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# Studies of the Electron-Promoted Cope Cyclization of 2,5-Phenyl-Substituted 1,5-Hexadiene Radical Anions

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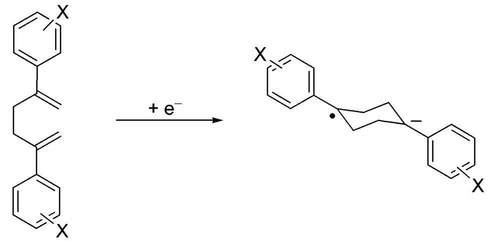
*Received September 11, 2006*



This work describes studies of the electron-promoted Cope cyclization of 2,5-phenyl-1,5-hexadiene radical anions in a flowing afterglow triple quadrupole mass spectrometer. The electronic properties of the hexadienes have been systematically modified by using aromatic substituents at the 2- and 5-positions of the hexedienes, including those with nitro, trifluoromethyl, fluoro, chloro, and acetyl groups. Ions were formed by the thermal attachment of electrons in the gas phase. Structures of the molecular radical anions were probed to determine whether they undergo cyclization to a cyclohexane-1,4-diyl anion structure by examining chemical reactivity with neutral reagents including carbon dioxide, carbon disulfide, and nitric oxide. First-order rate constants for the reactions of ions were measured, and the reaction efficiencies were determined. Based on the reactivity results, a thermochemical model has been developed, which predicts the reaction thermochemistry by using thermochemical properties of model systems. The observed reactivity from ion−molecule reactions and the study of reaction rates show that the ion of 2,5-dicyanohexadiene and 2,5-di(4,4′-trifluoromethyl phenyl)-1,5-hexadiene undergo Cope cyclization, whereas the radical anions having substituents such as the fluoro, nitro, chloro, and acetyl groups do not.

## Introduction

Theoretical and experimental studies in the field of cationic reactions[1−7] have led to increased understanding of the phenomenon of "hole catalysis".[8] In hole-catalyzed systems, ionization lowers the activation energy for a reaction and ultimately leads to reaction acceleration. Two notable examples are the hole-catalyzed Diels−Alder reaction[5,7] developed by Bauld and co-workers and olefin cyclodimerization[9] of 1,3-cyclohexadienes. The discovery of the hole-catalyzed Diels−Alder reaction paved the way for the exploration of other hole-catalyzed cation-radical pericyclic reactions.[7]

Over six decades ago, Cope reported the thermal rearrangement of hexa-1,5-dienes,[10−15] and since its discovery, the Cope rearrangement has diversified into many variants, including the oxy-Cope[16] and the anionic oxy-Cope[17] versions. The Cope rearrangement is part of a family of related [3,3] sigmatropic

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10.1021/jo0618775 CCC: $37.00

rearrangements that include the Claisen,[18] Caroll,[19,20] and Eschenmoser rearrangements[21,22] and other Claisen-related reactions.[23−27] These rearrangements are useful in organic synthesis because the parent reaction can be effected thermally and is tolerant to a variety of functional groups.

The Cope rearrangement has been extensively studied over the past decades,[28−30] and labeling studies have established that the rearrangement for 1,5-hexadiene proceeds through a chair pathway requiring 33.3 ± 0.5 kcal/mol, whereas the reaction involving a boat transition state requires an additional 11.4 ± 2.0 kcal/mol.[31,32] Although the details of the electronic structure of the Cope transition state have been debated,[31−48] labeling studies,[31,32] theoretical calculations,[49] and thermochemical estimates[50] support the assessment that the hydrocarbon undergoes rearrangement through an aromatic transition state,[51] although the extent of biradical character can be altered by substitution.[28,29,39,43,52−61]

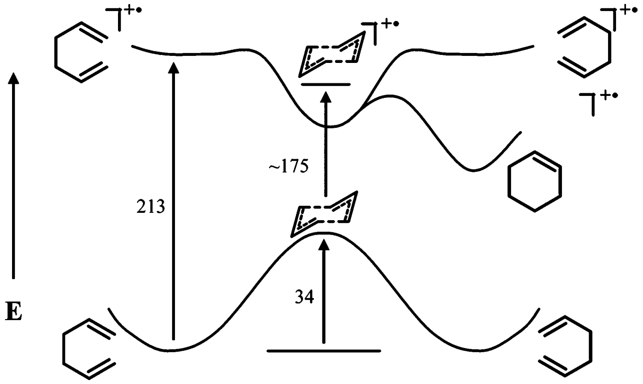

**FIGURE 1.** Schematic potential energy surface for neutral and cationic 1,5-hexadiene Cope rearrangement. The ionization energy of the hexadiene is obtained from photoelectron spectroscopy experiments,[66] whereas the ionization energy of the transition state is estimated to be similar to that of cyclohexyl radical.[68] The exothermic rearrangement of the cyclohexene-1,4-diyl radical cation is also indicated. Values are in kcal/mol.

