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Articles

Fickle Hexadienes. Manipulating the Relative Energies of Chairlike and Boatlike Transition Structures for the Cope Rearrangement

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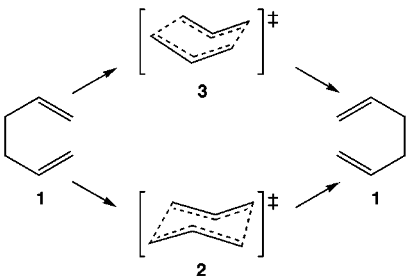
We report calculations on various hexadienes that can assume both chairlike and boatlike conformations, yet turn out (theoretically) to have transition structures for boatlike Cope rearrangement that are equal to or lower in energy than those of alternative chairlike structures. Pathways connecting boatlike and chairlike transition states in these systems also allow for unusual and facile isomerization pathways of certain strained alkenes.

Introduction

For the parent [3,3]-sigmatropic rearrangement of 1,5-hexadiene (**1**), the Cope rearrangement[1] (Scheme 1), labeling experiments[1b] have shown that the chairlike transition structure (**2**) is favored over a competing boatlike alternative (**3**) by 11 kcal/mol. While the chairlike pathway is favored for acyclic hexadienes, various ingenious polycyclic systems have been devised that effectively allow only boatlike rearrangements to occur. These include barbaralane (**4**),[2] semibullvalene (**5**),[3] and hypostrophene (**6**)[4] (Chart 1). Herein, we report calculations on several hexadienes that are free to adopt both chairlike and boatlike conformations, yet have activation barriers for boatlike Cope rearrangements that are equal to or lower than those for competing chairlike processes.

Scheme 1



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[1] For leading references, see: (a) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic: New York, 1981. (b) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 7147−7149. (c) See also ref 8a for a review of relevant computational studies. (d) For additional clever experiments aimed at estimating the difference in activation parameters between chairlike and boatlike Cope rearrangements, see: Shea, K. J.; Phillips, R. B. *J. Am. Chem. Soc.* **1980**, *102*, 3156−3162.

[2] For leading references, see: (a) Quast, H.; Seefelder, M.; Becker, C.; Heubes, M.; Peters, E.-M.; Peters, K. *Eur. J. Org. Chem.* **1999**, 2763−2779. (b) Doering, W. v. E.; Ferrier, B. M.; Fossel, E. T.; Hartenstein, J. H.; Jones, M., Jr.; Klumpp, G.; Rubin, R. M.; Saunders: M. *Tetrahedron* **1967**, *23*, 3943. (c) Williams, R. V. *Chem. Rev.* **2001**, *101*, 1185−1204.

[3] For leading references, see: (a) Williams, R. V. *Eur. J. Org. Chem.* **2001**, 227−235. (b) Jiao, H.; Nagelkerke, R.; Kurtz, H. A.; Williams, R. V.; Borden, W. T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1997**, *119*, 5921−5929. (c) See also ref 2c.

[4] For leading references, see: Das, B.; Sebastian, K. L. *Chem. Phys. Lett.* **2000**, *330*, 433−439.

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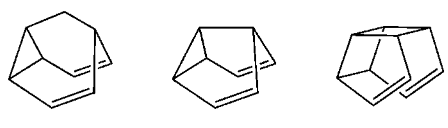
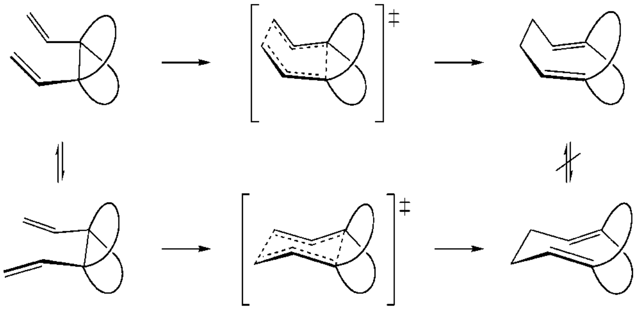
Published on Web 10/20/2001

Chart 1



4 **5** **6**

Scheme 2

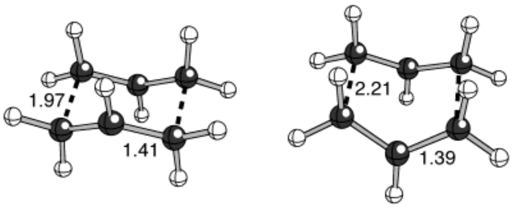


We refer to such systems as "fickle hexadienes", since they show no clear preference for one pathway over another.

Our basic system, co-opted from a design proposed by one of us decades ago, is shown in Scheme 2. 1,5-Hexadiene is tied into a bicyclic system by two hydrocarbon tethers[5] that produce torsional, transannular, and bridgehead strain that varies in magnitude between reactants, products and transition structures. The tethering is so designed as to leave the hexadiene free to follow either a boatlike or chairlike path for Cope rearrangement, but the products of the two modes of rearrangement are not easily interconvertible isomers.

Methods

All calculations were performed with GAUSSIAN 98.[6] Geometries were optimized at the B3LYP/6-31G(d) level,[7] which has been shown to be extremely effective for describing structures and energetics for pericyclic reactions, including [3,3]-sigmatropic shifts.[8] Moreover, the advantages and disadvantages of using B3LYP/6-31G(d) to compute structures and energetics for species involved in competing concerted closed-shell and stepwise diradical mechanisms have been described in detail by Houk and co-workers in the context of the Diels–Alder reaction of ethylene and butadiene.[9a] Based on comparisons of their B3LYP/6-31G(d) results with those of experiment and more intensive calculations for this and other pericyclic reactions, they concluded that the B3LYP/6-31G(d) method is an effective and economical means of comparing the energetics of competing concerted and stepwise mechanisms for potentially pericyclic reactions.[8,9a]



2 **3**

Figure 1. Selected interatomic distances (Å) for chairlike and boatlike transition structures for the Cope rearrangement of 1,5-hexadiene.

