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Thermal Rearrangements of Heteroatom-Bridged Diallenes

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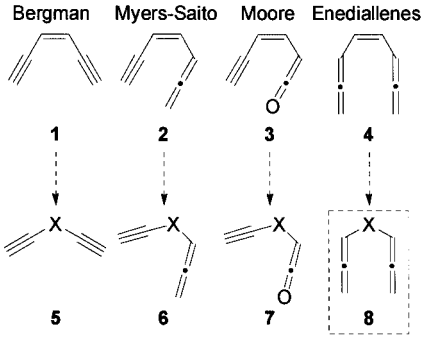
A systematic application of the BLYP/6-311+G*//BLYP/6-31G* computational scheme was utilized to identify the favored *aromatic* 2,6-reactions leading to the formally aromatic hetero-3,4-dimethylenecyclopentadienediyl derivatives from the thermal rearrangements of (hetero)atom-bridged diallenes (X = CH^-, NH, O, S). Protonation of the heteroatom substituent raises the respective 2,6-cyclization energy barrier, and the alternative 1,6-cyclization reaction forming the hetero-cyclohexadienediyl can compete.

Introduction

Under the umbrella of the Cope rearrangement, cyclizations of polyunsaturated systems, such as enediynes,[1,2] enyne–allenes[3–5] and enyne–ketenes,[6] have been grouped within larger "families of reactions"[7–9] in order to interpret systematically similar reactions. The corresponding Bergman, Myers–Saito and Moore reactions are analogous to the Cope reaction in the sense that there is a formation of a new σ-bond across the π-bonds. However, some of the reactions also involve a π-electron sextet that favors a reaction path leading to biradical intermediates that are stabilized by aromaticity. The formation of these π-electron sextets in the intermediates or products strongly affects the reaction barriers and energies. However, the nucleus-independent chemical shielding (NICS)[10] results of the Bergman and Myers–Saito reactions indicate that aromaticity is not developed fully in the transition structures.[9] Examining these reactions, we also systematically searched for new cyclization reactions. For instance, we studied heterosubstitued systems that included lone-pair-carrying heteroatoms in place of the central olefinic bonds of **1**, **2**, **3** and **4** (Scheme 1), i.e., **5**, **6**, **7**,[11–13] and **8**. Although experimental studies are available for the reactions of **8**,[14–21] this paper reports the necessary validation (as seen later) and computational analysis of other viable cyclization modes and delivers another building block for a new "reaction family", namely the heterosubstitued diallenic hydrocarbons.



Scheme 1.

Structures of type **8** are readily accessible through base-induced rearrangements[14,18,19] of the propargylic precursor **9** (Scheme 2). Subsequent cycloaromatizations of **8** were proposed to yield the five-membered biradical intermediate **12** (Scheme 2).[14] The existence of the singlet biradical **12** has been inferred by experimental studies by trapping with electron-deficient alkenes and oxygen and also by kinetic analysis of these heteroatom-bridged diallene rearrangements.[14,19,21] Diradical **12** was also generated and observed by an alternative route.[21] Although its singlet and triplet states must be close in energy, the absence of a chemically induced dynamic nuclear polarization (CIDNP) effect in the NMR spectra during the cyclization of **8** indicates that the cyclizations occur on the singlet manifold.[21]

Biradical **12** belongs to the class of non-Kekulé molecules[22] characterized by the contribution of the lone-pair of a heteroatom X to the π-conjugated hydrocarbon framework; also, **12** possesses a small singlet-triplet energy separation (ΔE_{ST}). Upon irradiation of some precursor diazenes (Scheme 3), Berson et al.[23,24] generated the hetero-biradical **12** (X = O, S and NH) for ΔE_{ST} "tuning" studies of these molecules.[22,25,26] Considering the heteroatom as a bridge connecting the two termini of the biradical tetra-

