, R.; Nerin, R. Substitutionsprodukte Des Cyclopentadiens, 9. Mitt.: Phenylcyclopentadien. *Monatsh. Chem.* **1960**, *91*, 829−835.

(6) Csicsery, S. M. Methylcyclopentadiene Isomers. *J. Org. Chem.* **1960**, *25*, 518−521.

(7) Mironov, V. A.; Sobolev, E. V.; Elizarova, A. N. Substituted Cyclopent Adienes and Related Compounds: Communication 10.

The Three Isomeric Methylcyclopentadienes. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1963**, *12*, 1467−1474.
(8) Mironov, V. A.; Sobolev, E. V.; Elizarova, A. N. Some General Characteristic Properties of Substituted Cyclopentadienes. *Tetrahedron Lett.* **1963**, *19*, 1939−1958.
(9) McLean, S.; Webster, C. J.; Rutherford, R. J. D. Kinetic Isotope Effect for the Thermally-Induced Migration of Hydrogen in Cyclopentadienes. *Can. J. Chem.* **1969**, *47*, 1555−1559.
(10) Roth, W. R.; König, J. Wasserstoffverschiebungen, IV. Kinetischer Isotopeneffekt der 1.5-Wasserstoffverschiebung im cis-Pentadien-(1.3). *Liebigs Ann. Chem.* **1966**, *699*, 24.
(11) Rondan, N. G.; Houk, K. N. Ab Initio Transition Structures for 1,5-Sigmatropic Hydrogen Shifts of 1,3-Pentadiene and Cyclopentadiene. *Tetrahedron Lett.* **1984**, *25*, 2519−2522.
(12) Roth, W. R. 1.5-Wasserstoff-Verschiebung im Cyclopentadien und Inden. *Tetrahedron Lett.* **1964**, *5*, 1009−1013.
(13) Datta, A.; Hrovat, D. A.; Borden, W. T. Calculations Predict Rapid Tunneling by Carbon from the Vibrational Ground State in the Ring Opening of Cyclopropylcarbinyl Radical at Cryogenic Temperatures. *J. Am. Chem. Soc.* **2008**, *130*, 6684−6685.
(14) Gonzalez-James, O. M.; Zhang, X.; Datta, A.; Hrovat, D. A.; Borden, W. T.; Singleton, D. Experimental Evidence for Heavy-Atom Tunneling in the Ring-Opening of Cyclopropylcarbinyl Radical from Intramolecular 12C/13C Kinetic Isotope Effects. *J. Am. Chem. Soc.* **2010**, *132*, 12548−12549.
(15) Schleif, T.; Mieres-Perez, J.; Henkel, S.; Mendez-Vega, E.; Inui, H.; McMahon, R. J.; Sander, W. Conformer-Specific Heavy-Atom Tunneling in the Rearrangement of Benzazirines to Ketenimines. *J. Org. Chem.* **2019**, *84*, 16013−16018.
(16) Wu, Z.; Feng, R.; Li, H.; Xu, J.; Deng, G.; Abe, M.; Bégué, D.; Liu, K.; Zeng, X. Fast Heavy-Atom Tunneling in Trifluoroacetyl Nitrene. *Angew. Chem., Int. Ed.* **2017**, *56*, 15672−15676.
(17) Jaklevic, R. C.; Lambe, J. Molecular Vibration Spectra by Electron Tunneling. *Phys. Rev. Lett.* **1966**, *17*, 1139−1140.
(18) Küchenhoff, S.; Brenig, W.; Chiba, Y. Vibrationally Assisted Sticking, Tunneling and Isotope Effect for Hydrogen on Cu Surfaces. *Surf. Sci.* **1991**, *245*, 389−400.
(19) Mil'nikov, G. V.; Kühn, O.; Nakamura, H. Ground-State and Vibrationally Assisted Tunneling in the Formic Acid Dimer. *J. Chem. Phys.* **2005**, *123*, 074308.
(20) Dormans, G. J. M.; Buck, H. M. The Mechanism of the Thermal [1,5]-H Shift in Cis-1,3-Pentadiene. Kinetic Isotope Effect and Vibrationally Assisted Tunneling. *J. Am. Chem. Soc.* **1986**, *108*, 3253−3258.
(21) Pegg, G.; Meehan, G. Quantum Mechanical Tunneling in Homodienyl Sigmatropic [1,5]-Hydrogen Shifts of (Hydroxymethyl)-Styrylcyclopropanes. *Aus. J. Chem.* **1990**, *43*, 1071.
(22) Johnson, B. A.; Hu, Y.; Houk, K. N.; Garcia-Garibay, M. A. Vibrationally Assisted Tunneling in a Hydrogen Atom Transfer Reaction. *J. Am. Chem. Soc.* **2001**, *123*, 6941−6942.
(23) Yamabe, S.; Tsuchida, N.; Yamazaki, S. Revisiting Hydrogen [1,5] Shifts in Cyclopentadiene and Cycloheptatriene as Bimolecular Reactions. *J. Chem. Theory Comput.* **2005**, *1*, 944−952.
(24) Check, C. E.; Gilbert, T. M. Progressive systematic underestimation of reaction energies by the B3LYP model as the number of C−C bonds increases: Why organic chemists should use multiple DFT models for calculations involving Polycarbon hydrocarbons. *J. Org. Chem.* **2005**, *70*, 9828−9834.