Structures of diradicals whose formation could compete with concerted Cope rearrangements in our systems were therefore optimized with unrestricted B3LYP/6-31G(d) (optimizations of singlet diradicals employed the "guess = (mix,always)" option).[9] Values of $\langle S^2 \rangle$[9b] for specific structures are noted below. Although spin-projection[9a,c,d] of the energies for the spin-contaminated singlet diradicals encountered in this study does not change any of our conclusions in a qualitative sense, both uncorrected and spin-projected energies are noted throughout the text. The stability[9e,f] of restricted B3LYP wave functions (toward unrestricted alternatives) for representative closed-shell transition structures was verified using the "stable" keyword in GAUSSIAN98[6] or by reoptimizing RB3LYP structures using UB3LYP and the "guess = (mix,always)" option.

All structures were characterized by frequency calculations at the B3LYP/6-31G(d) level, and zero-point energy corrections (scaled by 0.9806)[10] from these calculations are included in the reported energies.

The Parent Reaction

The parent [3,3]-sigmatropic shift of 1,5-hexadiene has been studied previously at many levels of theory,[8a] including B3LYP/6-31G(d). This level of theory predicts an activation energy of 34 kcal/mol for the chairlike rearrangement,[8a,11,12] in excellent agreement with the experimentally determined barrier of 33.5 ± 0.5 kcal/mol.[1] The boatlike transition structure is 8 kcal/mol less stable than the chairlike transition structure, using the same methodology.[11,12] The geometries of the chairlike (**2**) and boatlike (**3**) transition structures are shown in Figure 1.

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(5) Cope rearrangements in related systems have been examined experimentally as routes to molecules with two bridgehead double bonds. See: Shea, K. J.; Greeley, A. C.; Nguyen, S.; Beauchamp, P. D.; Wise, S. *Tetrahedron Lett.* **1983**, *24*, 4173–4176.

(6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I. R.; Gomperts, R.; Martin, L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M. P.; Gill, M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*, Revision A.9, Gaussian, Inc., Pittsburgh, PA, 1998.

(7) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372–1377. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

(8) (a) Wiest, O.; Montiel, D. C.; Houk, K. N. *J. Phys. Chem. A* **1997**, *101*, 8378–8388. (b) Houk, K. N.; Beno, B. R.; Nendel, M.; Black, K.; Yoo, H. Y.; Wilsey, S.; Lee, J. K. *THEOCHEM* **1997**, *398–399*, 169–179. (c) Hrovat, D. A.; Beno, B. R.; Lange, H.; Yoo, H.-Y.; Houk, K. N.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 7456–7460.

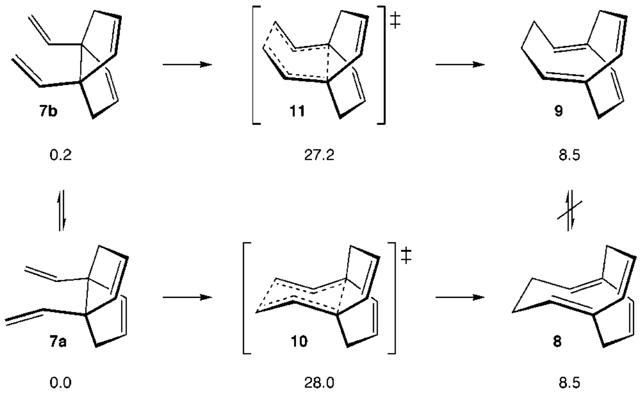
(9) (a) Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 6036–6043. (b) Gräfenstein, J.; Cremer, D. *Mol. Phys.* **2001**, *99*, 981–989. (c) Yamanaka, S.; Kawakami, T.; Nagao, H.; Yamaguchi, K. *Chem. Phys. Lett.* **1994**, *231*, 25–33. (d) Yamaguchi, K.; Jensen, F.; Dorigo, A.; Houk, K. N. *Chem. Phys. Lett.* **1988**, *149*, 537–542. (e) Bauemschmitt, R.; Ahlrichs, R. *J. Chem. Phys.* **1996**, *104*, 9047–9052. (f) Beno, B. R.; Fennen, J.; Houk, K. N.; Linder, H. J.; Hafner, K. *J. Am. Chem. Soc.* **1998**, *120*, 10490–10493. (g) Staroverov and Davidson have recently quantified and compared the diradical character of models for 1,4-cyclohexanediyl, a complex of two allyl radicals, and the concerted transition structure for the Cope rearrangement of 1,5-hexadiene: Staroverov, V. N.; Davidson, E. R. *J. Am. Chem. Soc.* **2000**, *122*, 186–187. The results of this study indicate that the concerted transition structure has the least diradical character among potential intermediates and transition structures in the Cope rearrangement and "can be justly referred to as predominantly aromatic."

(10) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502–16513.

(11) Wiest, O.; Black, K. A.; Houk, K. N. *J. Am. Chem. Soc.* **1994**, *116*, 10336–10337. See also: Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 334–337.

(12) Calculations on the parent Cope reaction were repeated in the course of this study, and no significant differences in geometries or energies compared to the previously reported results[11] were observed.