Bauld and co-workers have reported computational studies showing that a radical cation variant exists for the Cope rearrangement of 1,5-hexadiene.[62−64] The calculations predict that the hexadiene radical cation cyclizes to a lower energy chair intermediate, a situation characterized as an "inverted potential energy surface"[65] for the reaction, as shown in Figure 1.

As shown in Figure 1, the inverted potential energy surface results because the difference in ionization energies of the neutral hexadiene[66] and the transition state[67,68] is greater than the activation energy for rearrangement to the neutral product. Experimental evidence for the intermediacy of cyclohexane-1,4-diyl radical cation in the Cope rearrangement of 1,5-

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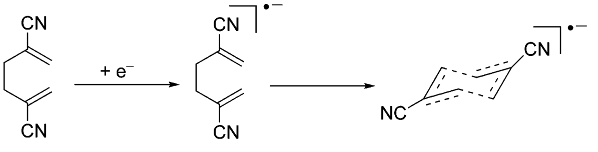
hexadiene radical cation has been provided by Williams and co-workers[65,69] in their matrix isolation studies and by Wenthold and Hu[70] in their gas-phase experiments. Matrix EPR studies of the1,5-hexadiene radical cation carried out by Williams and co-workers[65,69] have shown that it spontaneously undergoes cyclization to the cyclohexane-1,4-diyl radical cation, which rearranges to cyclohexene radical cation. Subsequent studies of 1,5-hexadiene radical cation in a flowing afterglow mass spectrometer are also consistent with the existence of the inverted potential energy surface, and a similar reaction sequence has been proposed to occur.[70] Photoinduced electron-transfer (PET) studies of 2,5-diaryl-1,5-hexadienes derivatives by Miyashi and co-workers[71] have shown that hole catalysis can indeed be used to effect slow Cope reactions.

In contrast to the phenomenon of hole catalysis is electron catalysis, where reduction is used to accelerate the reaction. Indeed, examples of electron-promoted electrocyclic[72−83] and cycloaddition[84−87] reactions have been previously reported. Sigmatropic rearrangement of radical anions[88,89] have also been proposed but likely occur through dianionic states rather than from radical anions. Perhaps, the most common example of electron catalysis is electron-induced olefin polymerization.[90]

Electronic structure calculations predict that, in select cases, single-electron reduction can effect an inverted potential energy surface for the Cope rearrangement.[91] This happens because the electron binding energy of the cyclic intermediate is greater than the electron affinity of the closed-shell hexadiene, leading to an inverted potential energy surface as shown in Figure 2.[91] For example, cyclization of the radical anion of 2,5-dicyano-1,5-hexadiene, **1**, to form the corresponding cyclohexane-1,4-diyl radical anion, **1**$^-$, is calculated at the B3LYP/6-31G* level of theory to be exothermic by 16.2 kcal/mol (eq 1).[91]



(1)

**1** **1**$^-$

We have recently reported experimental studies that confirm **1**$^-$ as the structure of the ion formed upon one-electron reduction of **1** in the gas phase,[92] providing the first example of an electron-promoted Cope cyclization.[92] In this work, we examine the scope of this reaction and the effect that substituents have on it, with the goal of elucidating the role that electronic structure has on the potential energy surfaces for reaction of 1,5-hexadiene radical anions.

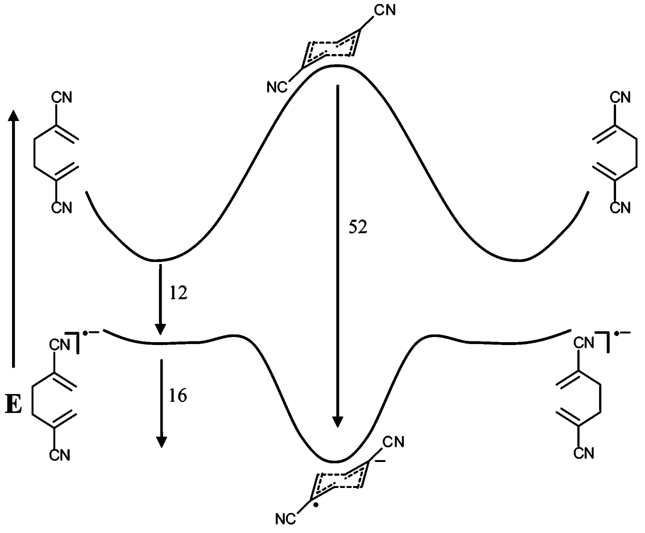
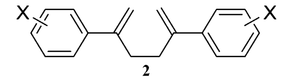


**FIGURE 2.** Potential energy surface for neutral and anionic 2,5-dicyano-1,5-hexadiene Cope rearrangement, calculated at the B3LYP/6-31 + G* level of theory, adapted from ref 91.