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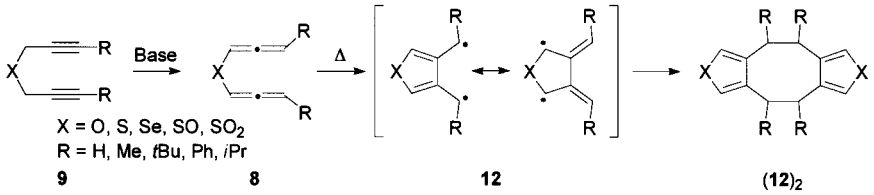
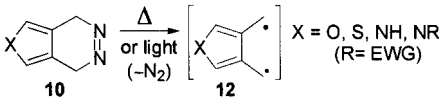


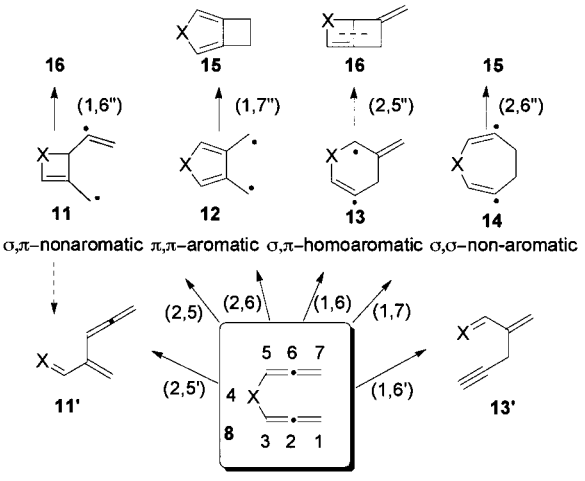
Scheme 2.

methyleneethane (TME), they found that it is possible to adjust ΔE_{ST} by means of the variable character of the heteroatom lone pair p_z-orbital acting on the non-bonding frontier π-orbitals (NBMOs) of TME.[25] Thus, the nature of the X heteroatom offers a tuning mechanism to control the total molecular electronic spin and ΔE_{ST}.



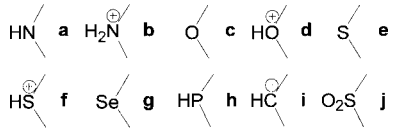
Scheme 3.

Apart from the 2,6-cyclizations of **8**, heteroatom-bridged diallenes have not been examined with respect to other cyclization modes, i.e., through $\mathbf{TS}_{25}$, $\mathbf{TS}_{16}$ and $\mathbf{TS}_{17}$ (Scheme 4). On the basis of our previous computational studies,[11,12] the 1,6-cyclization should be viable and competitive with the 2,6-reaction path. The present work provides insight into the various reaction possibilities and the importance of the X heteroatom in cyclizations. While the 2,6-cyclization product **12** demands X to be a π-donor to complete the aromatic π-electron sextet, the corresponding $\mathbf{TS}_{26}$ requires X to be a σ-acceptor because of its [2+2] addition nature in the early stages of the reaction coordinate.[27–29] The systematic selection of X with respect to the aforementioned criteria is depicted in Scheme 5 and we present the cyclizations of **8** to the formally aromatic hetero-3,4-dimethylenecyclopentadienediyl **12**, the homoaromatic hetero-cyclohexadienediyl **13**, the nonaromatic cyclobutene derivative **11** and the cycloheptadienediyl **14**



Scheme 4.

(Scheme 4). Other rearrangements of **8** leading to acyclic products such as 2-methylenepenta-3,4-dienes **11′** and 2-methylenepent-4-ynes **13′** were considered as well.



Scheme 5.

