J. Am. Chem. Soc. **1998,** *120,* 5741−5750

Rearrangements on the C_6H_6 Potential Energy Surface and the Topomerization of Benzene

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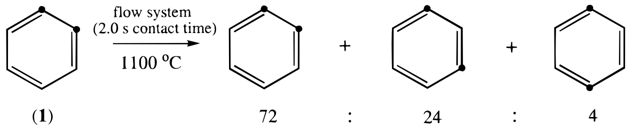
Received September 17, 1997. Revised Manuscript Received December 22, 1997

Abstract: The benzene potential energy hyperface was examined employing hybrid Hartree−Fock/density functional theory (B3LYP), second-order perturbation theory (MP2), and the coupled-cluster method with single, double, and perturbative triple excitations [CCSD(T)] in conjunction with DZP and TZ2P basis sets. All stationary points were characterized by harmonic vibrational frequency analyses; intrinsic reaction coordinates were calculated for all transition structures at B3LYP/DZP. Final energies were evaluated at the CCSD(T)/DZP//B3LYP/DZP level and corrected for $T = 1373$ K. There are three competing mechanisms for the high-temperature intramolecular topomerization of [1,2-$^{13}C_2$]benzene to [1,3-$^{13}C_2$]- and [1,4-$^{13}C_2$]benzene: (a) benzene ring contraction to benzvalene ($\Delta G^{\ddagger} = 93.5$ kcal mol^{-1}) followed by ring opening to benzene; (b) degenerate rearrangement of benzvalene via a $^1A''$ prefulvene TS ($\Delta G^{\ddagger} = 95.0$ kcal mol^{-1} relative to benzene) generating [1,4-$^{13}C_2$]benzene as a primary reaction product of [1,2-$^{13}C_2$]benzene; (c) [1,2]-H shift in benzene to yield 2,4-cyclohexadienylidene, followed by ring contraction to bicyclo[3.1.0]hexa-1,3-diene ($\Delta G^{\ddagger} = 96.7$ kcal mol^{-1}) and ring opening to fulvene. As these mechanisms are all within 3.2 kcal mol^{-1}, it is unlikely that benzene topomerizes at 1373 K exclusively via one mechanism.

Introduction

The prototype aromatic molecule, benzene (**1**), was obtained as a pyrolysis product by Michael Faraday in 1825.[1] Despite its positive heat of formation (ca. 20 kcal mol^{-1}), benzene is considered to be one of the most stable organic compounds. However, it undergoes polytopal rearrangements at high temperatures.[2] The first uncatalyzed thermal degenerate rearrangement of an aromatic compound, ^{13}C-labeled naphthalene, was reported by Scott and Apogian in 1977.[3] Degenerate rearrangements which violate the principle of minimal structural change, but which conserve both the molecular and the structural formula, have been called "automerizations".[4] Later the term "topomerization" was introduced[5] on the basis of Mislow and Raban's[6] as well as Eliel and Wilen's[7] more systematic stereochemical nomenclature for enantiotopic and diastereotopic ligands. Topomerization, now the more common name for degenerate isomerizations, describes reactions "converting a molecule into another that is superimposable with the original one but in which two or more atoms or ligands have exchanged place".[8]

Scheme 1. Topomerization of Benzene (**1**)



After Scott's initial discovery, thermal topomerizations of other aromatic compounds such as azulene,[9] pyrene,[10] benz[*a*]anthracene,[11] and acenaphthalene[12] also were observed. However, the topomerization of benzene (**1**) itself was not detected until 1987.[2] The reaction of doubly labeled [1,2-$^{13}C_2$]benzene in a quartz flow system with a contact time of 2.0 s at ca. 1100 °C gives a [1,2:1,3:1,4 $^{13}C_2$-benzene isotope ratio of 72:24:4 in the product (Scheme 1).

There has been much effort in elucidating the topomerization mechanisms for polyaromatic systems under Scott's experimental conditions (low substrate concentration and nitrogen as carrier gas).[3,9−14] The key step in the topomerization of naphthalene (**2**), according to experimental[14] and theoretical[13] data, is the reversible formation of benzofulvene (**3**) (Scheme 2).

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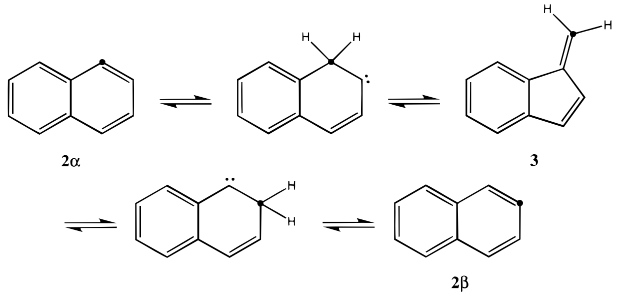
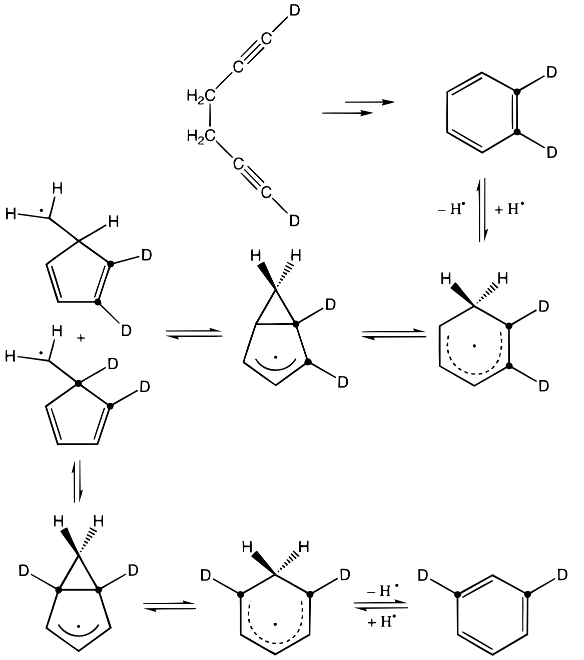
S0002-7863(97)03270-8 CCC: $15.00 © 1998 American Chemical Society
Published on Web 05/29/1998

Scheme 2. Suggested Unimolecular Mechanism for the Topomerization of Naphthalene

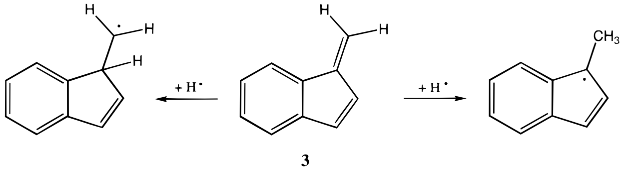


Scheme 3. Zimmermann's Suggestion for a Radical Mechanism for the Secondary Isomerization of 1,2-Dideuterobenzene[15]