**SCHEME 1**



**2**

| X | | X | |
|---|---|---|---|
| a: | H | f: | *p*-COCH$_3$ |
| b: | *p*-F | g: | *m*-Cl |
| c: | *m*-F | h: | *m*-CF$_3$ |
| d: | *p*-NO$_2$ | i: | *p*-CF$_3$ |
| e: | *p*-Cl | | |

For this study, the electronic properties of the hexadienes have been systematically modified by using aromatic substituents at the 2- and 5-positions, **2**, as shown in Scheme 1. The aromatic substituents include those with nitro, trifluormethyl, fluoro, chloro, and acetyl groups in the *meta* and *para* positions. Here we describe the results of reactivity studies of substituted hexadiene radical anions, with particular focus on determining whether they have acyclic or cyclic cyclohexane-diyl anion structures. From these reactivity studies, we propose a simple thermochemical model to predict whether an anion will have an inverted potential energy surface and hence spontaneously cyclize.

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**TABLE 1. Measured Rate Constants and Efficiencies for the Reactions between Diphenylhexadiene Radical Anions and $CO_2$, $CS_2$, and NO[a]**

| | | rate coefficient ($cm^3/s$) (efficiency, *eff*) | | |
|---|---|---|---|---|
| diene | X | $CO_2$ | $CS_2$ | NO |
| **2b** | *p*-F | *b* | $1.4 \pm 0.4 \times 10^{-12}$ (0.002) | $1.4 \pm 0.3 \times 10^{-11}$ (0.02) |
| **2c** | *m*-F | *b* | $2.2 \pm 0.4 \times 10^{-12}$ (0.002) | $2.6 \pm 1 \times 10^{-12}$ (0.002) |
| **2d** | *p*-$NO_2$ | *b* | $2.2 \pm 0.5 \times 10^{-12}$ (0.002) | $3.1 \pm 0.8 \times 10^{-12}$ (0.005) |
| **2e** | *p*-Cl | *b* | $2.0 \pm 0.2 \times 10^{-11}$ (0.02) | $2.4 \pm 0.8 \times 10^{-11}$ (0.04) |
| **2f** | *p*-$COCH_3$ | *b* | $3.4 \pm 1 \times 10^{-12}$ (0.004) | $2.3 \pm 0.8 \times 10^{-12}$ (0.003) |
| **2g** | *m*-Cl | *b* | $3.2 \pm 1 \times 10^{-11}$ (0.04) | $4.9 \pm 0.5 \times 10^{-12}$ (0.01) |
| **2h** | *m*-$CF_3$ | $2.7 \pm 1.5 \times 10^{-12}$ (0.004) | $4.8 \pm 0.5 \times 10^{-12}$ (0.01) | $2.8 \pm 0.8 \times 10^{-12}$ (0.01) |
| **2i** | *p*-$CF_3$ | $2.5 \pm 0.4 \times 10^{-11}$ (0.04) | $1.7 \pm 0.4 \times 10^{-11}$ (0.02) | $2.1 \pm 1 \times 10^{-10}$ (0.34) |
| **1** | CN[c] | $3.4 \pm 0.3 \times 10^{-10}$ (0.49) | $1.4 \pm 0.3 \times 10^{-10}$ (0.14) | $1.8 \pm 0.4 \times 10^{-10}$ (0.28) |

[a] Uncertainities correspond to one standard deviation. [b] Rate of the reaction is too slow to be measured ($<10^{-12}$ $cm^3/s$). [c] Substituted at the diene.

## Experimental Section

All experiments were carried out at room temperature (298 ± 2 K) in a flowing afterglow triple quadrupole mass spectrometer that has been described previously.[107] The radical anions of the 1,5-hexadienes were generated in the high-pressure flow reactor (P[He] = 0.400 Torr, flow[He] = 200 std/$cm^3$) by electron ionization (EI) of neutral 2,5-diphenyl-1,5-hexadienes, added 15 cm downstream of the electron source. Ion−molecule reactions were investigated by adding neutral reagent vapors through either of two fixed-position ring inlets situated downstream in the flow tube. Reactions were characterized by the loss of the reactant ion and the formation of the product. The ions in the flow tube, collisionally cooled to ambient temperature by the helium buffer gas, were extracted through a 1 mm orifice and focused into a low-pressure region containing a triple quadrupole mass analyzer. Reaction rates were measured by monitoring the yield of the reactant ion as a function of neutral flow.[107] The efficiency of the reaction, *eff*, was obtained by comparing the measured rate constant for the reaction with the collision rate constant, calculated by using the average dipole orientation (ADO) approach,[93] with $eff = k/k_{coll}$. None of the hexadienes investigated in this work are commercially available, but they were prepared by the $ZnCl_2$-based condensation[108] reaction of the substituted acetophenone and the corresponding bromoacetophenone followed by olefination by using Nysted reagent.[109] The bromoacetophenones that were not commercially available were synthesized by using known procedures.[110−112] All synthesis procedures and characterization data are included in Supporting Information. Helium was purified via a liquid nitrogen trap containing molecular sieves. Gas purities are as follows: He (99.995%), $CO_2$ (99%), $CS_2$ (99%), NO (99%), and $NO_2$ (99%).