Scheme 3



(energies in kcal/mol relative to that of **7a**)

The First Variation: Unsaturated 3-Carbon Tethers

The first tethered system examined is shown in Scheme 3. This system involves two 3-carbon tethers, each containing one double bond. Species on the chairlike reaction coordinate have C_2 symmetry, while the overall symmetries of boatlike species are just C_1. The computed geometries of the structures in Scheme 3 are shown in Figure 2. Overall, the transition structures in these tethered systems are looser than in the unconstrained parent system (compare Figures 1 and 2). As in the parent system, the forming bonds in the boatlike transition structure are slightly longer than those in the chairlike transition structure. The alkenes in the tethers are roughly orthogonal to the alkenes involved in the rearrangement, so their role is primarily a geometric one.

The computed relative energies of reactants, products, and transition structures are shown in Scheme 3. Compared to the parent Cope reaction (barriers of 34 kcal/mol for chairlike rearrangement and 42 kcal/mol for boatlike rearrangement at the same level of theory), the barriers for rearrangement in the tethered system are reduced significantly: by 6 kcal/mol for the chairlike rearrangement and by 15 kcal/mol for the boatlike rearrangement. This rate acceleration is no doubt due to strain imparted to the reactants upon tethering, strain that is greater than that of the transition structures.[3b]

Can one see structural evidence for such reactant and product strain? Consider an unsubstituted 1,5-hexadiene restricted to a boatlike (eclipsed) conformation analogous to that in **7b**. Optimization of such a 1,5-hexadiene with its central C−C−C−C dihedral angle fixed to 0° indeed leads to a slight lengthening of its central C−C bond (1.57 Å) compared to that in alternative gauche and anti 1,5-hexadiene structures (both 1.55 Å). The analogous bonds in **7a** and **7b** are lengthened even further (Figure 2), we think as a result of the additional strain which accompanies tethering.

The Cope rearrangements available to **7a** and **7b** are unusual in that the energetics along the rearrangement reaction coordinates are practically identical for both the chairlike and boatlike pathways (Scheme 3). The equalization of the barriers for the chairlike and boatlike rearrangement is due in large part to the fact that inclusion of the tethers enforces eclipsing interactions about the breaking bond[13] in the chairlike structures that are not present in the parent system (**2**, Figure 1).

The relative energies of the chairlike and boatlike products of rearrangement (**8** and **9**, respectively) are also equalized (Scheme 3). Although the newly formed bond is somewhat staggered in **8** while eclipsed in **9**, the chairlike product appears to suffer from slightly worse transannular interactions (Figure 2). The bridgehead carbons[14] in both structures do not exhibit any significant pyramidalization[15] (the sum of the bond angles for all of the bridgehead carbons in **8** and **9** is between 359° and 360°), while the remaining carbons comprising the bridgehead double bonds are all pyramidalized to the same extent (the sum of the angles at each of these carbons is 357°). However, the bridgehead alkenes in **8** are slightly more twisted and slightly lengthened (Figure 2) compared to those in **9** (the average deviation from planarity for the C−C═C−C dihedral angles is 28° for **8** and 24° for **9**).

Biradical Alternatives. Formation of a bis-pentadienyl biradical by homolytic cleavage of the doubly allylic C−C single bonds in structures **7**−**9** could possibly compete with Cope rearrangement. Highly delocalized C_2-symmetric biradical **12**[16] (Figure 3), for example, is only 19.2 kcal/mol less stable than **7a**, making it almost 9 kcal/mol more stable than concerted Cope transition structure **10**. A triplet structure ($\langle S^2 \rangle = 2.09$) of similar geometry lies 3.4 kcal/mol above **12**. The transition structure for formation of **12** from **7a** (**13**, $\langle S^2 \rangle = 0.72$, Figure 3), however, is 7.4 kcal/mol (3.3 kcal/mol when spin projected) higher in energy than transition structure **10**. Although biradical **12** enjoys the benefits of the extended conjugation afforded to its unpaired electrons by their inclusion in pentadienyl radical substructures, this conjugation is much less significant in transition structure **13** (Figure 3)—the dihedral angles between the incipient allyl fragments and the alkenes in the tethers are 47°—keeping the energy of **12** above that of **10** and allowing the pericyclic pathway to predominate.

Accomplishing a High Energy Alkene Isomerization via a Pericyclic Detour. While the direct interconversion of the bicyclic products **8** and **9** is most unlikely under thermal conditions, a formal cis/trans alkene isomerization of this type could occur by sequential thermally accessible Cope rearrangements. This detour connects **9** to **8** by a path through **11**, **7b**, **7a**, and **10** (Scheme 3). The highest barrier encountered along such a path is between **7a** and **10** and is only 28 kcal/mol.

The Second Variation: Saturating the First

The effects of hydrogenating the alkenes in the tethers of **7**−**11** were examined next. Any conjugation between these alkenes and the delocalized core of the transition structure will be removed upon saturation, and new torsional and transannular interactions will arise. Both partially and fully hydrogenated tethers were examined. The effects of partial and full hydrogenation were qualitatively similar, however, and therefore only the system with fully hydrogenated tethers is described

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(13) For leading references on “torsional steering” effects that minimize eclipsing interactions in the transition structures for addition reactions, see: Lucero, M. J.; Houk, K. N. *J. Org. Chem.* **1998**, *63*, 6973−6977.

(14) For leading references on bridgehead alkenes, see: (a) Bredt, J.; Thouet, H.; Schmitz, J. *Justus Liebigs Ann. Chem.* **1924**, *437*, 1−13. (b) Warner, P. M. *Chem. Rev.* **1989**, *89*, 1067−1093. (c) Wijsman, G. W.; Iglesias, G. A.; Beekman, M. C.; de Wolf, W. H.; Bickelhaupt, F.; Kooijman, H.; Spek, A. L. *J. Org. Chem.* **2001**, *66*, 1216−1227.