Computational Methods

All structures were optimized using DFT as implemented in the Gaussian03 package[30] utilizing Becke's pure gradient-corrected exchange function in conjunction with the Lee–Yang–Parr non-local correlation function[31] (BLYP) and the 6-31G* basis set. Open-shell single-state transition structures (TSs) and products were treated with an unrestricted broken-spin approach (BS-UBLYP). Analytical vibrational frequencies were computed using second-derivative computations to obtain the thermal and ZPVE corrections and also to identify the minima and TSs. Intrinsic reaction coordinate[32] (IRC) computations were utilized to confirm the TSs. Single-point energies, using the same function but with a larger basis set (6-311+G*), were computed for all species; Brueckner doubles coupled-cluster energies[33,34] utilizing a cc-pVDZ basis set [BD(T)/cc-pVDZ] were additionally computed for comparison in some critical cases. The validity of the use of these computational schemes for these types of molecules has been demonstrated in our previous studies and were confirmed by other groups.[9,29,35–40] NICS values[10] were computed at the geometric ring centers to assess the aromaticity of all cyclic structures.

Results and Discussion

Scheme 4 describes the reaction paths (through $\mathbf{TS}_{xy}$) of **8** as a function of X leading to products **11**–**14**, along with competing rearrangements ($\mathbf{TS}_{25'}$ and $\mathbf{TS}_{16'}$) that result in the acyclic products **11′** and **13′**. Domino cyclizations ($\mathbf{TS}_{xy''}$) of **11**–**14** give rise to bicyclic products **15** and **16**. Although all depicted reactions were computed, we have focussed our discussion on the most feasible and competitive reaction pathways, i.e., $\mathbf{TS}_{26}$, $\mathbf{TS}_{16}$ and $\mathbf{TS}_{17''}$, and their respective products **12**, **13**, and **15**. Relative Gibbs free acti-

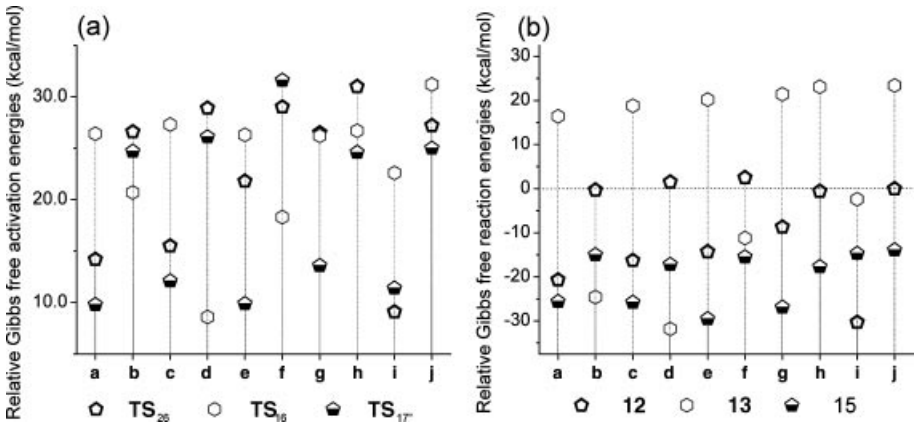


Figure 1. (a) Relative Gibbs free activation energies (kcal mol^{-1}, 298 K, at the UBLYP/6-31G* level) for the thermal cyclizations of **8** as a function of X to form **12**, **13** (**13d′**, **13f′**) and **15**; (b) relative Gibbs free reaction energies (kcal mol^{-1}, 298 K, at the UBLYP/6-31G* level) for the thermal cyclizations of **8** as a function of X to form **12**, **13** (**13d′**, **13f′**) and **15**.

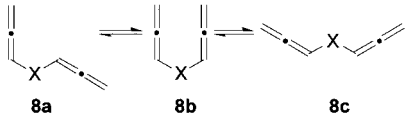
vation and reaction energies as a function of X are presented in Figure 1 (a) and (b). Table 1 provides relative energies at BLYP/6-311+G**//BLYP/6-31G* + ZPVE level as well as the NICS values for all cyclic species.

Table 1. Relative single point energies (kcal mol^{-1}) and NICS values (for the five- and six-membered ring compounds only) at the BLYP/6-311+G*//BLYP/6-31G*+ZPVE level for the **TS**s and products of the thermal cyclization of the heteroatom-bridged diallenes (**8**).