## Results

Most of the substituted diphenylhexadienes listed in Scheme 1 undergo electron attachment when added to the flow tube in the presence of thermal electrons. Of those listed in Scheme 1, only **2a**, 2,5-diphenyl-1,4-hexadiene, does not give a molecular radical anion, $\mathbf{2a}^-$, to any extent. Yields of diphenylhexadiene anions for the other systems vary from very high ($\mathbf{2h}$−, $\mathbf{2i}^-$) to very low ($\mathbf{2e}^-$, $\mathbf{2c}^-$). Fragmentation is also observed upon ionization, with fragmentation patterns dependent on the substituents. Full lists of EI products and relative yields are provided in Supporting Information.

Structures of the molecular radical anions, $M^{\bullet-}$, were probed by examining chemical reactivity with neutral substrates, including $CO_2$, $CS_2$, and NO. First-order rate constants for the reactions of ions $\mathbf{2b}^-$−$\mathbf{2i}^-$ and $\mathbf{1}^-$ are listed in Table 1. Also included in Table 1 is the reaction efficiency, the ratio of the measured rate to the ADO collision rate.[93] Most of the reactions examined in this work are relatively slow, with efficiencies generally below 0.05. Notable exceptions include the reactions of $\mathbf{1}^-$ and the reaction of $\mathbf{2i}^-$ with NO.

The products in the observed reactions are listed in Table 2. In most cases, the observed products correspond to simple adducts. The exceptions include the reaction of $\mathbf{1}^-$ with NO, which occurs by addition and loss of HCN to form the oximate anion as described previously,[92] and the reaction of $\mathbf{2d}^-$ with $CS_2$, which occurs by sulfur atom abstraction.

We have examined the reactivity of model systems to compare with the reactivity of ionized hexadienes. As indicated in Scheme 2, the acyclic radical anion of the hexadiene should

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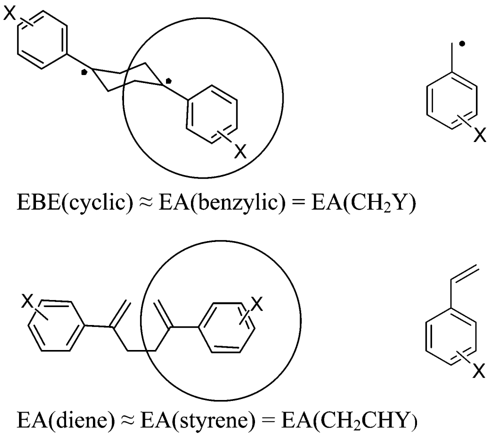
**TABLE 2. Ion−Molecule Reactivity with Neutral Reagent Gases for Diphenylhexadiene Radical Anions**

| diene | X | $CO_2$ | $CS_2$ | NO | $CO_2$ + NO[b] | $CO_2$ + $NO_2$[b] |
|---|---|---|---|---|---|---|
| **2b** | *p*-F | *a* | [M + $CS_2$] | [M + NO] | [M + NO] | *a* |
| **2c** | *m*-F | *a* | [M + $CS_2$] | [M + NO] | [M + NO] | *a* |
| **2d** | *p*-$NO_2$ | *a* | [M + S] | [M + NO] | [M + NO] | *a* |
| **2e** | *p*-Cl | *a* | [M + $CS_2$] | [M + NO] | [M + NO] | *a* |
| **2f** | *p*-$COCH_3$ | *a* | [M + $CS_2$] | [M + NO] | [M + NO] | *a* |
| **2g** | *m*-Cl | *a* | [M + $CS_2$] | [M + NO] | [M + NO] | *a* |
| **2h** | *m*-$CF_3$ | [M + $CO_2$] | [M + $CS_2$] | [M + NO] | [M + $CO_2$ + NO] | [M + $CO_2$ + $NO_2$] |
| **2i** | *p*-$CF_3$ | [M + $CO_2$] | [M + $CS_2$] | [M + NO] | [M + $CO_2$ + NO] | [M + $CO_2$ + $NO_2$] |
| **1** | CN[c] | [M + $CO_2$] | [M + $CS_2$] | [M + NO − HCN] | [M + $CO_2$ + NO] | [M + $CO_2$ + $NO_2$] |

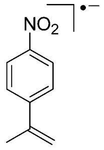
[a] No reaction is observed (see Table 1). [b] Indicates the product of sequential reaction of $CO_2$ and NO or $NO_2$. [c] Substituted at the diene.

**SCHEME 2**

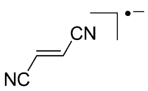


be electronically very similar to the radical anion generated from the corresponding methyl styrene.