Scott et al.[2] also proposed several plausible mechanisms for the topomerization of benzene, but the experimental evidence was not conclusive. Although radical chain reactions could not be ruled out, these were assumed to be improbable because of the low concentrations of benzene employed.[2] Zimmermann et al.[15,16] explained (Scheme 3) the observation of *m*- and *p*-dideuterobenzenes after the thermolysis of 1,6-dideutero-1,5-hexadiine at temperatures below 720 °C (0.3 s contact time) and in the presence of H_2 with a subsequent radical isomerization of the main product, 1,2-dideuterobenzene.[15,16] This mechanism also leads to ^{13}C scrambling in labeled benzene (Scheme 3).[16] On the basis of their results, Zimmermann et al.[16] challenged Scott's view of an unimolecular reaction mechanism. They suggested that under Scott's conditions (i.e., in the absence of hydrogen gas) radicals may be generated from some of the benzene molecules by "destructive adsorption at the inner surface of the reactor tube." Apart from the radical generation, all steps involved in the radical mechanism are only slightly endothermic, or even exothermic. Thus, this pathway may be a possible alternative to unimolecular processes if radicals are available as chain carriers.[16]

Scheme 4. Reaction of Benzofulvene with a Hydrogen Atom: Expected To Give the Methylindenyl Radical (Right) Rather Than the Indenylmethyl Radical (Left)



On the other hand, the unimolecular nature of the topomerization of naphthalene is firmly established.[13,14] Pyrolysis of labeled **3** gives a 21:79 ± 3 mixture of **2**α and **2**β (Scheme 2). If the reaction were a radical process, a hydrogen atom, generated by "destructive adsorption" of **3**, would react with **3** to give the methylindenyl radical rather than the indenylmethyl radical (Scheme 4). The latter, however, is the benzoannelated analogue of the cyclopentadienyl radical (see Scheme 3), an intermediate in Zimmermann's mechanism. The methylindenyl radical, on the other hand, cannot rearrange easily to **2**. Hence, it seems justified to assume a unimolecular reaction during the high-temperature topomerization of naphthalene and—by analogy—of benzene.

Since Scott et al.[2] were not able to detect any intermediate, current knowledge of the topomerization mechanism comes from the theoretical calculations (MP3/6-31G**//RHF/6-31G**) of Merz and Scott which favor a [1,2]-H shift reaction path similar to that of naphthalene involving carbenic intermediates.[17] An alternative mechanism with benzvalene (**4**) as intermediate is only 3 kcal mol^{-1} higher in energy, but this result is doubtful since the level of theory probably is insufficient for a clear distinction to be made. Since there possibly are alternative mechanisms not considered previously, we have now investigated a considerable part of the C_6H_6 potential energy surface (PES) using density functional theory as well as the highly correlated CCSD(T) ab initio method.

Methods

A rapidly growing body of evidence suggests that hybrid HF/DFT[18−20] methods give rather good geometries and energies for closed-shell as well as for open-shell systems.[21−25] Becke's[26] three-parameter gradient corrected exchange functional and the correlation functional of Lee, Yang, and Parr[27] (B3LYP) as implemented in Gaussian 94[28] are particularly effective. We employed a double−ξ quality basis set, consisting of Huzinaga's[29] (9s5p) primitive set for C and (4s) primitive set for H contracted by Dunning[30] to (4s2p) for C and (2s) for H, augmented with one set of polarization functions (DZP) on both carbon and hydrogen. The orbital exponents were $\alpha_d(C) = 0.75$ and $\alpha_p(H) =$

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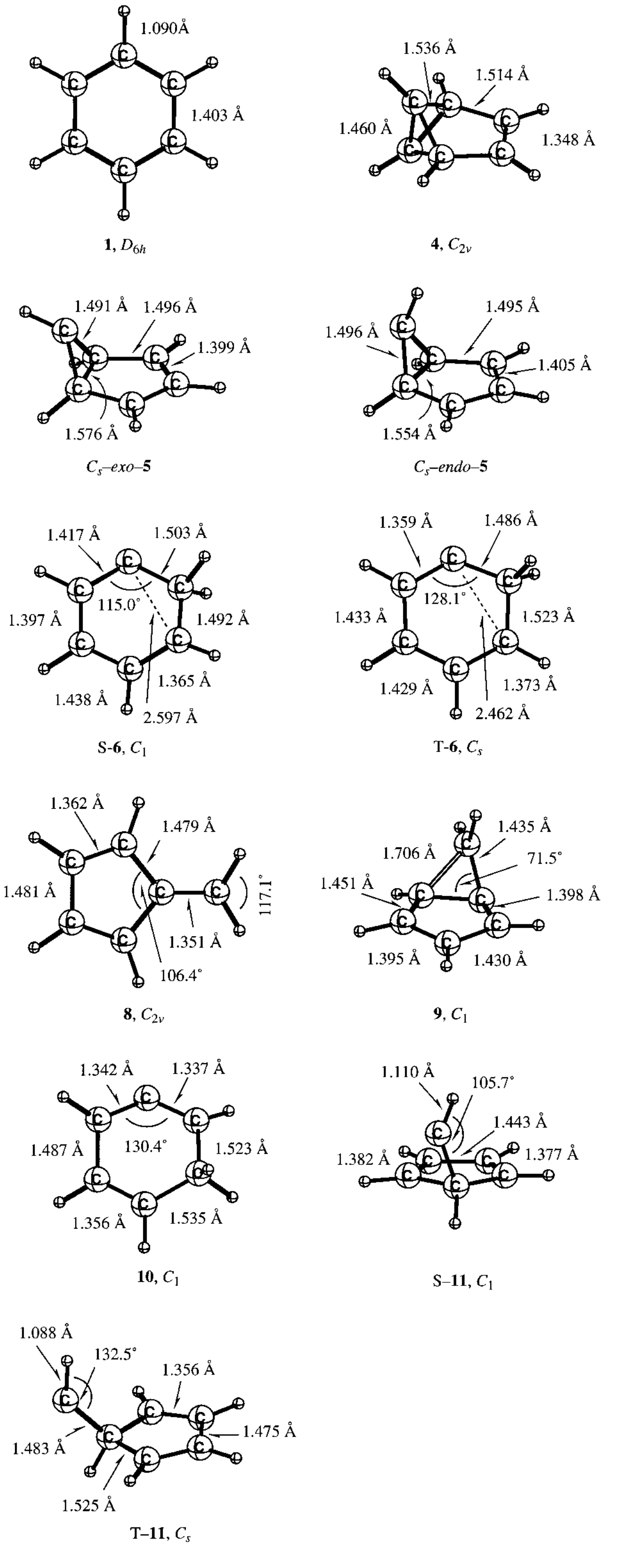
0.75. Furthermore, a TZ2P basis set, consisting of Huzinaga's[29] (10s6p) and (5s) primitive sets for C and H, contracted[31] to (5s3p) and (3s) for C and H, respectively, and augmented with two sets of polarization functions with orbital exponents $\alpha_d(\mathrm{C}) = 1.5$, 0.375 and $\alpha_p(\mathrm{H}) = 1.5$, 0.375, also was employed. Spherical harmonic polarization functions were used throughout this study. All geometry optimizations of closed-shell states were performed at the B3LYP/DZP level of theory. Spin-unrestricted procedures (UB3LYP/DZP) were employed for triplet and open-shell singlet states. The singlet–triplet energy separations of the carbenes were evaluated at the B3LYP/TZ2P//B3LYP/DZP level. In addition, 2,4-cyclopentadienylcarbene was studied with frozen-core second-order Møller–Plesset perturbation theory (MP2) using the DZP basis set for full geometry optimizations. Single points (frozen-core) with the coupled-cluster method involving single, double, and perturbative triple excitations [CCSD(T)][32–37] in conjunction with the DZP basis set gave the relative energies. A two-determinant coupled-cluster (TD-CCSD) single point calculation involving single and double excitations for the open-shell singlet $^1A''$ state of prefulvene employed the DZP basis set.[38,39]

