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Pericyclic Reactions between Aminoboranes $R_2B{=}NR_2'$ and Alkenes: [4+2] vs [2+2] Transition States

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Computational comparison of the [2+2] and [4+2] reactions between aminoboranes $R_2B{=}NR'_2$ and alkenes $CH_2{=}CH(R'')$ shows that the latter are strongly preferred. The preference arises from the [4+2] reactions exhibiting lower reaction barriers than do the [2+2] reactions; the products formed are of nearly equal stability. This behavior mimics that of reactions between alkenes and supports viewing aminoboranes, particularly $(F_3C)_2B{=}NMe_2$, as acting like polar alkenes.

Introduction

Aminoboranes $R_2B{=}NR_2$ have long been studied as heteroatom analogues of alkenes $R_2C{=}CR_2$.[2] While the two are isoelectronic, the polar nature of the B=N bond in aminoboranes manifests itself in myriad reactions that alkenes do not undergo. The example germane to this work is that aminoboranes containing small peripheral substituents dimerize readily in a [2+2] fashion to form 1,3-diaza-2,4-diboracyclobutanes, while the analogous reaction is symmetry-forbidden for alkenes.[3,4] Interestingly, if one treats an aminoborane such as $(F_3C)_2B{=}NMe_2$ with ethene in a crossover reaction, no reaction occurs.[5] $(F_3C)_2B{=}NMe_2$ reacts only with alkenes containing a peripheral methylene group [i.e., $H_2C{=}CH(CH_2R)$] in a [4+2] ene-type process to give alkenyl-substituted dimethylamine-boranes $H(Me)_2N{\rightarrow}B(CF_3)_2(CH_2CH{=}CHR)$, which may then rearrange (Scheme 1).[6] This provides further reaction-based evidence that the B=N bond in aminoboranes contains substantial double-bond character.[7] While to our knowledge no multistep syntheses have employed this hetero-ene rearrangement yet, applications of amine-boranes and aminoboranes containing alkenyl substituents have been reported.[8]

We showed previously[9] that computationally modeling the [4+2] Diels−Alder-like reactions between butadiene and several aminoboranes $R_2B{=}NR'_2$ provides considerable insight into the mechanistic details of such reactions and supports the view that $(F_3C)_2B{=}NMe_2$ in particular contains a B=N double bond with reaction characteristics similar to those of a C=C double bond. To expand this view, we report here modeling studies of the [2+2] reactions between aminoboranes $R_2B{=}NR'_2$ (R = H, CF_3; R′ = H, Me) and ethene, and [2+2] and [4+2] ene-type reactions between the aminoboranes and propene. While all the products show similar stabilities, the [4+2] reactions exhibit lower transition state barrier energies than do the [2+2] processes. This behavior mimics the symmetry-based behavior of alkenes.[3] Thus despite their polar nature, aminoboranes behave chemically as if they contain B=N double bonds.

Computational Methods

All calculations were performed with the Gaussian 98 suite of programs.[10] Each molecule and transition state was fully optimized without constraints using the Hartree−Fock/6-31+G(d) approach. The natures of all stationary point structures were determined by analytical frequency analysis, which also provided zero-point energies (ZPEs). ZPEs were scaled by 0.9153 when used to correct the raw energy values.[11] The structures were then reoptimized using the models given in Table 1 and the 6-311++G(d,p) basis set. The large basis set was selected because the [4+2] reactions involve the transfer of a hydrogen atom, making it advisable to model hydrogens as completely as the heavier atoms. The 6-311++G(d,p) basis set augments the triple-ζ functions on the hydrogens with diffuse and polarization functions.

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Scheme 1

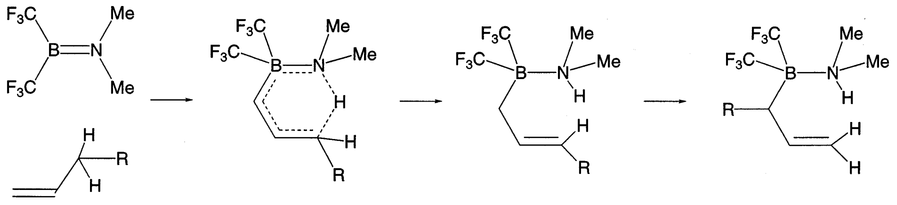

Table 1. Predicted Energies [6-311++G(d,p) basis set, kcal mol^{-1}] for [2+2] Cyclization and [4+2] Ene-Type Reactions between $R_2B{=}NR'_2$ and $H_2C{=}CH(R'')$ (R = H, F_3C; R′ = H, Me; R″ = H, Me) Using Various Models