(25) Zhao, Y.; Truhlar, D. G. Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **2008**, *41*, 157−167.
(26) Schreiner, P. R. Relative Energy Computations with Approximate Density Functional Theory—A Caveat! *Angew. Chem., Int. Ed.* **2007**, *46*, 4217−4219.
(27) Wodrich, M. D.; Corminboeuf, C.; Schleyer, P. v. R. Systematic Errors in Computed Alkane Energies Using B3LYP and Other Popular DFT Functionals. *Org. Lett.* **2006**, *8*, 3631−3634.
(28) Pieniazek, S. N.; Clemente, F. R.; Houk, K. N. Sources of Error in DFT Computations of C−C Bond Formation Thermochemistries: $\Pi \rightarrow \sigma$ Transformations and Error Cancellation by DFT Methods. *Ang. Chem. Int. Ed.* **2008**, *47*, 7746−7749.
(29) Kruse, H.; Goerigk, L.; Grimme, S. Why the Standard B3LYP/6-31G* Model Chemistry Should Not Be Used in DFT Calculations of Molecular Thermochemistry: Understanding and Correcting the Problem. *J. Org. Chem.* **2012**, *77*, 10824−10834.
(30) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. A Fifth-Order Perturbation Comparison of Electron Correlation Theories. *Chem. Phys. Lett.* **1989**, *157*, 479−483.
(31) Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. Natural Triple Excitations in Local Coupled Cluster Calculations with Pair Natural Orbitals. *J. Chem. Phys.* **2013**, *139*, 134101.
(32) Sparta, M.; Neese, F. Chemical Applications Carried out by Local Pair Natural Orbital Based Coupled-Cluster Methods. *Chem. Soc. Rev.* **2014**, *43*, 5032−5041.
(33) Neese, F.; Wennmohs, F.; Becker, U.; Riplinger, C. The ORCA Quantum Chemistry Program Package. *J. Chem. Phys.* **2020**, *152*, 224108.
(34) Liakos, D. G.; Neese, F. Is It Possible To Obtain Coupled Cluster Quality Energies at near Density Functional Theory Cost? Domain-Based Local Pair Natural Orbital Coupled Cluster vs Modern Density Functional Theory. *J. Chem. Theory Comput.* **2015**, *11*, 4054−4063.
(35) Bootsma, A. N.; Doney, A. C.; Wheeler, S. E. Predicting the Strength of Stacking Interactions between Heterocycles and Aromatic Amino Acid Side Chains. *J. Am. Chem. Soc.* **2019**, *141*, 11027−11035.
(36) Karton, A.; Goerigk, L. Accurate Reaction Barrier Heights of Pericyclic Reactions: Surprisingly Large Deviations for the CBS-QB3 Composite Method and Their Consequences in DFT Benchmark Studies. *J. Comput. Chem.* **2015**, *36*, 622−632.
(37) Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom−atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615−6620.
(38) Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057−65.
(39) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648.
(40) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; DeFrees, D. J.; Pople, J. A.; Gordon, M. S. Self-Consistent Molecular Orbital Methods. 23. A polarization-type basis set for 2nd-row elements. *J. Chem. Phys.* **1982**, *77*, 3654−65.
(41) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16*, Rev. A.03; Gaussian Inc.: Wallingford, CT, 2016.
(42) Luchini, G.; Alegre-Requena, J. V.; Funes-Ardoiz, I.; Paton, R. S. GoodVibes: Automated Thermochemistry for Heterogeneous Computational Chemistry Data. *F1000research* **2020**, *9*, 291.
(43) Legault, C. Y. *CYLview20*; Université de Sherbrooke, 2020; http://www.cylview.org.
(44) Caramella, P.; Quadrelli, P.; Toma, L. An Unexpected Bispericyclic Transition Structure Leading to 4 + 2 and 2 + 4 Cycloadducts in the Endo Dimerization of Cyclopentadiene. *J. Am. Chem. Soc.* **2002**, *124*, 1130−1131.
(45) Wassermann, A. Kinetics of an Inverse Diene Synthesis in the Pure Liquid State. *Nat.* **1936**, *138*, 369−369.