	BLYP/6-311+G*//BLYP/6-31G*+ZPVE						
X	$<S^2>$		ΔH_o			NICS	
	TS_{26}	TS_{16}	TS_{26}	TS_{16}	$TS_{17''}$[a]	TS_{26}	TS_{16}
a	0.00	0.00	13.9	25.3	10.0	–11.2	–11.1
b	0.00	0.00	26.5	19.3	25.5	–4.3	–18.8
c	0.00	0.00	15.7	26.1	12.4	–10.1	–11.5
d	0.00	0.00	28.9	7.1	26.9	–5.6	–11.4
e	0.00	0.00	21.5	25.2	9.5	–12.1	–19.5
f	0.00	0.00	28.5	16.7	31.2	–6.7	–20.0
g	0.00	0.00	24.5	23.3	11.5	–11.5	–19.8
	0.00	0.00	30.9	25.3	24.6	–1.3	–20.2
i	0.00	0.00	5.5	17.6	10.0	–8.6	–8.2
j	0.00	0.00	27.0	29.6	25.9	–3.9	–15.6
	12	**13**	**12**	**13**	**15**	**12**	**13**
a	0.00	0.00	–19.9	15.1	–23.7	2.2	–1.1
b	1.01	0.00	1.0	–25.2	–13.4	–2.7	–2.5
c	0.58	0.70	–14.7	18.8	–24.1	0.1	–2.2
d	1.04	0.00	3.2	*–33.5*	–15.3	–4.1	n/a[b]
e	0.67	0.92	–13.9	20.5	–27.8	3.4	–2.6
f	0.97	0.00	3.8	*–12.5*	–14.2	–3.2	n/a[b]
g	0.79	0.82	–9.6	19.7	–27.1	5.3	–3.0
	1.04	0.75	0.9	23.0	–15.5	–0.5	–3.6
i	0.00	0.00	–31.5	–7.8	–14.8	7.0	4.1
j	0.82	1.02	1.2	25.0	–12.2	–1.9	–2.3

[a] The actual barriers for these domino cyclizations are relative to structures **12** instead of the reactants (**8**). [b] Unaccounted NICS values for products without ring formation due to either the C^3–X or C^5–X cleavages; this also indicates that their corresponding **TS**s lead to acyclic products (**13′**), whose energies are listed in *italics.*

The two-fold base-catalyzed propargyl–allene isomerization of **9** (Scheme 2) yields the diallenes **8** that displays three conformers (Scheme 6). Their energy differences depending on X are in the range of 0.2–8.8 kcal mol^{-1}, mostly in favor of **8c** (for X = **a**, **b**, **g**, **i** and **j**) then **8a** (for X = **c**, **d** and **e**). The ΔG and $\Delta G^{\ddagger}$ values were computed with respect to the global minimum of the conformers, i.e., **8a**, **8b**, or **8c**, depending on the nature of X.



Scheme 6.

Diallenes **8** rearrange to form **12**[21] through a [2+2] bond formation across the central allene carbon atoms; the absence of a kinetic isotope effect signals little or no rotation of the terminal methylene units in the **TS**.[19] This suggests an early transition structure for this exothermic reaction, which is confirmed by the computed negative ΔG value (**12**) except for X = **d** and **f** [Figure 1 (b)].