The intrinsic reaction coordinate analysis[40–42] of transition structures employed Gonzalez and Schlegel's algorithm[43,44] at B3LYP/DZP. For all species, thermodynamic corrections at $T = 1373$ K were applied using unscaled B3LYP/DZP harmonic vibrational frequencies for comparison with experimental data. The enthalpies of activation $\Delta H^{\ddagger}$, free enthalpies of activation $\Delta G^{\ddagger}$, and activation energies E_a at 1373 K were obtained using standard procedures.[45] However, at the high temperature considered in this study, uncertainties in the thermodynamic functions may be higher than usual as they were derived from harmonic vibrational frequencies. All B3LYP and MP2 calculations were carried out with Gaussian 94;[28] the CCSD(T), and the TD-CCSD calculations used PSI2.0.8[46] and ACES2,[47] respectively.

Results and Discussion

Structures and Relative Energies. The structures considered are depicted in Figures 1 and 2 and their relative energies are summarized in Tables 1 and 2.



1, D_{6h}

4, C_{2v}

C_s–*exo*–**5**

C_s–*endo*–**5**

S-**6**, C_1

T-**6**, C_s

8, C_{2v}

9, C_1

10, C_1

S–**11**, C_1

T–**11**, C_s

Figure 1. Structures of **1**–**11** at the B3LYP/DZP level of theory.

A. Benzvalene Mechanism. Differentiation between concerted and stepwise pathways is difficult in pericyclic reactions involving diradical intermediates,.[22,48–53] The ring opening of benzvalene[54,55] (**4**, Scheme 5), a challenging example, has been

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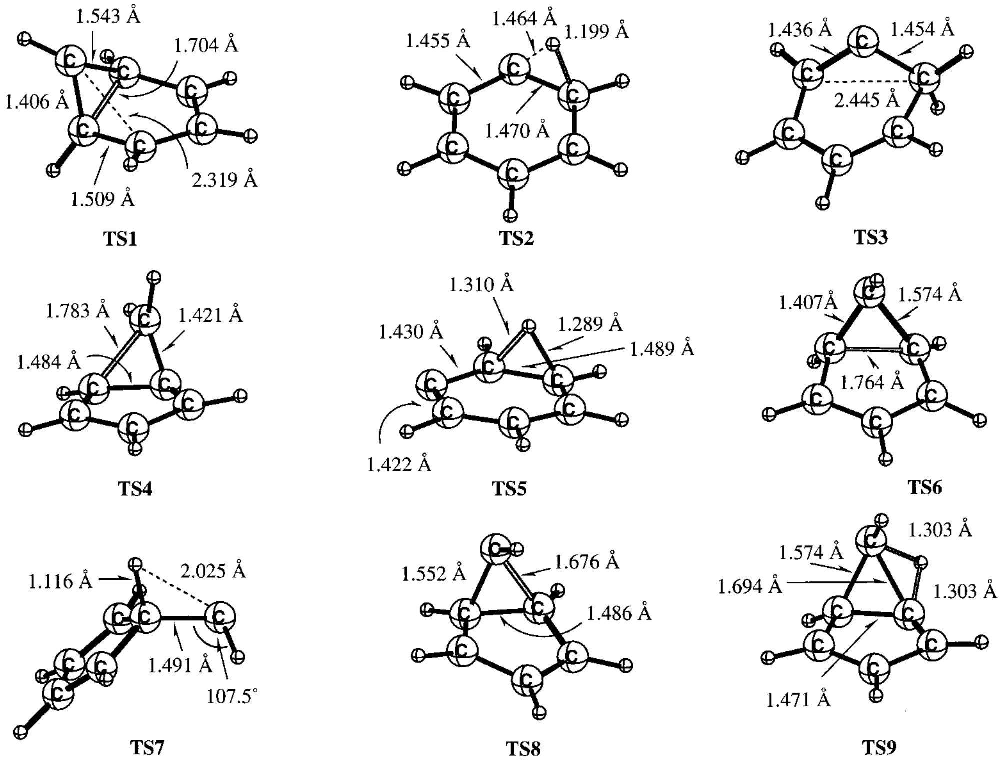


Figure 2. Transition structures **TS1**−**TS9** at the B3LYP/DZP level of theory.

Table 1. Zero-Point Corrected Relative Energies E_{rel} (kcal mol^{-1}) for Stationary Points on the C_6H_6 PES at CCSD(T)/DZP//B3LYP/DZP + ZPVE

structure	E_{rel}/(kcal mol^{-1})	structure	E_{rel}/(kcal mol^{-1})	structure	E_{rel}/(kcal mol^{-1})
1	0	**10**	73.7	**TS5**	107.3
4	72.4	S−**11** inward	107.1	**TS6**	114.7
C_S-exo-**5**	102.9	**TS1**	100.9	**TS7**	111.7
S-**6**	87.9	**TS2**	89.4	**TS8**	109.7
8	30.5	**TS3**	104.7	**TS9**	133.0
9	72.4	**TS4**	72.8		

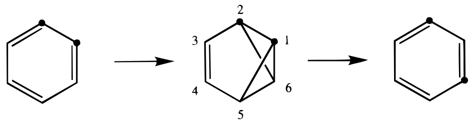
Table 2. Energies of **TS1** and C_s-*down*-**5** Relative to **4** at B3LYP and Coupled-Cluster Levels Using the DZP Basis Set

species	B3LYP	CCSD	CCSD(T)
4	0	0	0
TS1	27.7	35.4	30.3
C_s-exo-**5**	27.7[a]	33.5,[b] 30.8[a]	32.9[a]

[a] Spin-unrestricted treatment. [b] Two-determinant coupled-cluster method.

investigated experimentally[56] and theoretically.[17,57,58] Although the disrotatory−disrotatory opening of bicyclobutane is "forbidden", the involvement of the adjacent double bond in **4** "allows" a six electron concerted process.[57] Turro's experiments demonstrated that this reaction was concerted:[56] thermolysis of 1,6-dideuterobenzvalene (1,6-dideuterotricyclo[3.1.0.0^{2,6}]hexene) yields 1,2-dideuterobenzene exclusively. The lack of benzene-1,3-d_2 and benzene-1,4-d_2 suggests that the ring opening of 1,6-dideuterobenzvalene is stereospecific without an intermediate biradical. The energy of concert for the ring opening reaction, defined as the difference between the energy required to form the diradical intermediate (estimated via group additivity: 40 kcal mol^{-1}) and the measured enthalpy of activation (27 kcal mol^{-1}), is 13 kcal mol^{-1}.[56] These data indicate that the participation of a diradicaloid intermediate is unlikely. Another observation made by Turro, that "benzvalene is essentially non-chemiluminescent" indicates that the ground state and triplet state surfaces do *not* cross and corroborates the "allowed" and concerted nature of the reaction.[56] A surface crossing, which would generate long-lived chemiluminescent triplet states, is predicted for forbidden reactions involving biradical intermediates.