	G3(MP2)		MP2		B3LYP		MPW1K		mPW91	
reaction	ΔE_{ts}[a]	ΔE[a]	ΔE_{ts}	ΔE	ΔE_{ts}	ΔE	ΔE_{ts}	ΔE	ΔE_{ts}	ΔE
$H_2B{=}NH_2 + H_2B{=}NH_2 \rightarrow H_2BNH_2BH_2NH_2$, **1D**	9.9	−14.7	9.6	−15.7	14.3	−6.0	9.5	−16.5	10.9	−11.6
$(F_3C)_2B{=}NMe_2 + (F_3C)_2B{=}NMe_2 \rightarrow (F_3C)_2BNMe_2B(CF_3)_2NMe_2$, **2D**					28.3	−0.4	20.7	−15.9	26.2	−3.0
$H_2B{=}NH_2 + H_2C{=}CH_2 \rightarrow H_2BNH_2CH_2CH_2$, **1C**	41.4	10.9	39.6	7.7	43.5	17.5	37.2	5.1	35.7	10.8
$(F_3C)_2B{=}NMe_2 + H_2C{=}CH_2 \rightarrow (F_3C)_2BNMe_2CH_2CH_2$, **2C**	23.8	−15.3	20.0	−20.7	33.4	−0.8	24.9	−15.3	27.2	−5.8
$H_2B{=}NH_2 + H_2C{=}CH(CH_3) \rightarrow H_2BNH_2CH(CH_3)CH_2$, **3N**	37.5	9.8	35.2	6.6	40.9	18.1	36.1	5.6	34.7	11.8
$(F_3C)_2B{=}NMe_2 + H_2C{=}CH(CH_3) \rightarrow (F_3C)_2BNMe_2CH(CH_3)CH_2$, **4N**			15.5	−19.3	30.2	2.8	21.6	−11.7	24.9	−2.1
$H_2B{=}NH_2 + H_2C{=}CH(CH_3) \rightarrow H_3NBH_2CH_2CHCH_2$, **3O**	29.3	9.3	25.7	7.9	31.7	15.9	26.6	9.0	21.0	11.4
$(F_3C)_2B{=}NMe_2 + H_2C{=}CH(CH_3) \rightarrow Me_2HNB(CF_3)_2CH_2CHCH_2$, **4O**			7.9	−16.8	23.1	1.4	15.8	−7.7	14.2	−1.0

[a] ΔE_{ts} is the energy required to reach the transition state from the reactants (the barrier); ΔE is the overall reaction energy.

Relative energies for the reactions studied appear in Table 1. As one can see, the commonly used B3LYP and MP2 models differ substantially in their predictions. The B3LYP model routinely predicts considerably less exothermic reactions, with somewhat higher barriers. To assess which model was more likely to match experiment, we compared the results with those from G3(MP2) calculations when possible (Table 1). This composite method, which incorporates high-level QCISD(T) and MP2(full) calculations, has been shown to give average absolute deviations from experiment of 1.3 kcal mol^{-1} for the G2 test set,[12] and so is the most likely of the models to match the putative experimental energies. One sees in the table that the G3(MP2) results agree reasonably with those from the MP2 method and less well with those from the B3LYP approach. The rms deviation of the MP2 predictions from the G3(MP2) predictions is 3.0 kcal mol^{-1}, while that of the B3LYP predictions is 7.4 kcal mol^{-1}.