(15) (a) Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095−1109. (b) Haddon, R. C. *J. Am. Chem. Soc.* **1990**, *112*, 3385−3389.

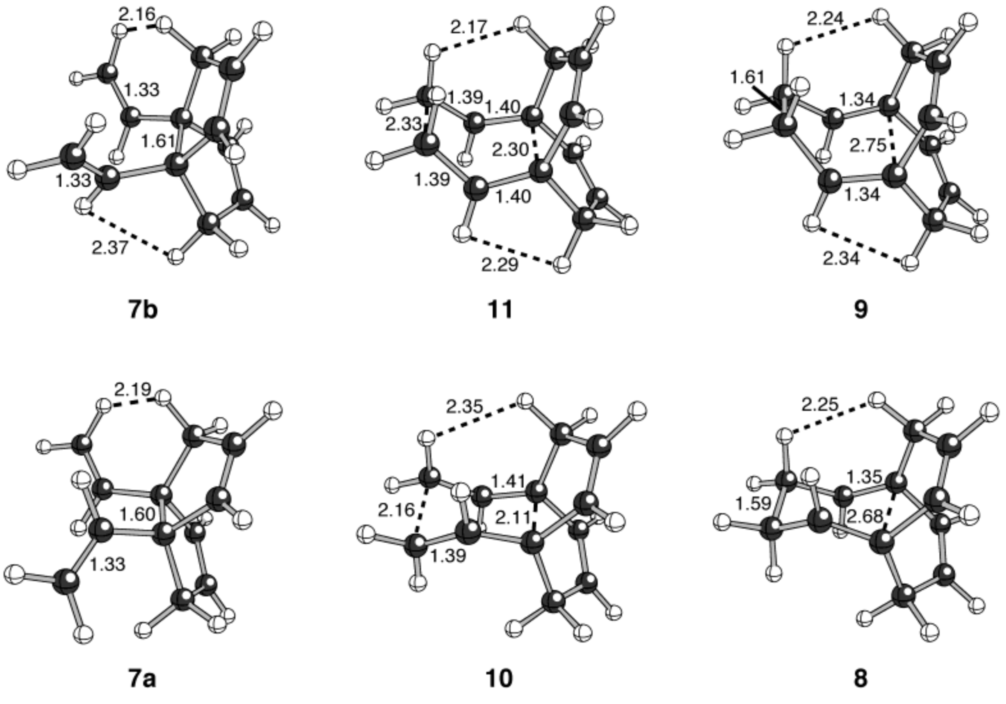

Figure 2. Selected interatomic distances (Å) for species shown in Scheme 3.

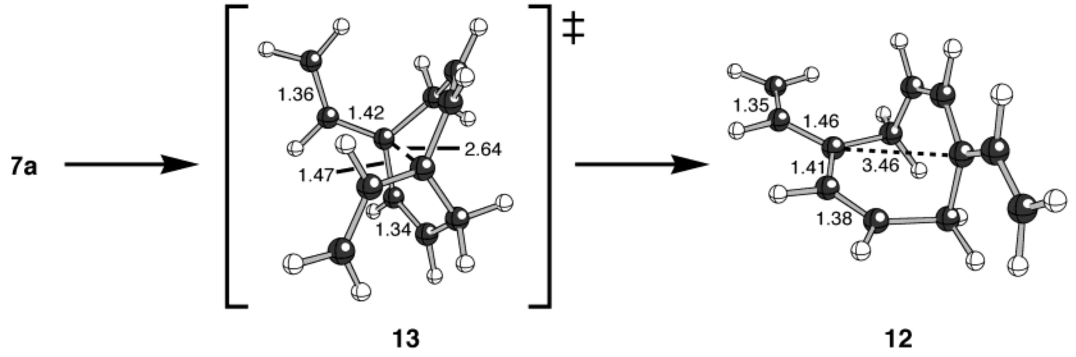

Figure 3. Selected interatomic distances (Å) for diradical **12** and the transition state (**13**) for its formation from **7a**.

in detail below; geometries and energetics for the partially hydrogenated cases can be found in the Supporting Information.

Fully Hydrogenated Tethers. Hydrogenation of both bridges in **7**−**11** produces the system shown in Scheme 4 and Figure 4. The competing effects of reduced angle strain and increased transannular and 1,3-strain result in barriers similar to those for the doubly unsaturated system. In agreement with previous force-field calculations,[17] boatlike bridgehead diene **16** is several kcal/mol less stable than its chairlike isomer **15**. However, similar to the more highly unsaturated systems, the bridgehead carbons in **15** and **16** are not pyramidalized, and each adjacent alkene carbon is pyramidalized to the same small extent. In addition, the bridgehead alkenes in both structures are twisted to the same degree (the average deviation from planarity for the C−C═C−C dihedral angles is 25°). **16** has worse transannular and eclipsing interactions than **15**, however, in contrast to the situation for equienergetic **8** and **9**, where **8** has more severe transannular interactions but **9** has worse eclipsing interactions.

Not surprisingly, biradical formation is even less favorable in this system, since less conjugation of the incipient radicals is possible than in the previous system. No singlet biradicals could be found in this case, most likely as a result of the enforced proximity of the radical-bearing carbons.[18] A triplet biradical derived from **14a** ($\langle S^2 \rangle = 2.06$) is 39.7 kcal/mol less stable than **14a**, and the radical centers in this structure are only 3.01 Å away from each other. The energy of a singlet constrained to the triplet geometry is 2.5 kcal/mol ($\langle S^2 \rangle = 0.96$) lower than that of the triplet. Clearly, the pericyclic pathway is predicted to predominate once again.