Therefore, reactions were also carried out with conventional radical anions, including **3** and **4**. These ions were found to be essentially unreactive with $CO_2$, $CS_2$, and NO. Similarly, because these are all phenyl-substituted systems, the cyclized ion would be expected to undergo benzyl-anion-like reactivity.



**3**

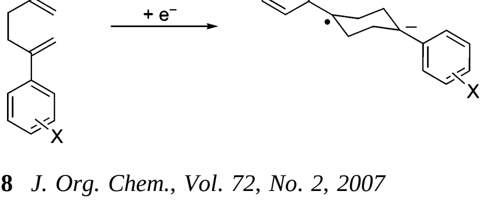


**4**

First-order rate constants for reaction of *p*-$NO_2$, *p*-$CF_3$, and *p*-$COCH_3$ benzyl anions with neutral reagents $CO_2$, $CS_2$, and NO have been measured and are listed in Table 3.

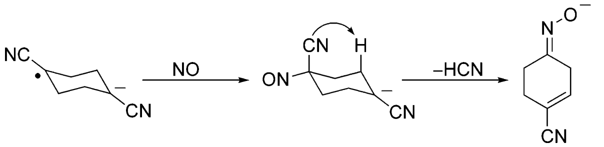
## Discussion

**Reactivity as a Probe of Ion Structure.** The reactivity described in the previous section provides insight into the structure of hexadiene radical anions. The most important question addressed by these studies is whether the ion has undergone Cope cyclization to the cyclohexane-diyl structure (eq 2).



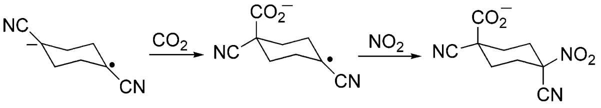
(2)

Ion **1**$^-$ is used as a model for the cyclized product. The cyclic structure of **1**$^-$ has been established previously[92] by using the reaction with nitric oxide to convert it to an oximate (eq 3) that has CID behavior indistinguishable from the authentically prepared ion.



(3)

Characteristic reactions for **1**$^-$ include efficient reactions with $CO_2$, $CS_2$, and NO. Moreover, the $CO_2$ adducts of **1**$^-$ are found to undergo subsequent reactions with radical substrates, including NO and $NO_2$ (Table 2). The reactivity can be readily understood in the light of the electronic structure of the cyclic anion. Reaction with $CO_2$ results in the formation of the carboxylate radical, **1a**$^-$, that can undergo radical coupling with other open-shell reagents (eq 4). This reaction sequence is common for distonic radical anions,[94] and has been observed previously for ions including *o*-, *m*-, and *p*-benzyne anions[95,96] and the *m*-xylylene radical anion.[92,95,96]



(4)

**1**$^-$ **1a**$^-$

The reactivity of **1**$^-$ with $CO_2$ can be contrasted with that for conventional radical anions, such as α-methyl-*p*-nitrostyrene radical anion, **3**, which serves as a model for ring-opened structures of the hexadiene anions, and fumaronitrile anion, **4**, unreactive with $CO_2$. Unlike most benzylic ions, conventional radical anions with olefinic and styrenyl moieties do not appear to react with $CO_2$ to any appreciable extent, and we interpret the formation of adduct in reaction with $CO_2$ for those systems that form a stable radical anion as evidence for an ion with closed-shell character, which would be the case for the cyclized product.[97] Thus, we can use the reaction with $CO_2$ as a probe for cyclization.

The reaction with NO also provides insight into the structure of the ion.[94] Although reaction of NO is found to occur with all the ions in Table 1, it appears to be significantly more efficient with the cyclized dicyano system. This is also true for $CS_2$, although the reaction of **1**$^-$ with $CS_2$ is not as efficient as those with $CO_2$ or NO. Of the diphenylhexadiene anions listed in Table 1, only **2i**$^-$ (X = *p*-$CF_3$) is clearly evidenced to have a cyclic structure. It undergoes a marginally efficient reaction

**TABLE 3. Reactivity of Benzyl Anions with Neutral Reagents[a]**

| | rate coefficient, ($cm^3/s$) (efficiency, *eff*) | | |
|---|---|---|---|
| benzyl anion | $CO_2$ | $CS_2$ | NO |
| *p*-$NO_2$ | $1.3 \pm 0.3 \times 10^{-12}$ (0.002) | $1.3 \pm 0.2 \times 10^{-10}$ (0.13) | $0.9 \pm 0.7 \times 10^{-11}$ (0.01) |
| *p*-$CF_3$ | $2.2 \pm 0.9 \times 10^{-10}$ (0.32) | $3.3 \pm 1.3\times 10^{-10}$ (0.34) | $3.4 \pm 1.5 \times 10^{-11}$ (0.05) |
| *p*-$COCH_3$ | $1.8 \pm 1.3 \times 10^{-11}$ (0.10) | $8.4 \pm 1 \times 10^{-11}$ (0.08) | $3.7 \pm 1.2 \times 10^{-11}$ (0.05) |