Scheme 5. Benzvalene Mechanism



1 4 1'

As found in semiempirical[57] and earlier ab initio[17] studies, the transition structure **TS1** for ring opening of benzvalene is quite asymmetric. Remarkably, the lengths of the two breaking bonds differ by 0.6 Å (Figure 2). In Dewar's words, the ring opening of **4** is an "allowed" concerted but not a synchronous "double" electrocyclic reaction.[57] An intrinsic reaction coordinate calculation[40−44] confirms that **TS1** connects **1** and **4**. Our activation parameters for the ring opening of benzvalene at 298 K (E_a = 29.3 kcal mol^{-1}, $\Delta S^‡$ = 2.6 eu, $\Delta G^‡$ = 27.9 kcal mol^{-1}) agree much better with the experimental values[56] (E_a = 26.7 kcal mol^{-1}, $\Delta S^‡$ = 1.6 e.u., $\Delta G^‡$ = 25.4 kcal mol^{-1}) than the parameters obtained by Merz and Scott (E_a = 39.9 kcal mol^{-1}, $\Delta S^‡$ = 3.2 eu, $\Delta G^‡$ = 38.3 kcal mol^{-1}) at MP3/6-31G**//HF/6-31G**.[17]

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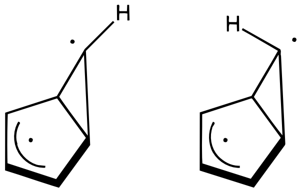
Chart 1. Bicyclo[3.1.0]hexenyl-6-yl (**5**); *exo* Conformer (Left) and *endo* Conformer

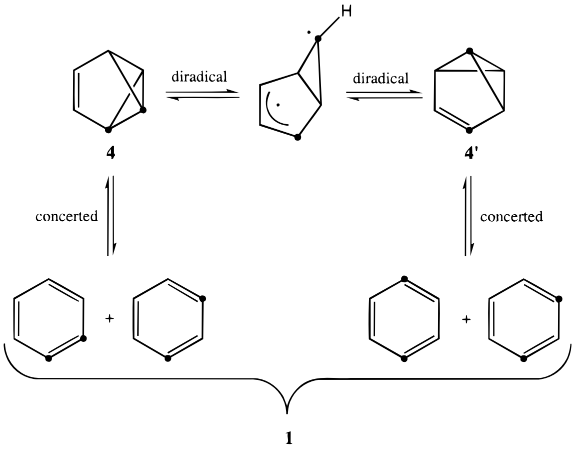


However, the assumption of a concerted reaction has been challenged by a recent CASSCF(6,6)/4-31G study,[58] which identified an asymmetric diradical intermediate, bicyclo[3.1.0]-hexenyl-6-yl (**5**, Chart 1), as an intermediate. Due to the pyramidal radical center at the three-membered ring, an *endo* and an *exo* form of **5** can exist. The C_s symmetric *exo* conformer, $^1A''$ prefulvene (C_s-*exo*-**5**), is an intermediate in the photochemistry of benzene according to low-level ab initio investigations.[59−61] Photochemically generated S_1 benzene relaxes via a conical intersection and yields C_s-*exo*-**5**, the first intermediate on the S_0 surface. However, Palmer et al.[58] characterized C_s-*exo*-**5** as a transition structure (at CASSCF-(6,6)/4-31G) which connects to two slightly distorted enantiomeric asymmetric *exo*-**5** forms (C_1-*exo*-**5**), termed "*pre-benzvalene*".[58] The suggestion that C_1-*exo*-**5** connects **1** and **4** via TS's with barriers of only 0.1−1.3 kcal mol^{-1} could not be verified in Dreyer and Klessinger's recent paper.[62] They also characterized C_s-*exo*-**5** as a transition structure at CASSCF(6,6)/3-21G, but C_1-*exo*-**5** only exists at the CASSCF(6,6)/STO-3G level; attempted optimization of C_1-*exo*-**5** using larger basis sets yielded **4**.[62] The C_s-*endo*-**5** conformer is a minimum at CASSCF(6,6)/3-21G.[62] Thus, the existence of a low-lying biradical reaction channel from **4** to **1** might be possible, although the theoretical evidence is not entirely convincing.

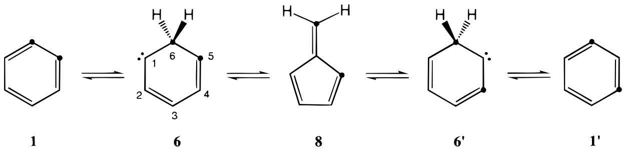
Recent results demonstrate that simple multiconfiguration SCF treatments (e.g. CASSCF) are biased, favoring diradicaloid structures.[63] Experiences in our[21,23] and other laboratories[22] show that B3LYP can provide a balanced description of closed-shell and open-shell species. This encouraged us to study the C_6H_6 PES in the pre-fulvene region using spin-unrestricted B3LYP. For C_s-*exo*-**5** and C_s-*endo*-**5** the spin operator expectation values $\langle S^2 \rangle$ are 1.025 and 1.032, respectively. Serious errors might arise in the UB3LYP and UCCSD(T) treatments due to the spin contamination of the spin-unrestricted open-shell singlet wave function. Thus, we also computed the energy of C_s-*exo*-**5** using the TD-CCSD method developed for open-shell singlets. All three quantum mechanical methods employed give similar energies for **TS1** and C_s-*exo*-**5** (Table 2), and the qualitative agreement with TD-CCSD strengthens our confidence in the spin-unrestricted B3LYP and CCSD(T) results for open-shell singlets, despite the spin contamination.

At UB3LYP/DZP the $^1A''$ C_s pre-fulvene *endo* conformation (C_s-*endo*-**5**) is a minimum, whereas the $^1A''$ *exo* form is a first-order saddle point with a low imaginary frequency (A″, 135 *i* cm^{-1}), in agreement with the CASSCF studies.[58,62] The IRC from C_s-*exo*-**5** leads to **4**. The C_s-*exo*-**5** is almost isoenergetic with **TS1** at the levels employed (Table 2). Thus, our calculations show that there exists a low energy path via $^1A''$ pre-fulvene for the degenerate isomerization, i.e., topomerization, of **4** into **4′**. This reaction path has considerable significance for the 1,2-^{13}C label scrambling in benzene. Once **4** is formed, it could rearrange stereospecifically to **1** via a *concerted* mechanism giving [1,2-$^{13}C_2$]benzene or [1,3-$^{13}C_2$]-benzene. The energetically very similar *diradical* mechanism, however, would also allow an isomerization of **4** to **4′** (Scheme 6). Thus, there exists a 1,2- into 1,4-^{13}C scrambling pathway *not* involving a [1,3-$^{13}C_2$]benzene intermediate. This scrambling possibility has not been considered in previous interpretations of experimental results.