The experimental activation energy (E_a) barriers for the cyclization associated with TS_{26} are 14.3 ± 1.7, 22.0 ± 2.4 and 34.2 ± 3.6 kcal mol^{-1} for X = **e**, **c** and **j**, respectively.[21] It was rationalized that the increase in the observed activation energies corresponds to a decrease in aromatic stabilization in the respective products **12**.[21] The lone pairs of X completing the π-electron sextet govern the reaction barriers. However, the computed $\Delta G^{\ddagger}(\mathbf{TS}_{26})$ values are 21.8, 15.5 and 27.2 kcal mol^{-1} for X = **e**, **c** and **j**, respectively. Obviously, our calculations show a different order for the activation energies, i.e., $\Delta G^{\ddagger}(\mathbf{TS}_{26}\mathbf{c}) < \Delta G^{\ddagger}(\mathbf{TS}_{26}\mathbf{e}) < \Delta G^{\ddagger}(\mathbf{TS}_{26}\mathbf{j})$, which is supported by the computed thermodynamic stabilization order of $\Delta G(\mathbf{12c}) < \Delta G(\mathbf{12e}) < \Delta G(\mathbf{12j})$. Previous computational studies[11–13] on the cycloaromatizations of **5**, **6** and **7** to the formally aromatic five-membered rings resulted in a similar computational trend (for X = **c** and **e**). Thus, it is questionable if the lone-pair contribution of the sulfur atom instead of the oxygen atom favors the aromatic stabilization. Furthermore, Salzner and Schleyer concluded from their studies on the anomeric effect and hyperconjugation that the orbital interactions with the lone-pair of sulfur or higher row atoms of the same group are less effective than those of oxygen.[41] Additional

computations at the BD(T)/cc-pVDZ level of theory were utilized to verify the computed activation energy ordering above; the comparison is provided in the Supporting Information (Table S2).

Figure 2 displays the linear correlation found between $\Delta G^{\ddagger}$(**TS**$_{26}$) and the corresponding ΔG(**12**); this correlation supports the notion of an aromatic π-electron sextet stabilizing the products. As X's ability to donate a lone pair of electrons[42] to the π-electron system decreases, in the order of X (**i**, **a**, **c**, **e**, **g**, **j**, **h**), the activation energy barrier increases similarly. Note that the exergonicities also decrease proportionally to the decreasing electron-donating ability of X.

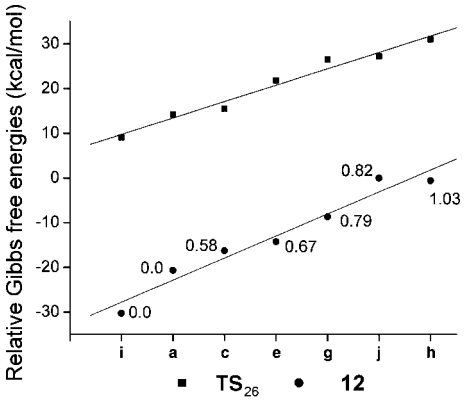


Figure 2. Relative Gibbs free activation (kcal mol^{-1}) of **TS**$_{26}$ (■) and reaction energies of products **12** (●) computed at the UBLYP/6-31G* level. The expected values for the Slater determinants (<S^2>) of **12** are listed next to each of the energetic data points, but not for those of **TS**$_{26}$ whose <S^2> values are equal to zero.

The computed NICS values (Table 1) provide a more detailed interpretation of the plots in Figure 2. While all NICS values of the products are rather small, those of the transition structures are large. Hence, aromaticity is a key factor for the transition structures but not for the products, at least according to the NICS analysis. Oddly, there seems to be a direct relationship between the magnitude of the energy barrier and the NICS value: high energy barriers have large negative NICS values. Hence, while delocalization is clearly important from a structural viewpoint, the initial [2+2] approach during the ring closure[27,28] is more important for the energy barriers than cyclic delocalization. Rotations of the two methylene groups occur late on the reaction path (Figure 3) and result in the conjugation of their two lone-pair p_z-orbitals with the molecular π-system; this greatly diminishes the cyclic π-delocalization in the products. As a consequence of this analysis, we conclude that bis(allyl) stabilization is the most important contribution to the relative ease of generating products **12**.[8,9]

The analyses of the frontier molecular orbitals of **TS**$_{26}$ and the product for X = NH confirm the notion of early electronic development in the transition structure (Figure 4). Early on in the reaction path (Figure 3), little or no rotation of the terminal methylene groups is observed.[21] Note that the increasing overlap of the HOMO of the starting materials lowers its energies as the reaction progresses towards the transition structure. In the transition structure,