[a] Uncertainities correspond to one standard deviation

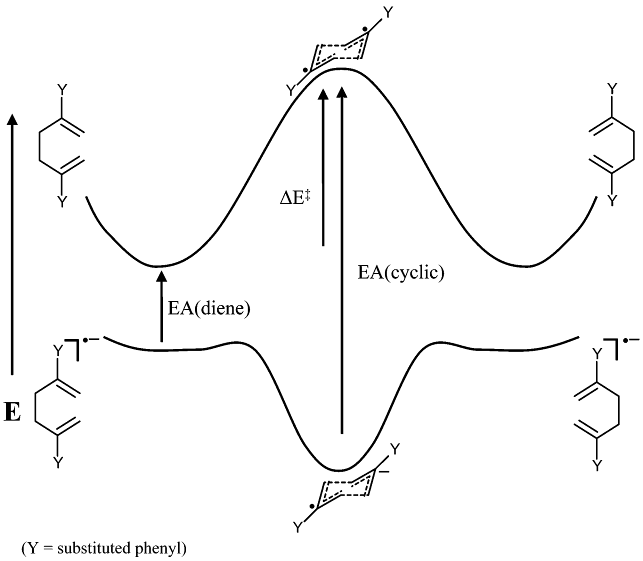


**FIGURE 3.** Parameters used to predict thermochemistry of the Cope cyclization of radical anions. The key parameters are the electron affinity of the hexadiene, EA(diene), the vertical electron binding energy of the cyclic anion, EBE(cyclic), and the activation energy for the neutral Cope rearrangement, $\Delta E^{\ddagger}$.

with $CO_2$, although it is about 10 times less efficient than the reaction of $CO_2$ with $\mathbf{1}^-$. Similarly, the efficiency for the reaction of **2i** with $CS_2$ is 10 times lower than that for $\mathbf{1}^-$. However, $\mathbf{2i}^-$ also undergoes efficient addition of NO, occurring in about one-third of all collisions. Moreover, as indicated in Table 2, the $CO_2$ adduct of $\mathbf{2i}^-$ undergoes addition with both NO and $NO_2$. The results are consistent with those expected for cyclic ion but not for ring-opened radical anion.

The results for $\mathbf{2h}^-$ (X = *m*-$CF_3$) are less clear. Although it does undergo slow reaction with $CO_2$ and even undergoes sequential addition of $CO_2$ and NO/$NO_2$, neither the reaction with $CS_2$ nor that with NO is indicative of a cyclic structure. Hence, the results are inconclusive, potentially indicating an exceptionally reactive ring-opened structure, an unreactive cyclic structure, or even a mixture of two forms. In contrast to the above, $\mathbf{2b}^-$−$\mathbf{2g}^-$ radical anions are completely unreactive to $CO_2$ and exhibit very little reactivity with $CS_2$ and NO. It is most likely that they have conventional $\pi$-radical anion structures.

**Thermochemical Model of Reactivity.** From the reactivity studies, we conclude that ions $\mathbf{1}^-$ and $\mathbf{2i}^-$ likely have cyclic structures and $\mathbf{2b}^-$−$\mathbf{2g}^-$ are acyclic hexadiene ions, whereas the structure of $\mathbf{2h}^-$ is unclear. The observed cyclization reactivity of the hexadiene radical anions can be explained by using a simple model based on potential energy surfaces as shown in Figure 3.

From Figure 3 we identify three important thermochemical properties for predicting the thermochemistry of the cyclization reaction. In order for the cyclization to be energetically favorable, the electron binding energy of the cyclic anion, EBE(cyclic), must be greater than the combined electron affinity of the hexadiene, EA(diene), and the activation energy for the Cope rearrangement of the hexadiene, $\Delta E^{\ddagger}$, as reflected in eq 5a. Alternatively, the cyclization is energetically favorable if the difference between EBE(cyclic) and EA(diene) is greater than the activation energy for the Cope rearrangement, as shown in eq 5b.

**TABLE 4. Predicted Electron Affinity (EA) Values for the Reactivity Model[a]**

| diene | X | EA (benzyl) | EA (styrene) | ΔEA (eV) | cyclizes? |
|---|---|---|---|---|---|
| **2a** | H | 1.0 | 0 | 1.0 | n/a |
| **2b** | *p*-F | 1.0 | 0 | 1.0 | no |
| **2c** | *m*-F | 1.0 | 0 | 1.0 | no |
| **2d** | *p*-$NO_2$ | 2.1 | 1.0 | 1.1 | no |
| **2e** | *p*-Cl | 1.2 | 0 | 1.2 | no |
| **2f** | *p*-$COCH_3$ | 1.7 | 0.5 | 1.2 | no |
| **2g** | *m*-Cl | 1.2 | 0 | 1.2 | no |
| **2h** | *m*-$CF_3$ | 1.4 | 0 | 1.4 | maybe[b] |
| **2i** | *p*-$CF_3$ | 1.5 | 0 | 1.5 | yes |
| **1** | CN[c] | 1.54[d] | 0 | 1.54 | yes |