The Third and Fourth Variations: Reducing the Tether Length

Removing One Methylene per Tether. Reducing the length of the saturated tethers in **14** from three to

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(16) All attempts to optimize the geometry of this structure using UB3LYP led to **12**. Curiously, $\langle S^2 \rangle = 0.00$ for this species (even when "guess=(mix, always)" and "nosymmetry" keywords were employed), indicating that there is no spin contamination from the triplet state.

(17) (a) Warner, P.; Peacock, S. *Tetrahedron Lett.* **1983**, *24*, 4169−4172. (b) McEwan, A. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 3951−3960.

(18) This is true even when the "guess=(mix, always)" option was employed.

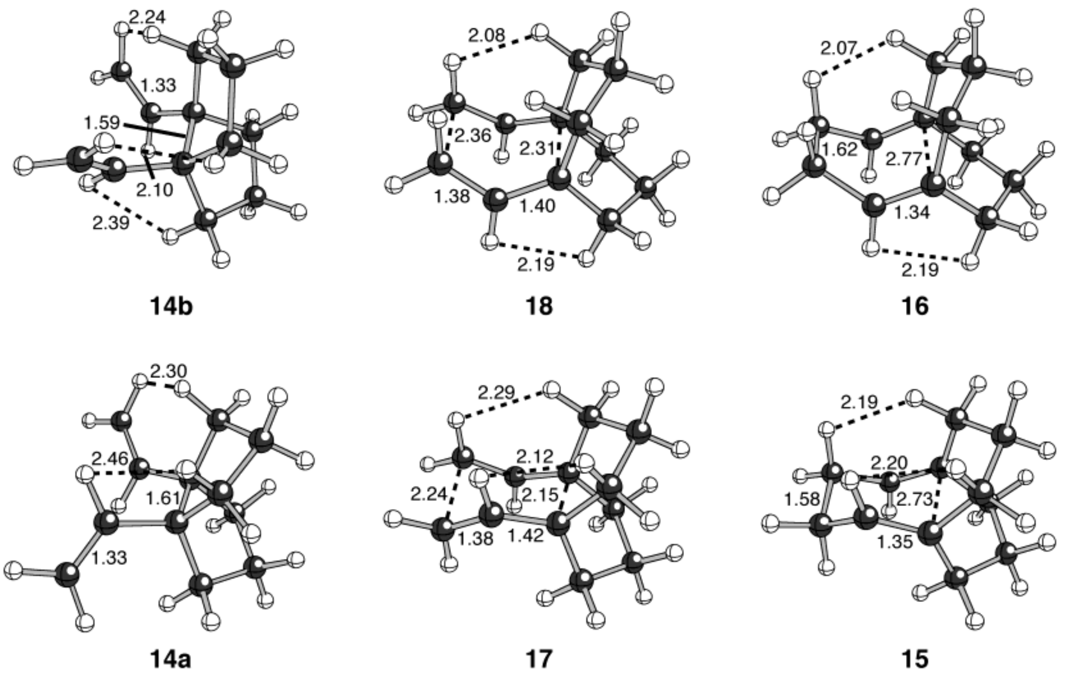
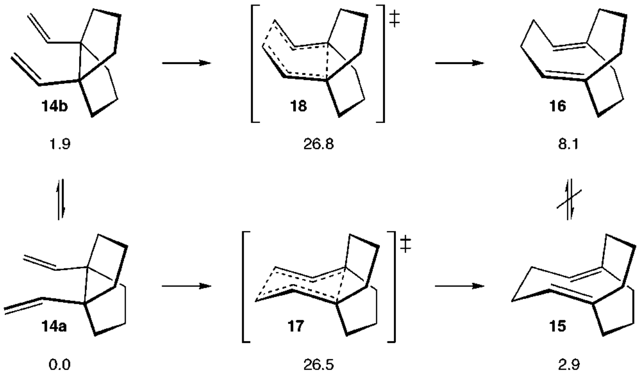


Figure 4. Selected interatomic distances (Å) for species shown in Scheme 4.

Scheme 4



(energies in kcal/mol relative to that of **14a**)

two methylene units has a significant effect on the energetics of rearrangement. This situation is summarized in Scheme 5 and Figure 5. The activation barriers in this system are considerably lower than those in the previous systems. Unlike the cases with longer tethers, the rearrangement to both chairlike and boatlike products in this system is exothermic. Apparently, accommodating two bridgehead alkenes in systems such as **20** and **21** is accompanied by less strain than fusing two cyclobutanes (as in **19**). Moreover, transannular steric repulsions are less severe in **20** and **21** than in **15** and **16** due to the geometric constraints of the shorter tethers. Eclipsing interactions in the tethers are comparable in all species **19**−**23**. The strain in **19** is reduced along both the chairlike and boatlike reaction coordinates, resulting in quite low barriers for rearrangement. In contrast to the parent system and the systems with longer bridges, the transition structures for Cope rearrangement in this system are extremely unsymmetrical. Due to the constraints of the shorter tethers, the forming bridgehead bonds are considerably shorter than the other partial bonds, which are particularly long. As predicted previously with force-field calculations,[17] the boatlike product in this case is more stable than its chairlike isomer.

A Variation on the Variation. Since the shorter bridges in this system affect lower barriers for rearrangement, we decided to examine the effects of including additional ethylene tethers. Inspired by the search for delocalized homoaromatic ground states or “stable transition states” in related systems based on **4** and **5**,[2c,3b] we computed the barrier for the degenerate Cope rearrangement of **24** via transition structure **25**. While a fully delocalized ground state is not predicted for this system, the **24** → [**25**]‡ → **24** reaction does have the lowest barrier we have seen in our tethered systems, only 8.1 kcal/mol (Scheme 6).