Scheme 6. Scrambling Possibilities during the Rearrangements of Benzvalene (**4**)



Scheme 7. [1,2]-H Shift Mechanism



B. 1,2-Hydrogen Shift Mechanism. [1,2]-H shifts are known to be extremely facile carbene reactions.[64−67] For example, the methylcarbene (H_3C-CH, ethylidene) [1,2]-H shift barrier is only 1.2 kcal mol^{-1} according to high-level ab initio calculations.[68] The reverse reaction, the shift of a hydrogen to the adjacent carbon yields cyclohexa-2,4-dienylidene (**6**) from benzene (Scheme 7) via **TS2**. Not surprisingly, the corresponding barrier (**1** → **6**, 89.3 kcal mol^{-1}) is quite large.[17] The reverse reaction **6** → **1** only requires 3 kcal mol^{-1} activation. To our knowledge, there are no reports on the ground state of **6**. The closely related C_{2v} isomer, cyclohexa-2,5-dienylidene (**7a**), has a triplet $^3B_1$ ground state, and its first excited state, $^1A_1$, is 12 kcal mol^{-1} higher in energy at CASPT2//CASSCF(6,6) using tightly contracted ANO-type basis sets with polarization functions.[69] 4,4-Dimethylcyclohexa-2,5-dienylidene (**7b**), known through ESR spectroscopy to have a triplet ground state,[70] readily undergoes radical fragmentation reactions in the gas phase-yielding phenyl radicals (Scheme 8).[71] Recently, the photochemistry of **7b** was explored by matrix isolation tech-

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Scheme 8. Reactions of 4,4-Dimethylcyclohexa-2,5-dienylidene (**7b**) in the Gas Phase and in Solution

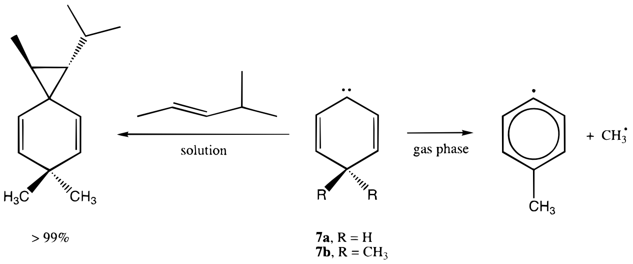


Table 3. Zero-Point Corrected Relative Energies E_{rel} (kcal mol^{-1}) of Carbenes Methylene, **6**, and **11** at the (U)B3LYP/TZ2P//(U)B3LYP/DZP + ZPVE Level of Theory

structure	E_{rel}	structure	E_{rel}
T-CH_2	0	S-**6** open-shell	2.9
S-CH_2	11.4 (9.1[a])	S-**11** inward	0
T-**6**	0	T-**11** inward	1.2
S-**6**	4.9	T-**11** outward	2.1

[a] Far infrared laser magnetic resonance. Reference 107.

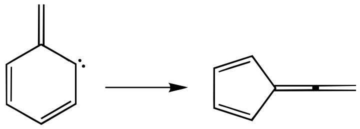
niques and ab initio calculations.[70] Its triplet ground state was found to have C_{2v} symmetry at the UMP2/6-31G* level. Most addition reactions of **7b** are stereospecific in solution, implying either a high reactivity of the singlet carbene compared to the rate of intersystem crossing to the more stable triplet ground state or a rather small singlet−triplet energy separation (ΔE_{ST}).[72]

The electronic structure of carbene **6** is very interesting, as it unites both an alkyl and an α,β-unsaturated substitution pattern. Both singlet and triplet states of alkylcarbenes are stabilized by hyperconjugation.[25,45,73] Since singlet carbenes have an empty p orbital, they are stabilized by alkyl groups about twice as much as the triplet states, where the carbene p orbital is semioccupied.[73] Thus, 2-propylidene has a singlet ground state.[73−75] On the other hand, vinyl substituted carbenes, as e.g., cyclopentadienylidene[76,77] and vinylmethylene,[78] have triplet ground states and low-lying $^1(\sigma\pi)$ singlet states. As with **7**,[69,70] the triplet state of **6** has a planar six-membered ring; the closed-shell singlet, however, is asymmetric (C_1). At B3LYP/TZ2P, **6** has a triplet ground state (Table 3). While the closed-shell σ^2 singlet state is 4.9 kcal mol^{-1} higher in energy, a $\sigma^1\pi^1$ open-shell singlet state exists which is only 2.9 kcal mol^{-1} above the triplet ground state. This result is in pronounced contrast to **7a** where the open-shell $^1B_1$ state is 3.4 kcal mol^{-1} less stable than the $^1A_1$ state, which in turn is 12 kcal mol^{-1} above the $^3B_1$ ground state.[69]

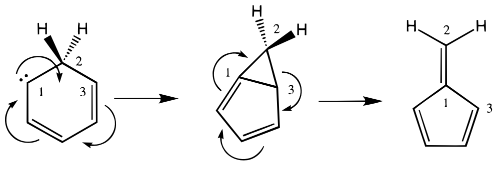
Cyclic carbene **6** could undergo an intramolecular CC insertion to yield fulvene (**8**). A similar reaction was observed for methylene cyclohexadienylidene, which gives fulvenallene (Scheme 9).[79]

Merz and Scott's calculations indicate that the rearrangement of **6** to **8** is not a one-step reaction but involves bicyclo[3.1.0]hexa-1,3-diene (**9**) as an intermediate (Scheme 10).[17] Dreyer and Klessinger's recent CASSCF study suggested **9** to be a possible intermediate in the photochemical formation of fulvene from benzene.[62] The barrier of the reaction **6** → **9** via **TS3**, 16.8 kcal mol^{-1} at CCSD(T), is similar to the [1,2]-C shift barrier of 2-butylidene to 2-methylpropene (17.3 kcal mol^{-1} at CCSD(T)/DZP).[67] Since the ensuing barrier for ring opening of **9** to **8** is only 0.4 kcal mol^{-1} (**TS4**), **9** is unlikely to be observable experimentally. Note that the C2−C3 bond in **9** (Scheme 10), which has to be broken to yield **8**, is unusually long (1.706 Å vs 1.535 Å in ethane).[80,81] Thus, the reaction from **8** to **1** is a two-step process with an overall barrier of 74 kcal mol^{-1}. The experimental high-pressure activation energy is $E_\infty = 64{-}68$ kcal mol^{-1} and was obtained by very low-pressure pyrolysis (VVLP) at 1050−1150 K using a RRKM fit assuming a concerted reaction mechansim.[82] A similar discrepancy between experiment and theory was found by Madden et al. at the G2M(rcc,MP2) level and attributed to neglected surface effects in the VVLP experiment.[83]

Scheme 9. Formation of Fulvenallene

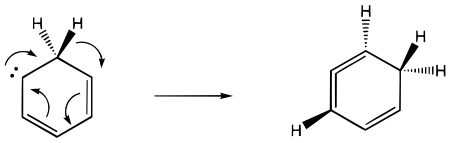


Scheme 10. Bicyclo[3.1.0]hexa-1,3-diene (**9**) as an Intermediate in the Reaction **6** → **8**



6 **9** **8**

Scheme 11. [1,2]-H Shift in **6** To Give Isobenzene (**10**)