Some of the difference between the B3LYP and MP2 models stems from the differences in the approximations used.[13] However, a substantial fraction was traced in other work from us[14] and others[15] to the inability of the B3LYP functional to properly model dispersion forces and weak dative[16] bonding interactions such as those between the four-coordinate boron and nitrogen atoms. We therefore undertook calculations using the hybrid MPW1K[17] and "pure DFT" mPWPW91[18] (hereafter shortened to mPW91) models. The former was designed to accurately determine transition state energies, and so probably models weak dative interactions well; the latter seems to model dispersion forces more accurately than does the B3LYP approach,[15] thereby giving good results for both ground state energies and structures.[19] In addition, each represents a different DFT approach (hybrid vs pure) and gives predictions similar to those from the MP2 model for the structures and B−N bond dissociation energies in $R_3B{-}NR'_3$ complexes,[14] which represent B−N binding analogous to that here. One sees in Table 1 that the MP2 and MPW1K models agree reasonably and that the latter agrees with the G3(MP2) method (rms deviation of 3.3 kcal mol^{-1}), while the mPW91 approach generally agrees well with the other models for reactions involving $H_2B{=}NH_2$ [rms deviation from G3(MP2) of 4.5 kcal mol^{-1}], but predicts insufficiently exothermic reactions involving $(F_3C)_2B{=}NMe_2$. This probably denotes incomplete assessment of dispersion forces /dative bonding by this model. One notes that the mPW91 model predicts lower barriers and more exothermic reactions than does the B3LYP model, in keeping with the view that the former better includes weak interactions than does the latter.

The MP2 model thus matches the predictions of the G3(MP2) approach best; however, it demands too many resources to be broadly useful. We could not examine the dimerization of $(F_3C)_2B{=}NMe_2$ using it, and examining the substituted aminoborane/propene reactions with the large basis set required substantial time and memory space. As a consequence, we generally discuss below only the MPW1K energies (and structural data), because these are most probably accurate for the barrier calculations, on which the conclusions of the work depend. However, the reader should note all the energies predicted for a reaction in Table 1, as the extremes represent bounds on the likely experimental values. While these cover a large range, as was recently noted, the "best" DFT functional currently yields an rms error of 6.3 kcal mol^{-1} in comparison with experiment for a large test set.[19] We cannot therefore be certain that the MPW1K values predict the experimental results well; we can only say that, of the DFT approaches examined here, they are the most likely to.

Except as noted in the Results and Discussion section, the structural data for the species studied are unexceptional. In general, all models predicted similar structures for the reaction components. The only exceptions involved the transition state structures, for which the DFT-based and MP2-based models tend to predict somewhat different distances for the forming B−C and N−C bonds. Some important bond lengths (MPW1K/

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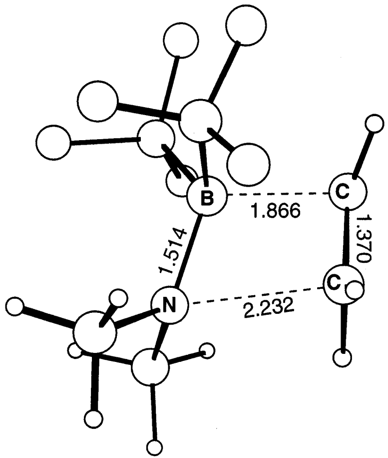
6-311++G(d,p) level) appear in the figures. Optimized Cartesian coordinates and absolute energies at this level for all the species reported are stored as Supporting Information.