Competing Pathways. There are several pathways that may compete with the desired Cope rearrangements of **19**−**21**. For example, because of the length of the tethers in **21**, two additional Cope rearrangements are possible (involving bonds b and c of **21**, Scheme 7). These lead to bicyclo[4.2.0] systems **26a** and **26b**, which are considerably less strained than both **19b** and **21**. The transition structures for the alternative Cope rearrangements leading to **26a** and **26b** (**27** and **28**, respectively) are slightly lower in energy than transition structure **23**.

The possibility of competitive diradical formation looms large in this system. We examined the formation of diradicals resulting from the cleavage of bonds a, b, and c in **21** (Scheme 7). We could not locate a singlet diradical arising from cleavage of bond b,[18] most likely because the *trans,trans*-octadiene-like framework in such a diradical would constrain the unpaired electrons to be in close proximity. In fact, in the analogous triplet biradical structure **29** (Scheme 7), the bridgehead carbons are only 2.83 Å apart. For the diradical species arising from cleavage of bonds a and c (**30** and **31**, Scheme 7), fully optimized singlet and triplet species could be found.[19]

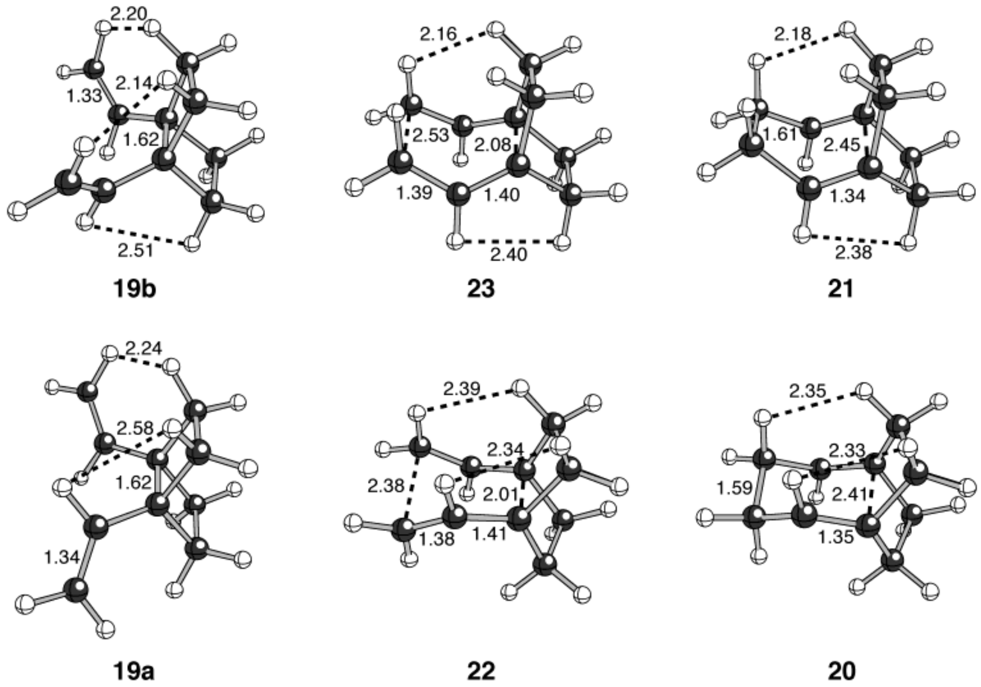
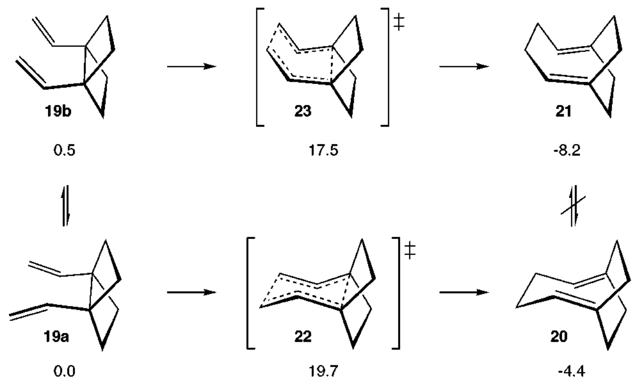


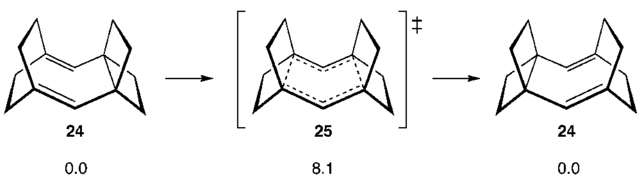
Figure 5. Selected interatomic distances (Å) for species shown in Scheme 5.

Scheme 5



(energies in kcal/mol relative to that of **19a**)

Scheme 6



(energies in kcal/mol relative to that of **24**)

Because the energies of biradicals **30** and **31** are lower than the energy of all three Cope rearrangement transition structures (**23**, **27**, and **28**), we sought transition structures for the formation of **30** and **31** from **21**. Attempted optimizations of transition structures involving the cleavage of bonds a and c consistently led to the transition structures for Cope rearrangement.[18] This is likely a result of the fact that the tethers in **21** constrain the carbons of the bridgehead alkenes to be in close proximity when the lengths of breaking bonds a and c are reasonably small. Transition structures for formation of **30** and **31** from **19b** and **26a**, respectively, were located; however, the geometric constraints in these systems are relaxed compared to those in **21**. Although the energies of these transition structures are comparable to or slightly lower than those of the Cope rearrangement transition structures, they are not directly accessible from **21**, implying that the chemistry of **21** should be dominated by pericyclic rearrangements rather than homolytic bond cleavage reactions.