6 **10**

Another interesting benzene isomer, isobenzene (1,2,4-cyclohexatriene, **10**), is accessible from **6** by [1,2]-H shift via **TS5** (Scheme 11). Only recently trapping studies provided ample experimental evidence for the existence of **10** and its derivates.[84,85] Previous semiemperical studies[86] suggest a chiral allene-type structure for **10** similar to the well-studied 1,2-cyclohexadiene.[66,86−88] The allenic CC bonds are slightly longer (1.342 and 1.337 Å, Figure 1) and the −HC=C=CH− angle

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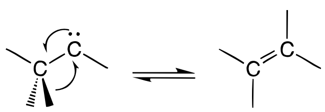
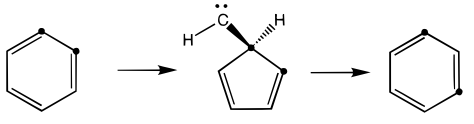
Scheme 12. [1,2]-C Shift in Carbenes



Scheme 13. [1,2]-C Shift Mechanism



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is slightly smaller (130.4°) than in asymmetric 1,2-cyclohexadiene (1.330−1.331 Å, 132.1°) at B3LYP/DZP due to the increased ring strain in **10**.[88] The barrier for the rearrangement of **6** via **TS5** to **10** is 19.4 kcal mol^{-1}, only 2.6 kcal higher than the competing reaction pathway from **6** to **8**. A transition structure for the direct isomerization of **1** into **10** circumventing carbene **6** could not be found. As a CC bond cleavage does not occur along the reaction path **1** → **10**, this reaction sequence does not contribute to a label scrambling of [1,2-$^{13}C_2$]benzene.

C. 1,2-Carbon Shift Mechanism. The first step of the 1,2-carbon shift mechanism involves the reverse of the well-known intramolecular insertion of a carbene into a CC bond to yield an alkene or an aromatic compound (Schemes 12 and 13).[89−91] The rearrangement of an alkene to a carbene has only been observed for highly strained bridgehead alkenes.[92−95] For instance, in 1(9)-homocubene the [1,2]-C shift to 9-homocubylidene is by far easier than the alternative [1,2]-H shift.[96] Despite the fact that 2,4-cyclopentadienylcarbene (**11**) may form from benzene under high-energy conditions, Merz and Scott[17] could not locate a transition structure for this reaction at the RHF level. They also found **11** to be quite high in energy (120 kcal mol^{-1} relative to **1**), leading them to conclude that the [1,2]-C shift mechanism is unimportant for the topomerization of benzene.[17]

Since Dreyer and Klessinger's[62] recent CASSCF study identified **11** as a key intermediate in the photochemical isomerization of **1** to **8**, we decided to include **11** in our examination as well. Evanseck et al.[97] reported two asymmetric conformations of singlet **11** differing in the orientation of the methylene hydrogen. The conformation with the H pointing toward the center of the ring ("inward" using the terminology of ref 97) is 5.5 kcal mol^{-1} (MP2/6-31G*//RHF/3-21G) more stable than the "outward" conformation which is assumed to be disfavored by electron−electron repulsion involving the π electrons of the diene system and the σ^2 electrons of the carbene.[97] An essentially free rotation around the C1−C2 bond (see Figure 3) was found by Dreyer and Klessinger at CASSCF(6,6)/3-21G.[62] All our optimization attempts to locate the "outward" form using B3LYP only resulted in benzvalene. To make sure that this result is not due to an insufficiency of the B3LYP method, we also employed MP2 in our study of S-**11** and obtained the same result. Thus, we conclude that singlet 2,4-cyclopentadienylcarbene adopts only the "inward" conformation and that the "outward" form does not exist on the C_6H_6 PES.

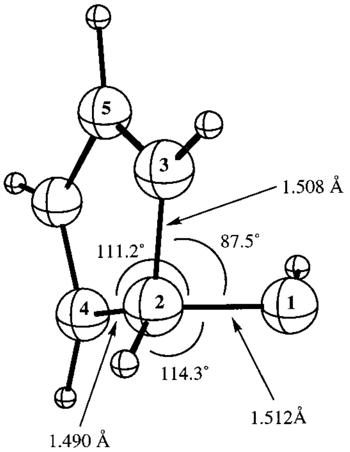

Figure 3. Geometry distortions of S-**11** at the B3LYP/DZP level of theory. Note the small angle C1−C2−C3.

The B3LYP/DZP geometry of S-**11** shows the characteristic features of hyperconjugative stabilization of the carbene center by the adjacent C2−C3 bond (Figure 3). The C2−C3 bond is longer than the C2−C4 bond by 0.018 Å. The C1−C2−C3 angle is only 87.5°, compared to 113.8° in T-**11** and 114.5° in 1-methylcyclopenta-2,4-diene. Thus, the hyperconjugative interaction leads to a considerable distortion of the geometry of S-**11**, similar to that found for *tert*-butylcarbene by Armstrong et al.[98] and by Sulzbach et al.[73] Besides the geometrical changes, the electron distribution reveals the stabilization in S-**11**. The NBO analysis of Reed et al.[99] shows an occupancy of 0.29 for the carbene p orbital. Charge transfer from the C2−C3 σ-bonding NBO as well as from the C3−C5 π-bonding NBO to the carbene p orbital is identified by second-order perturbation theory analysis of the Fock matrix in the NBO basis. The C1−C3 Wiberg bond index is 0.28. Thus, the carbene center is stabilized not only by hyperconjugation but also by an electrophilic interaction between the π system and the carbene p orbital.

The lowest triplet state of **11** is the C_s symmetric "inward" conformer; the triplet C_s "outward" structure is a 1.4 kcal mol^{-1} higher lying saddle point at UB3LYP/TZ2P. For carbene **11** we obtain a singlet ground state with $\Delta E_{\mathrm{ST}} = -1.2$ kcal mol^{-1} at B3LYP/TZ2P. Considering the error in the methylene singlet−triplet gap at this level of theory, $\Delta E_{\mathrm{ST}}(\mathbf{11})$ should be around -3.5 kcal mol^{-1}.

S-**11** is a high-lying shallow minimum on the C_6H_6 PES, 107.1 kcal mol^{-1} above benzene; there are several rearrangement pathways for **11** (Scheme 14). Besides the retroreaction to benzene via [1,2]-C shift (**TS6**), **11** can also undergo [1,2]-H shift to yield **8** via **TS7**. Intramolecular 1,4-cycloaddition leads to **4**. Indeed, the ease of cycloaddition is exploited in the synthesis of **4**:[55] reaction of lithium cyclopentadienide with methyllithium and dichloromethane gives **4** via either 2,4-cyclopentadienylcarbene or its 1-lithio-1-chloro-carbenoid precursor. The exclusive generation of 1-methylbenzvalene from

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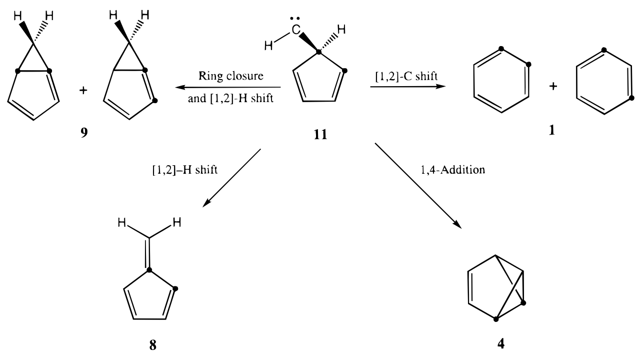
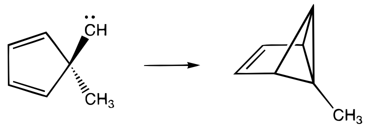
Scheme 14. Reactions of **11**



Scheme 15. Intramolecular 1,4-Addition of 5-Carbena-5-methyl-1,3-cyclopenta-1,3-diene, Yielding 1-Methylbenzvalene



5-carbena-5-methylcyclopenta-1,3-diene provides evidence that the benzvalene skeleton forms via stereospecific 1,4-addition of the singlet carbene S-**11** (Scheme 15).[100] Both HF[97] and semiempirical[101,102] calculations showed that the barrier for concerted (although not synchronous) 1,4-addition is 3 kcal mol^{-1} lower than that for 1,2-addition.