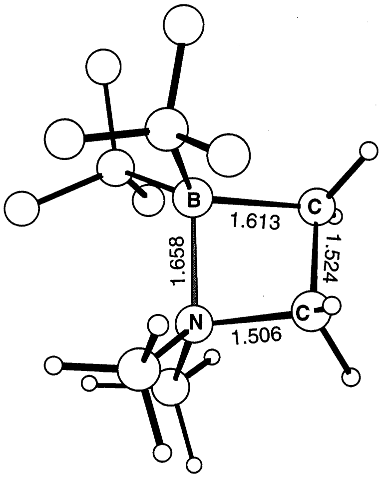
Results and Discussion

[2+2] Reactions between Aminoboranes and Ethene. Computational studies of the [2+2] dimerizations of $H_2B{=}NH_2$ and $(F_3C)_2B{=}NMe_2$, using the B3LYP/6-31G(d) approach, appeared previously.[9a] Using the larger 6-311++G(d,p) basis set changes the energies significantly. The B3LYP barrier energy decreases by 3.6 and 5.8 kcal mol^{-1}, respectively, while the reaction energy becomes less exothermic by 6.7 kcal mol^{-1} for both. This results in the prediction that the dimerization of $(F_3C)_2B{=}NMe_2$ is nearly thermoneutral (Table 1). Given the experimental reactivity of this molecule and the sizable Lewis acidity of the boron,[20] such a result seems unlikely and suggests a problem with using the B3LYP model for these systems. As discussed in the Computational Methods section, it appears that the B3LYP functional predicts aminoborane reaction energetics poorly, and we consider the MPW1K model more appropriate for this work. At the MPW1K/6-311++G(d,p) level, we predict rather exothermic dimerizations for both aminoboranes. However, the parent $H_2B{=}NH_2$ exhibits a barrier of only 9.5 kcal mol^{-1}, consistent with the ready dimerization of this compound under experimental conditions, while the substituted $(F_3C)_2B{=}NMe_2$ exhibits a barrier more than twice as large, consistent with its inertness toward dimerization.

Figure 1 shows the transition state and product for the [2+2] reaction between $(F_3C)_2B{=}NMe_2$ and $CH_2{=}CH_2$. This represents a crossover reaction analogous to the spin-forbidden dimerization of ethene. The parent reaction involving $H_2B{=}NH_2$ exhibits structurally similar stationary points. Characteristically,[9,20] the transition state is quite asymmetric, with a short $B-C_B$ distance and a long $N-C_N$ distance.[21] The parent system transition state **1Cts**[22] lies at quite high energy (37.2 kcal mol^{-1}), while the substituted **2Cts** lies at about two-thirds this. Both transition states lie well below that predicted for the [2+2] dimerization of ethene (ca. 80 kcal mol^{-1}),[23] but still high enough to make the process difficult to accomplish.



2Cts



2C

Figure 1. MPW1K/6-311++G(d,p)-optimized structures of the transition state **2Cts** and product **2C** of the [2+2] cyclization between $(F_3C)_2B{=}NMe_2$ and ethene. Distances are in Å.

The product 1-aza-2-boracyclobutane **2C** shows rather long B−N and N−C bonds (as does the analogous parent compound **1C**), but no other unusual features. Presumably the bonds lengthen to lessen ring strain, which is probably in excess of 15 kcal mol^{-1}.[24] The models predict that forming **1C** is endothermic, while forming **2C** is exothermic. This points to the sizable Lewis acidity of the trifluoromethyl-substituted boron atom in the substituted aminoborane.[20]

[2+2] and [4+2] Reactions between Aminoboranes and Propene. The [2+2] cyclization between an aminoborane and propene can occur with two orientations: one where the propene methyl group is attached to the carbon that binds to the boron (giving product **3B** or **4B**), and one where the methyl group is attached to the carbon that binds to the nitrogen (giving product **3N** or **4N**). The former orientation requires a higher barrier and generally gives a less exothermic reaction regardless of the model or aminoborane used. As a result, we have not included data for **3Bts**, **3B**, **4Bts**, or **4B** in Table 1, although their structures and absolute energies are available as Supporting Information. We will not discuss these isomers further, save to note that the energetic behavior contrasts with that of the [4+2] Diels−Alder cyclizations between aminoboranes and 2-methylbutadiene, where the methyl-substituted carbon preferred a position near the boron.[25]

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[21] Hereafter, the carbon bonding to boron will have the symbol C_B and that bonding to nitrogen C_N.

[22] Transition states and products are labeled systematically as follows. An odd number implies a structure derived from $H_2B{=}NH_2$; an even number implies a structure derived from $(F_3C)_2B{=}NMe_2$. The letter D means a structure formed by dimerization of the aminoborane, while C means a structure formed by the crossover [2+2] cyclization between an aminoborane and ethene. The letter N means a structure in which the methyl group of the added propene lies near the nitrogen atom of the aminoborane, while B means a structure in which the methyl group lies near the boron atom. The open chain structures formed from the [4+2] ene-type reactions are designated with the letter O. Transition states are labeled ts.

[23] We calculate the barrier energy for this process at the MPW1K/6-311++G(d,p) level to be 81.7 kcal mol^{-1}. This is dramatically higher than the experimental barrier (43.8 kcal mol^{-1}), which points to the fact that the reaction probably occurs through a transition state containing tetramethylene biradicals. See: Bernardi, F.; Bottoni, A.; Celani, P.; Olivucci, M.; Robb, M. A.; Venturini, A. *Chem. Phys. Lett.* **1992**, *192*, 229−235.