We predict barriers of 22.3−25.7 kcal/mol for the three possible Cope rearrangements **21** → **19b**, **21** → **26a**, and **21** → **26b** (Scheme 7). These barriers are extremely close to the barrier of 25.4 kcal/mol which we predict for the Cope rearrangement of tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (**34** → **35**, Scheme 8), a value that compares nicely with the measured activation enthalpy of 28 ± 1.5 kcal/mol.[20] Due to the presence of an additional tether in **34**, however, it can never choose to rearrange via a chairlike pathway.

Compound **21** has been synthesized and reportedly rearranges to **26** via Cope rearrangement.[21] The experimentally derived E_a for this reaction is 19.6 kcal/mol,[21] in good agreement with our predicted barriers of 22.3 and 22.6 kcal/mol for conversion of **21** to **26a** and **26b**, respectively. In addition, Wiseman and Vanderbilt[21] monitored the evolution of the Raman spectrum of a mixture of **21** and **26** over time and assigned bands at 1620 and 1637 cm^{-1} to the double bond stretches in **21** and **26**, respectively. We predict bands of 1640 and 1647 cm^{-1} (from frequency calculations at the B3LYP/6-31G(d) level, scaled by 0.9614 as suggested by Scott and Radom[10]) for the asymmetric and symmetric stretches of the double

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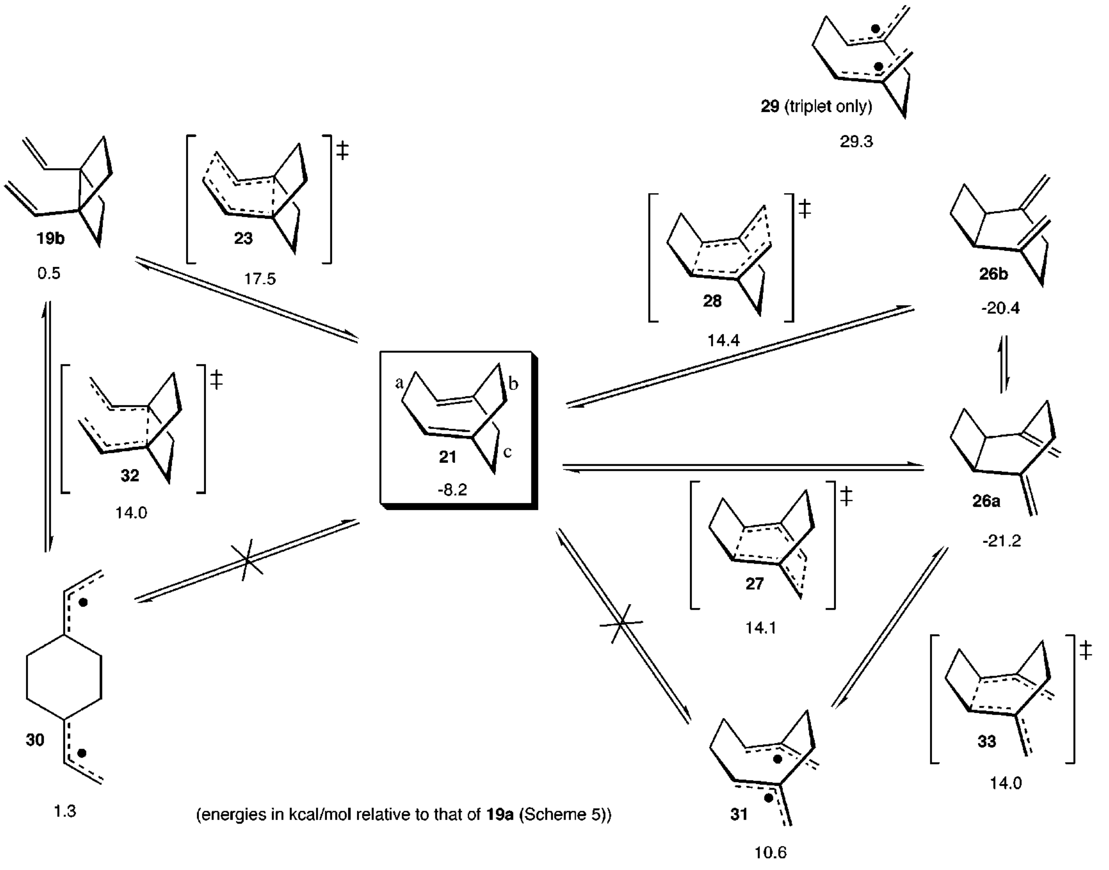
(19) Singlet−triplet gaps in both cases were less than 0.1 kcal/mol, favoring the singlet, and ⟨S^2⟩ values for both singlets were 1.06, implying a roughly equal mix of singlet and triplet contributions to the computed singlet energies. Adjustment of the energies for the singlets by spin projection[9] resulted in changes in energy of only 0−0.05 kcal/mol, due to the small singlet−triplet gaps.

(20) Wiberg, K. B.; Matturo, M.; Adams, R. *J. Am. Chem. Soc.* **1981**, *103*, 1600−1602.

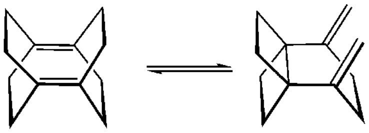
(21) Wiseman, J. R.; Vanderbilt, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 7730−7731.