The barriers for the reactions of S-**11** to **1**, **4**, **8**, and **9** range from 3 to 26 kcal mol^{-1}. In agreement with experimental findings,[55,100] the intramolecular 1,4-addition to the π system (via **TS8**) is the most facile reaction of S-**11**, requiring an activation barrier of only 2.6 kcal mol^{-1} relative to S-**11**. Clearly, the electrophilic interaction between the carbene p orbital and the π-system of the diene is responsible for the very low barrier for 1,4-addition. The exocyclic hydrogen is still oriented "inward" in the B3LYP/DZP optimized **TS8**, in contrast to the TS obtained by Evanseck et al. at HF/3-21G,[97] and thus has to move "outward" during the 1,4-addition (Figure 4). An IRC calculation confirms that **TS8** connects S-**11** with benzvalene. Note that a TS for 1,2-addition does not exist at the B3LYP/DZP level. Evanseck's HF/3-21G 1,2-addition TS,[97] which is characterized by an "outward" standing exocyclic hydrogen, results in benzvalene upon reoptimization at B3LYP/DZP and MP2/DZP.

As expected, the [1,2]-H shift (**TS7**, $E_a = 4.6$ kcal mol^{-1}) is favored over the [1,2]-C shift (**TS6**, $E_a = 7.6$ kcal mol^{-1}) by 3 kcal mol^{-1}. Compared to Dreyer and Klessinger's[62] CASSCF(6,6)/3-21G structure, our B3LYP/DZP geometry for **TS7** is more educt-like with a very unsymmetrically bridging hydrogen (Figure 2), similar to recent B3LYP/6-31G* results.[83] The bond to the migrating hydrogen is stretched only slightly, from 1.094 Å in S-**11** to 1.116 Å, and it is still 2.025 Å away from the carbene center. The much lower energy of **TS7** with respect to S-**11** at our level of theory (6.1 kcal mol^{-1} at B3LYP/DZP vs 15.6 kcal mol^{-1} at CASSCF(6,6)/3-21G) shifts the TS along the reaction coordinate toward the educt, in agreement with Hammond's postulate.[103]

The transition structure **TS6** for the [1,2]-C shift reaction **1** → **11** is product-like (Figure 2) due to its high barrier of 114.7 kcal mol^{-1}. The distance between C2 and C3, 2.430 Å in **1** and 1.508 Å in S-**11** (see Figure 3), has decreased to 1.764 Å in **TS6**. The evolving carbene center at C1 is 66.7° out of the ring plane. Calculation of the IRC confirms that **TS6** does connect **11** and **1**.

A [1,2]-H shift accompanied by a simultaneous ring closure via **TS9** to yield bicyclic **9** is another reaction channel originating from S-**11**. However, the **TS9** geometry is very similar to the CASSCF(6,6)/3-21G transition structure Dreyer and Klessinger[62] assigned to the rearrangement of pre-benzvalene (**5**) into **9**, although a minimum corresponding to **5** could not be found at CASSCF. Our intrinsic reaction coordinate calculation shows that **TS9** connects S-**11** with **9** at a barrier of 25.9 kcal mol^{-1}. Since there are lower lying alternative pathways, this reaction is not important experimentally.

D. Dyotropic Shift Mechanism. A dyotropic rearrangement[104] shift for benzene (**1**) involving a hydrogen shift from C1 to C2 while C3 migrates from C2 to C1, might give fulvene (**7**) directly (Scheme 16).

However, Merz and Scott[17] were not able to locate a TS for this dyotropic benzene rearrangement at HF/6-31G*; instead, they found a high-lying TS connecting **1** and **9**. Hence, the process involves two steps with **9** as the intermediate at this level. Thus, the mechanism is *not* strictly dyotropic.[104] Our preliminary HF/6-31G* calculation gave Merz and Scott's transition state, but we noticed that its geometry was very similar to that of **TS9**. Moreover, intrinsic reaction coordinate calculations at both HF/6-31G* and B3LYP/DZP show that the Merz–Scott transition state[17] is the same as **TS9** but that it does *not* connect **9** and **1**. Instead, **TS9** describes the pathway between **9** and **11**.

Thermochemical Corrections and the Thermal Topomerization of Benzene. For comparisons with experiment, we evaluated the free enthalpies ΔG at 1373 K of the ground and transition states possibly involved in the topomerization of benzene (Table 4). For the benzvalene mechanism, a $\Delta G^{\ddagger}$ value of 93.5 kcal mol^{-1} is computed for the **1** → **4** reaction via **TS1**. A very similar free activation enthalpy relative to benzene, $\Delta G^{\ddagger} = 95.0$ kcal mol^{-1}, is obtained for the biradical topomerization of **4**. The three-step [1,2]-H shift mechanism is more complicated. When the thermochemical parameters are included, the energy of **TS2** is lowered more than **6**, resulting in a negative activation barrier ($\Delta G^{\ddagger} = -1.4$ kcal mol^{-1}) for the **6** → **1** reaction. This suggests that the carbene **6** does not exist at very high temperatures. The highest free activation enthalpy of the [1,2]-H shift mechanism, 96.6 kcal mol^{-1}, thus corresponds to the rearrangement of **1** to **9**. The [1,2]-C shift mechanism does not seem to be a viable topomerization mechanism under Scott's experimental conditions, due to its 9 kcal mol^{-1} higher $\Delta G^{\ddagger}$.

Conclusions

The investigation of the reactions on the C_6H_6 potential energy surface reveals that benzvalene (**4**) is one of the key intermediates in the thermal intramolecular topomerization of benzene (**1**). Besides the conventional concerted **1** → **4** mechanism, there exists a biradical pathway similar in energy for the degenerate isomerization of benzvalene. This biradical **1** → **4** → **4′** → **1′** reaction, not considered previously in the interpretation of experimental results, allows the generation of [1,4-$^{13}C_2$]benzene as a primary reaction product from [1,2-$^{13}C_2$]benzene. The competing [1,2]-H shift mechanism is only slightly higher in energy. Thus, we conclude that, for the intramolecular topomerization of benzene, several mechanisms operate simultaneously.