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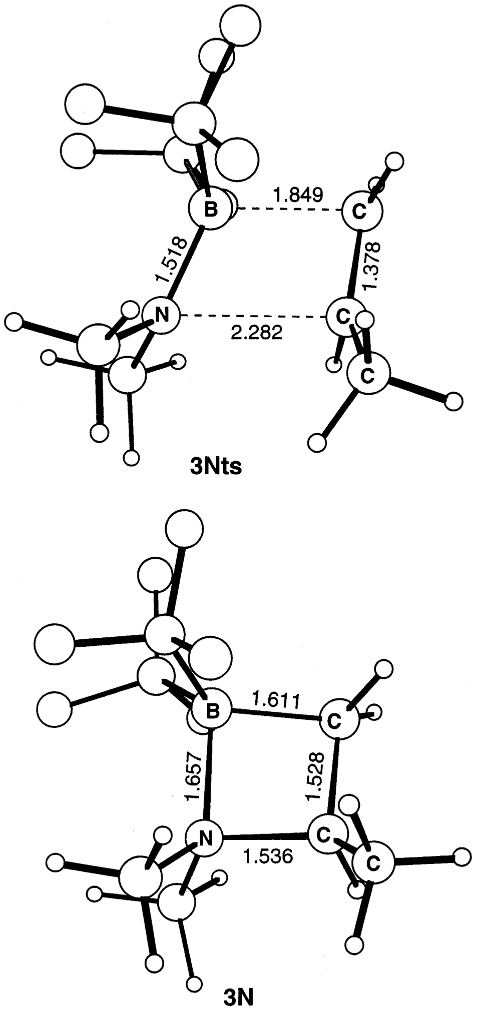

Figure 2. MPW1K/6-311++G(d,p)-optimized structures of the transition state **3Nts** and product **3N** of the [2+2] cyclization between $(F_3C)_2B{=}NMe_2$ and propene. Distances are in Å.

The [2+2] cyclization of $(F_3C)_2B{=}NMe_2$ with propene to form **4N** appears in Figure 2. The cyclization involving the parent aminoborane forming **3N** shows structurally similar species. Both the transition state **4Nts** and the product display structural features similar to those seen in the cyclizations of aminoboranes and ethene (Figure 1). The combination of increased bulk and increased electron density on C_N manifests itself in longer $N{-}C_N$ distances in **4Nts**/**4N** versus **2Cts**/**2C**. The energetics of the cyclizations are similar as well. The propene reaction shows a slightly lower barrier and is slightly less exothermic. However, the barrier is similar to that of the dimerization of $(F_3C)_2B{=}NMe_2$ to form **2D**, which does not occur under known conditions. These energetic details generally hold for the parent reaction as well.

That the barriers for [2+2] crossover cyclization are similar to those for [2+2] dimerization implies that the aminoborane B=N double bond behaves chemically like a polar C=C bond. That the barriers are significant provides the system with the need to find an alternative reaction path, a requirement that the [4+2] ene-type reaction meets.