[a] Styrene EAs correspond to EAs of the corresponding substituted benzene. Benzyl EAs are estimated using the gas-phase acidities[99] and the procedure described by Fattahi and Kass,[98] unless otherwise noted. [b] Inconclusive as to whether the ion is cyclized or not. [c] Substituted at the diene. [d] Reference 100.

$$\mathrm{EBE(cyclic)} > \mathrm{EA(diene)} + \Delta E^{\ddagger} \qquad (5a)$$

$$\mathrm{EBE(cyclic)} - \mathrm{EA(diene)} > \Delta E^{\ddagger} \qquad (5b)$$

Unfortunately, none of these hexadienes have known gas-phase EAs, and the EBE values for the cyclic ions are similarly unknown. However, we can estimate these values by using the thermochemical properties of comparable systems. For example, the electron affinity of the hexadiene should be similar to that of the corresponding styrene ($CH_2CHY$), indicated in Scheme 2, and consequently the corresponding substituted benzene. For the EBE of the cyclic ion, we use the EA value estimated for the triplet biradical. Because these are phenyl-substituted systems, the electron affinity of the biradical is approximately that of the corresponding substituted benzyl radical, which is more likely to be known or readily estimated from the acidity.[98] The predicted electron affinity values are listed in Table 4.

With these approximations, in light of eq 5b, we predict the cyclization to be energetically favorable when the relation in eq 6 is satisfied. The model is reasonably consistent with known

$$\mathrm{EA(CH_2Y)} - \mathrm{EA(CH_2CHY)} = \Delta\mathrm{EA} > \Delta E^{\ddagger} \qquad (6)$$

experimental results and/or reported electronic structure calculations. For example, for the dicyano-substituted diene, **1**, the electron affinity of the diene is estimated to be that of the acrylonitrile, $CH_2CHCN$. Acrylonitrile does not form a valence bound state but only forms a dipole bound anion with a small binding energy of 7 meV.[101] The electron affinity of cyanomethyl radical (EA($CH_2CN$)) has been measured by using negative ion photoelectron spectroscopy to be 1.543 ± 0.014 eV.[100] Therefore, according to eq 4, the cyclization of the ion derived from hexadiene **1** (Y = CN) should be favorable because ΔEA, ca. 1.54 eV, is greater than the barrier for Cope rearrangement of **1**, 23.2 kcal/mol (1.0 eV).[52,102] Similarly, for the 1,5-hexadiene hydrocarbon (Y = H), the values are EA($CH_3$) = 1.8 kcal/mol[103] and EA($HC_2{=}CH_2$) = 0 kcal/mol, giving ΔEA = 1.8 kcal/mol, well below the 33.3 kcal/mol Cope rearrangement barrier.[31] Indeed, electronic structure calculations predict that the cyclohexan-1,4-diyl anion is unbound with respect to electron detachment and ring opening.[91] We can also use this thermochemical model with substituted phenyl hexadienes to predict the reactivity of their anions toward Cope cyclization. For example, for diphenylhexadiene **2a** (X = H), the value of EA($YCH_2$) is that for benzyl, 0.912 ± 0.006 eV,[104] and the value of EA($CH_2CHY$) is that for styrene, which does not form a stable anion and has EA = 0. This gives ΔEA = 0.9 eV (21 kcal/mol), slightly less than the 25 kcal/mol barrier for the Cope rearrangement of 2,5-dipenyl-1,5-hexadiene.[41] To estimate the ΔEA for 2,5-di(4,4′-nitro phenyl)-1,5 hexadiene, **2d**, we need the electron affinity of *p*-nitrobenzyl radical. Although this has not been measured, it can be estimated by using the approach described by Fattahi and Kass[98] to give a value of 49 kcal/mol (2.1 eV). Similarly the electron affinity of *p*-nitrostyrene is not experimentally known but is likely similar to that of nitrobenzene, 1 eV.[105] The difference in EA is thus found to be 1.1 eV = 25 kcal/mol, similar to the barrier for Cope rearrangement for aromatic substituted hexadiene.[59] However, empirically it is found that $\mathbf{2d}^-$ does not cyclize. EA values for the substituted hexadiene systems, ΔEA values,[99] and cyclization results for $\mathbf{1}^-$ and $\mathbf{2b}^-{-}\mathbf{2i}^-$ are shown in Table 4. A clear pattern is observed, as the ΔEA values for the phenylhexadienes that do not cyclize are all in the range of 1.0−1.2 eV. For those that cyclize, which include $\mathbf{2i}^-$ (*p*-$CF_3$) and $\mathbf{1}^-$ (-CN) the ΔEA values are ca. 1.5 eV. The *m*-$CF_3$-substituted system, **2h**, has a ΔEA value of 1.4 eV and appears to be near the threshold at which cyclization occurs. Therefore, on the basis of our experimental results, it appears that the cyclization occurs only if ΔEA > 1.4 eV (32 kcal/mol).