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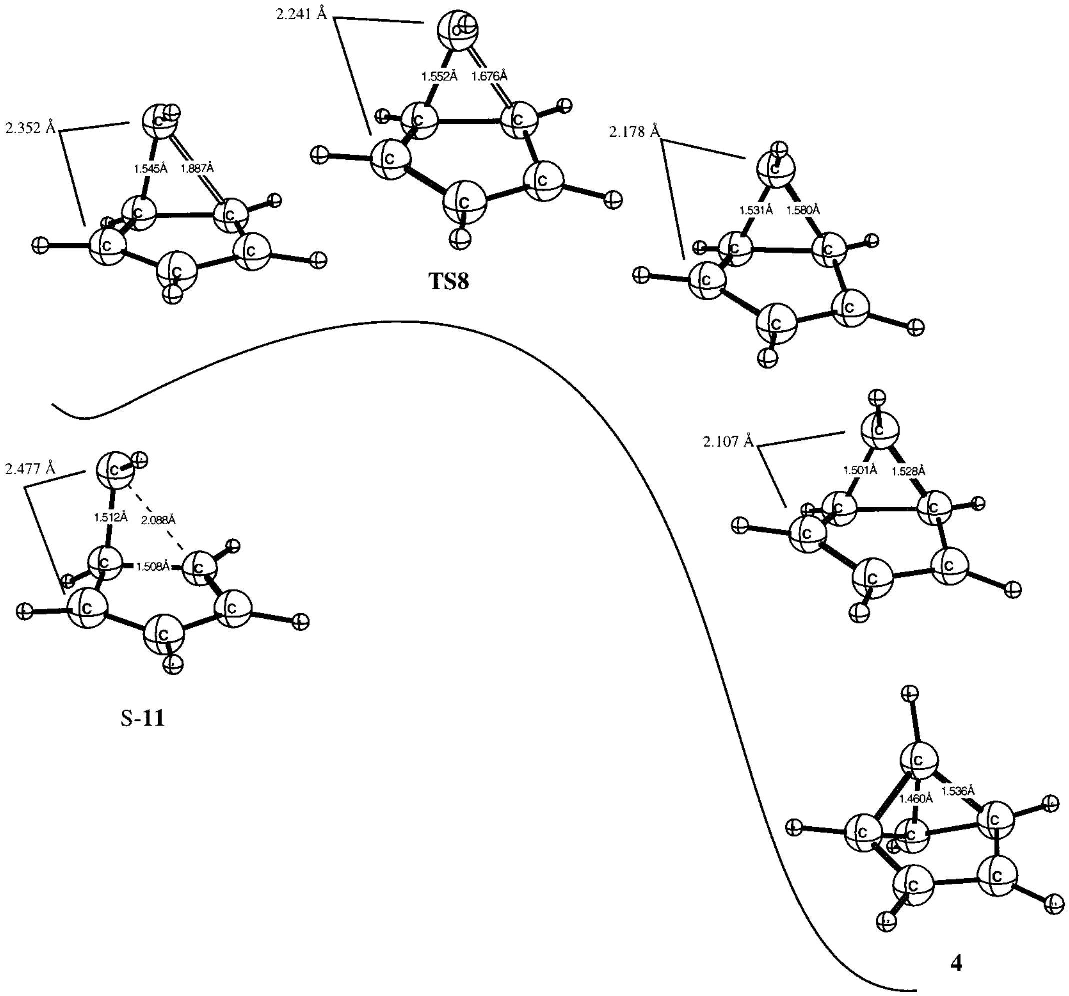
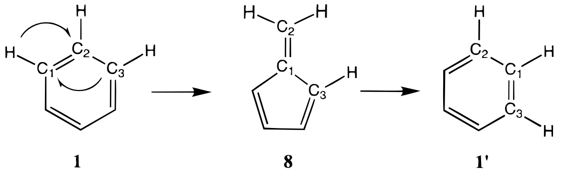


Figure 4. Schematic representation of the pathway S-**11** to **4**. Geometries were obtained from an intrinsic reaction coordinate calculation (IRC) at the B3LYP/DZP level. Note the motion of the methylene hydrogen from an "inward" position in S-**11** to an "outward" position in **4**. Bond lengths are given in angstroms.

Scheme 16. Dyotropic Shift Mechanism



However, we expect the benzvalene mechanism and its biradical extension to be disfavored for condensed aromatic molecules, like naphthalene. In such a system the aromaticity of both benzene rings has to be destroyed for the **2**α → **2**β scrambling via benzvalene derivatives. In contrast, the [1,2]-H shift mechanism involving carbene intermediates does not suffer from such drawbacks and will be the most feasible reaction pathway for naphthalene and similar hydrocarbons.

The carbenic isomers of **1**, 2,4-cyclohexadienylidene (**6**) and 2,4-cyclopentadienylcarbene (**11**), have close-lying singlet and triplet states and are 16−35 kcal mol^{-1} less stable than **4**. Since these carbenes resemble minima on the PES, they should in principle be observable experimentally in spite of very low barriers (2−3 kcal mol^{-1}) for [1,2]-H shift and intramolecular cycloaddition. The allene isomer of **1**, 1,2,4-cyclohexatriene (**10**), is thermodynamically as stable as **4**. Although small cyclic allenes are still considered to be exotic intermediates, recent theoretical studies find them to be energetically low lying.[23,24,105,106] Their elusive nature is not surprising, however, considering the electrophilic character of the allenic carbon atom which makes these compounds susceptible to intermolecular reactions.

Table 4. Relative Energies (kcal mol^{-1}), Enthalpies (kcal mol^{-1}), Entropies (eu), and Activation Parameters (kcal mol^{-1}) Relative to Benzene at 1373 K

molecule	E_{rel}	H_{rel}	S_{rel}	ΔH	ΔG
1	0	0	0		
4	74.2	−0.7	4.4	73.5	67.5
S-**6**	90.8	−1.1	5.2	89.7	82.6
8	31.9	−0.2	7.3	31.7	21.7
9	74.4	−0.6	8.5	73.8	62.1
S-**11** inward	110.3	−1.1	10.5	109.2	94.8

	E_{rel}	H_{rel}	S_{rel}	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	E_a
TS1	104.4	−3.8	5.2	100.6	93.5	103.3
C_s-*exo*-**5**	107.1	−4.1	5.8	103.0	95.0	105.7
TS2	93.3	−4.4	5.6	88.9	81.2	91.6
TS3	107.9	−3.7	5.5	104.2	96.7	106.9
TS4	75.2	−3.4	3.9	71.8	66.4	74.5
TS6	118.6	−3.9	6.7	114.7	105.5	117.4
TS7	116.3	−4.3	7.4	112.0	101.8	114.7
TS8	113.5	−3.8	6.1	109.7	101.3	112.4
TS9	138.3	−4.9	6.9	133.4	123.9	136.1

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Acknowledgment. The authors are grateful to Prof. L. T. Scott for helpful comments. The work in Erlangen was supported by the Stiftung Volkswagenwerk, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie. H.F.B. thanks the Bavarian State and the DAAD for fellowships. P.R.S. is grateful for a Liebig-Fellowship through the Fonds der Chemischen Industrie and acknowledges the support by Prof. A. de Meijere. The work in Georgia was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Fundamental Interactions Branch, Grant No. DE-FG05-94ER14428.

JA973270Z