https://doi.org/10.1021/acs.joc.2c02145
J. Org. Chem. 2022, 87, 14995−15000

(46) Guner, V.; Khuong, K. S.; Leach, A. G.; Lee, P. S.; Bartberger, M. D.; Houk, K. N. A Standard Set of Pericyclic Reactions of Hydrocarbons for the Benchmarking of Computational Methods: The Performance of ab Initio, Density Functional, CASSCF, CASPT2, and CBS-QB3Methods for the Prediction of Activation Barriers, Reaction Energetics, and Transition State Geometries. *J. Phys. Chem. A* **2003**, *107*, 11445−11459.
(47) Turnbull, A. G.; Hull, H. S. A thermodynamic study of the dimerization of cyclopentadiene. *Aust. J. Chem.* **1968**, *21*, 1789−97.
(48) Herndon, W. C.; Grayson, C. R.; Manion, J. M. Retro-Diels-Alder reactions. III. Kinetics of the thermal decompositions of exo- and endo-dicyclopentadiene. *J. Org. Chem.* **1967**, *32*, 526−529.
(49) Werstiuk, N. H.; Sokol, W. Density functional theory computational study on Diels−Alder reactions of cyclopentadiene with selected vinylsilanes and methylenecyclopropane. *Can. J. Chem.* **2011**, *89*, 409−414.
(50) Jorgensen, W. L.; Lim, D.; Blake, J. F. Ab Initio Study of Diels-Alder Reactions of Cyclopentadiene with Ethylene, Isoprene, Cyclopentadiene, Acrylonitrile, and Methyl Vinyl Ketone. *J. Chem. Soc.* **1993**, *115*, 2936−2942.
(51) Tehrani, F. N.; Assaf, K. I.; Hein, R.; Jensen, C. M. E.; Nugent, T. C.; Nau, W. M. Supramolecular Catalysis of a Catalysis-Resistant Diels−Alder Reaction: Almost Theoretical Acceleration of Cyclopentadiene Dimerization inside Cucurbit[7]uril. *ACS Catal.* **2022**, *12* (4), 2261−2269.
(52) Dewar, M. J. S.; Merz, K. M.; Stewart, J. J. P. Vibrationally Assisted Tunnelling (VAa standard T) in a 1,5 Hydrogen Shift? *J. Chem. Soc., Chem. Commun.* **1985**, 166−168.
(53) Shelton, G. R.; Hrovat, D. A.; Borden, W. T. Tunneling in the 1,5-Hydrogen Shift Reactions of 1,3-Cyclopentadiene and 5-Methyl-1,3-Cyclopentadiene. *J. Am. Chem. Soc.* **2007**, *129*, 164−168.
(54) Clarke, J.; Fowler, P. W.; Gronert, S.; Keeffe, J. R. Effect of Ring Size and Migratory Groups on [1, N] Suprafacial Shift Reactions. Confirmation of Aromatic and Antiaromatic Transition-State Character by Ring-Current Analysis. *J. Org. Chem.* **2016**, *81*, 8777−8788.
(55) Bachrach, S. M. Theoretical studies of the [1,5] sigmatropic hydrogen shift in cyclopentadiene, pyrrole, and phosphole. *J. Org. Chem.* **1993**, *58*, 5414−5421.
(56) Jiao, H.; Schleyer, P. v. R. Electrostatic Acceleration of Electrocyclic Reactions by Metal Cation Complexation: The Cyclization of 1,3-cis-5-Hexatriene into 1,3-Cyclohexadiene and the 1,5-Hydrogen Shift in Cyclopentadiene. The Aromaticity of the Transition Structures. *J. Am. Chem. Soc.* **1995**, *117*, 11529.
(57) Caramella, P.; Quadrelli, P.; Toma, L. An Unexpected Bispericyclic Transition Structure Leading to 4 + 2 and 2 + 4 Cycloadducts in the Endo Dimerization of Cyclopentadiene. *J. Am. Chem. Soc.* **2002**, *124*, 1130−1131.
(58) Alabugin, I. V.; Manoharan, M.; Breiner, B.; Lewis, F. D. Control of Kinetics and Thermodynamics of [1,5]-Shifts by Aromaticity: A View through the Prism of Marcus Theory. *J. Am. Chem. Soc.* **2003**, *125*, 9329−9342.
(59) Alkorta, I.; Elguero, J. 1,2-Proton shifts in pyrazole and related systems: a computational study of [1,5]-sigmatropic migrations of hydrogen and related phenomena. *J. Chem. Soc., Perkin Trans.* **1998**, *2*, 2497−2504.

https://doi.org/10.1021/acs.joc.2c02145
J. Org. Chem. 2022, 87, 14995−15000