According to eq 5, the cyclization reaction should be exothermic if ΔEA is greater than $\Delta E^\ddagger$, which is ca. 25 kcal/mol for the aromatic substituted system.[59] The difference between $\Delta E^\ddagger$ and the empirical threshold of 32 kcal/mol likely results from systematic errors in the estimation that is used and particularly in the approximation that the electron affinity of the diene is similar to that of the styrene. The increased size and the potential group interactions of the diene are expected to lead to a larger EA for the hexadiene than for the styrene. For example, the electron affinity of of 2,5-dicyanohexadiene radical anion to form the ring-opened structure is calculated to be 13 kcal/mol higher than that of acrylonitrile.[91] The experimental results in this work suggest that the EAs of diphenylhexadiene are ca. 0.3−0.4 eV higher than those of the corresponding styrenes. This leads us to a revised thermochemical model, where EA(diene) is estimated as EA($CH_2CHY$) + 0.3 eV as shown in Figure 4. With this revision, the reaction is predicted to occur if eq 7 is satisfied.

$$\mathrm{EA(CH_2Y)} - \mathrm{EA(CH_2CHY)} > \Delta E^\ddagger + 0.3\ \mathrm{eV} \tag{7}$$

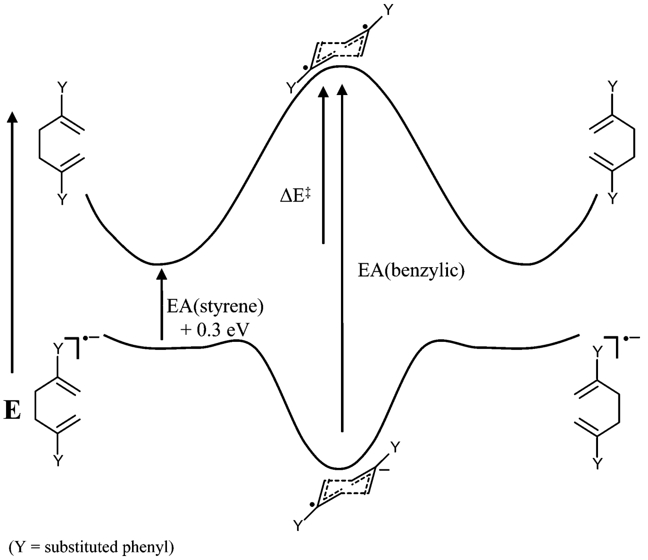


**FIGURE 4.** Revised thermochemical model for predicting the thermochemistry of the Cope cyclization of radical anions, in which the quantity EA(diene) is estimated to be 0.3 eV higher than the electron affinity of the corresponding styrene, the electron binding energy of the cyclic anion is estimated to be that of the model benzyl anion.

**Reaction Dynamics.** The thermochemical model described in the previous section predicts the reactivity of hexadiene radical anions solely on the basis of reaction thermochemistry, in that a reaction is predicted to occur if it is exothermic but not if it is endothermic. It does not take into account any energy barriers that separate the ring-opened anion from the cyclic structure. Calculations of the acyclic dicyanohexadiene radical anion predict that the ion is a stable minimum on the potential energy surface,[91] which means there exists a barrier for the cyclization. Potential energy surface calculations carried out in our lab[106] suggest that the barrier for cyclization is very small (<1 kcal/mol) and thus is not large enough to have a significant effect on the rate of the cyclization reaction at room temperature. Moreover, the energy of electron attachment to the hexadiene provides energy that can be used to overcome larger barriers for the reaction, such that reaction thermochemistry is the overriding consideration.

## Conclusions

Reactivity studies of ionized 2,5-diphenyl-1,5-hexadienes indicate that electron-promoted cyclization occurs for those radical anions with trifluoromethyl substituents on the aromatic ring. Systems with electron-withdrawing (nitro, acetyl) or electron-donating (halogens) substituents form stable radical anions that apparently do not cyclize. The occurrence of cyclization can be predicted by using a simple thermochemical model based on electron affinities of model substrates and the activation energies of the neutral Cope rearrangement. According to this model, $CF_3$ groups are optimal because they stabilize the benzyl-like anion without extensively stabilizing the open-shell, $\pi$-radical anion.

Although the other radical anions examined in this work do not form stable cyclic structures, this does not preclude the possibility that the ionization does not accelerate the Cope rearrangement, as compared to the neutral substrates. Establishing this to be the case will require the determination of the kinetics for rearrangement.

**Acknowledgment.** Funding for this work was provided by the National Science Foundation (CHE04-54874). We also thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support.

**Supporting Information Available:** Fragmentation patterns and syntheses for the 2,5-biphenyl hexadienes **2b**−**2i**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0618775