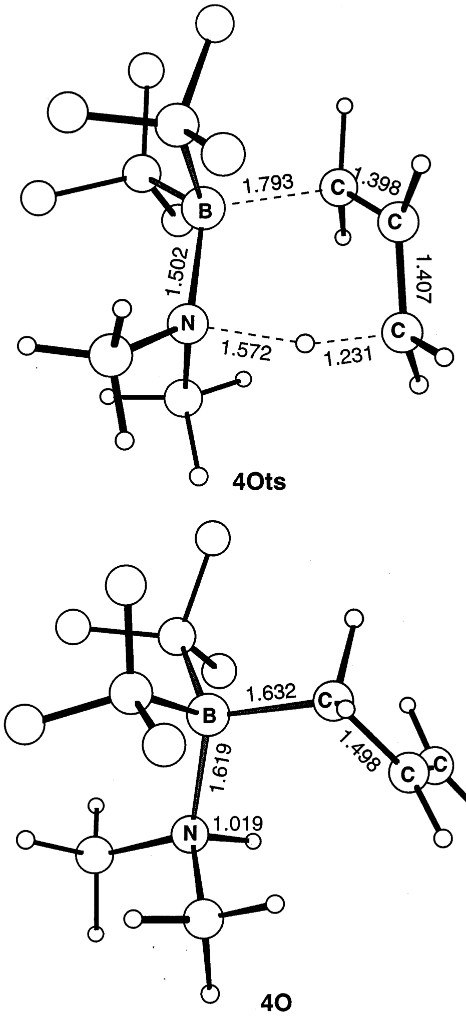

Figure 3. MPW1K/6-311++G(d,p)-optimized structures of the transition state **4Ots** and product **4O** of the [4+2] ene-type reaction between $(F_3C)_2B{=}NMe_2$ and propene. Distances are in Å.

As above, the [4+2] ene-type reaction can occur in two ways: with the boron accepting the hydrogen from the propene methyl group, or with the nitrogen doing so. The former case exhibits a high barrier and is less exothermic than the latter, and so will not be further discussed. Structural and energetic data for these isomers (designated **3Xts**, **3X**, **4Xts**, and **4X**) are available as Supporting Information.

The lower energy transition state **4Ots** and product **4O** for the [4+2] reaction appear in Figure 3. Transition state **4Ots** lies early along the reaction coordinate, as denoted by the modest lengthening of the breaking C−H bond (0.11 Å) and the long N−H interaction distance (1.572 Å). Structurally, **4Ots** takes the common "six-membered chair ring" form. The transition state barrier to **4Ots** is some 6 kcal mol^{-1} smaller than that to **4Nts** (Table 1). Internal reaction coordinate scans of the potential energy surface preceding and succeeding **4Nts** indicate that the ene-type process is concerted; no other transition states or intermediate minima are apparent. These observations are consistent with the experimental result and support viewing the B=N double bond as behaving like a C=C double bond.

The acyclic product **4O** shows a normal N−H bond distance, 0.55 Å shorter than the distance in **4Ots**. Once

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(25) Gilbert, T. M. *Organometallics* **2003**, *22*, 3748−3752.

the carbon delivers its hydrogen to the nitrogen, the ethenyl group formed swings well away from the B−N axis. Assuming this happens in all the aminoborane/alkene ene-type reactions, it is surprising that rearrangements requiring the boron to bind to the unsubstituted ethenyl carbon atom occur. The system appears to have little desire to put the two atoms in proximity.

The model suggests the acyclic **3O** and **4O** are approximately as stable as their cyclic counterparts **3N** and **4N** (and **3B** and **4B**). This allows an estimation of the ring strain energy (RSE) in the cyclic molecules as the difference between the sum of the energies of the C═C double bond and the N−H bond in the acyclic species and the sum of the energies of the N−C, C−CH_3, and C−H bonds present in the cyclic molecules. Using representative averages of these values,[26] we find RSE = 9 kcal mol^{-1}, in reasonable agreement with RSEs (ca. 12−16 kcal mol^{-1}) determined differently for unsubstituted 1-aza-2-boracyclobutane.[24]

Conclusions

The work described above constitutes the strongest evidence we have modeled that aminoboranes, especially $(F_3C)_2B{=}NMe_2$, contain polar, but alkene-like B═N double bonds. Support comes from the facts that the crossover [2+2] cyclization of $(F_3C)_2B{=}NMe_2$ requires traversing a barrier nearly isoenergetic with that for aminoborane dimerization, that the [4+2] cyclizations appear concerted, just as in alkene ene reactions, and that [4+2] ene-type reactions show detectably lower barriers than do the [2+2] reactions. That aminoboranes with small substituents dimerize readily could be cited as evidence that aminoboranes should be viewed as containing a nitrogen atom with a free lone pair and an electron-deficient boron atom. However, the data here are inconsistent with such a view.

While the preference of aminoboranes for ene-type reactions supports viewing their B═N bonds as double bonds, further support would come from observing variations on the “six-membered transition state” reaction theme well-known in organic chemistry, such as in Cope rearrangements and similar electrocyclic processes. While some of these have been observed,[5] many remain to be found. We hope the work above will spur searches for such reactions.

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Supporting Information Available: Cartesian coordinates and absolute energies of all molecules examined at the MPW1K/6-311++G(d,p) level. This material is available free of charge via the Internet at http://pubs.acs.org.

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