Scheme 7



(energies in kcal/mol relative to that of **19a** (Scheme 5))

Scheme 8

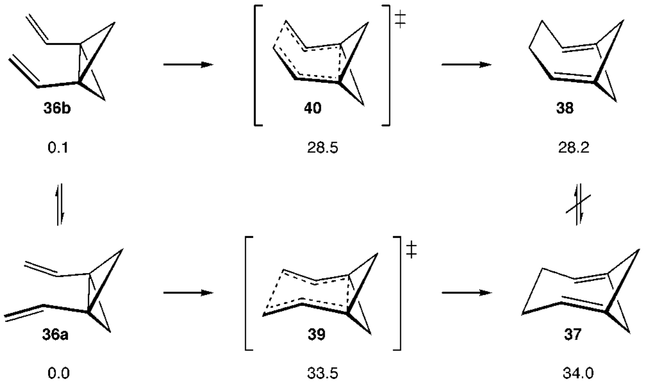


bonds in **21** and four bands ranging from 1656 to 1671 cm^{-1} for the stretching of the double bonds in **26a** and **26b**. Our predicted stretching frequencies thus reproduce the shift to higher wavenumbers upon rearrangement of **21** to **26**.

In summary, the preferred pericyclic reactivity of **21** outlined in Scheme 7 is consistent with all available experimental results of which we are aware.[22] Moreover, boatlike transition structures for Cope rearrangement (**23**, **27**, and **28**) again have slightly lower energies than their isomeric chairlike transition structure **22**.

Removing a Second Methylene per Tether. Next we examined the Cope rearrangements available to **36a** and **36b** (Scheme 9). The extremely short tethers in this system result in increased strain associated with the bridgehead double bonds in products **37** and **38**. Earlier force-field calculations indicated that the chairlike bicyclo[4.1.1] system **37** is extremely highly strained.[17] In contrast to the previous systems, both the bridgehead carbon atoms and the adjacent carbon atoms in the alkenes in **37** and **38** are highly pyramidalized (the sum of the angles at the bridgehead carbons is 344° in **37** and 334° in **38**, and at the adjacent carbons is 349° in **37** and 352° in **38**), hinting that alternative diradical structures may be extremely important in this system (see below).

Scheme 9



(energies in kcal/mol relative to that of **36a**)

Comparable strain seems to be present in the transition structures for Cope rearrangement (**39** and **40**), which are extremely similar in energy to **37** and **38**. In fact, chairlike transition structure **39** is actually slightly lower in energy than the chairlike product **37** when zero point energy is taken into account, indicating that the conversion of **37** to **36a** would be effectively barrierless. Overall, reducing the tether length so severely reduces the differential strain between the reactants and products that the barriers for rearrangement increase considerably (Scheme 9). Clearly ethylene tethers (as in **19**−**23**) are

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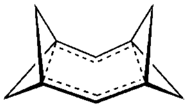
[22] An attempt to access biradical **30** via photolysis of a bicyclic diazene precursor has also been reported: Engel, P. S.; Nalepa, C. J. *Pure Appl. Chem.* **1980**, *52*, 2621−2632. In this reaction, however, only a tetraene product was observed and no intermediates (**19b**, **21**, or **31**) were detected, even during photolysis under matrix isolation conditions at 26K.

the optimum for promoting Cope rearrangements in the series of molecules we have examined.

Structures analogous to **24** and **25**, but with each tether shortened by one methylene unit, can also be envisioned. Calculations show that the minimum for such a system is a fully delocalized structure (**41**). This agrees nicely with the findings of Jiao et al. on closely related annelated semibullvalenes.[3b]



41

Avoiding the Pericyclic Pathways. In **36**, however, strain relief via biradical formation likely precludes Cope rearrangement. We calculate that the singlet bis-allyl radical that would arise from homolytic carbon−carbon bond cleavage in **36b** or **38**, for example, is only 15.0 kcal/mol ($\langle S^2 \rangle = 1.05$, 17.7 kcal/mol with spin projection) higher in energy than **36b**, making it much lower in energy than products **37** and **38** and the transition structures leading to them. The analogous triplet biradical is even more stable than the singlet (by 0.6 or 3.3 kcal/mol using the spin projected energy of the singlet). This is consistent with an experimental study (involving photolysis of a divinyl diazabicyclohexene precursor to these biradicals), which suggested that the ground state is likely a triplet.[23] Furthermore, we calculate that the transition structure for biradical formation from **36b** is only 16.7 kcal/mol higher in energy than **36b** ($\langle S^2 \rangle = 0.94$, 14.4 kcal/mol with spin projection), making homolytic cleavage much more facile than Cope rearrangement in this system.

Conclusions

In all of the doubly tethered hexadiene systems described above, both chairlike and boatlike transition structures for Cope rearrangement of similar energy exist. This is in contrast to the chairlike and boatlike transition structures employed by 1,5-hexadiene itself, which differ in energy by roughly 10 kcal/mol, favoring, of course, the chairlike structure. In fact, the only structure studied for which the boatlike transition structure is not slightly lower in energy than the chairlike alternative is **14**. When the tether length is reduced to a single methylene unit, biradical formation overwhelms Cope rearrangement, but in systems with longer tethers, pericyclic pathways are likely. By linking these chairlike and boatlike pathways together, new routes for alkene isomerization arise.

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Supporting Information Available: Structures and energetics for the Cope rearrangements of partially hydrogenated **7**. Coordinates and energies of structures **7a**−**41** and **S1a**−**S7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Jain, R.; Sponsler, M. B.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 1356−1366.