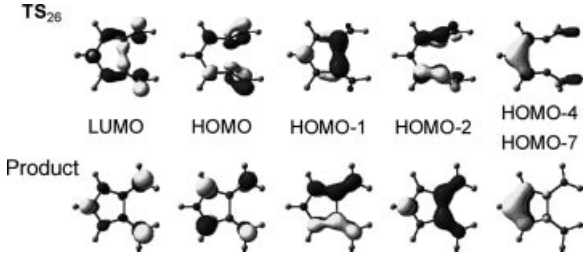


Figure 4. Frontier molecular orbitals of the transition structure and product of the 2,6-cyclization of **8** to form **12** with X = NH.

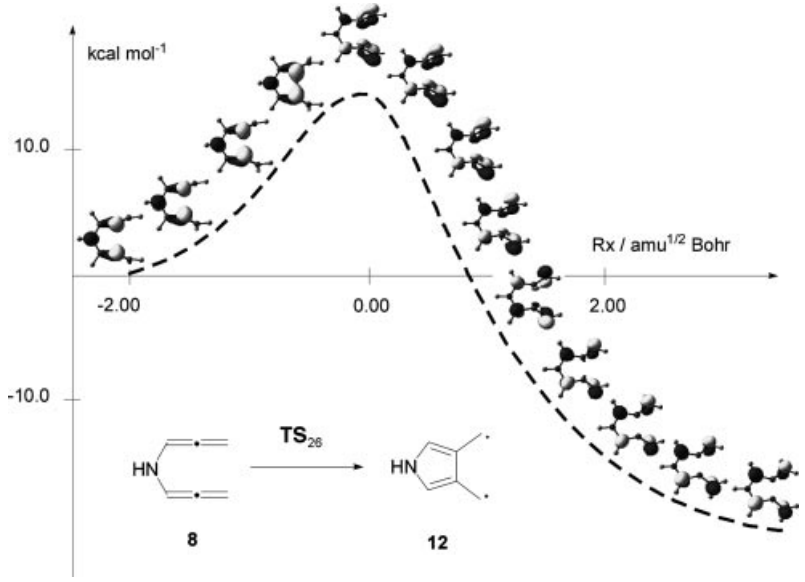


Figure 3. Transformation of the HOMO along the reaction path of the 2,6-cyclization of **8** to form **12** with X = NH.

the former HOMO has become HOMO–1 and the character of the new HOMO no longer describes the σ-bond formation. Instead, the π-HOMO takes over and determines the second half of the reaction path. Transformation of the in-plane π-orbitals into the σ-orbitals (**TS**'s HOMO) requires reactant **8** to assume the proper conformation (**8b**, Scheme 5). The antibonding character of the HOMO is too small to result in a significant σ-π-mixed MO across the C–C bond formation. Hence, the character of the HOMO along the reaction path changes from a σ-bond to a π-space interaction shortly before the transition structure.

The electronic perturbation of the heteroatom in products **12** and $\mathbf{TS}_{26}$ can be analyzed with the help of frontier molecular orbitals (FMOs) (Figure 4). For X = **i**, **a**, **c**, **e**, **g**, **j** and **h**, the available electron lone-pair interacts with the molecular π-system to complete the π-electron sextet (HOMO–2). The strong perturbation of the heteroatom X lowers the activation barrier (Figure 2), increasing the HOMO and LUMO energy separation and brings about the singlet nature of the products.[25] Vice versa, when the donor ability of X diminishes, the HOMO and LUMO of the products approach degeneracy allowing singlet-triplet (S–T) mixing (Figure 2).

The contribution of the electron lone-pair of X can be turned off by protonation (X = **b**, **d** and **f** vs. **a**, **c** and **e**) and $\Delta G^{\ddagger}(\mathbf{TS}_{26})$ increases accordingly by 7.2–13.4 kcal mol^{-1}. The computed NICS values of $\mathbf{TS}_{26}$ (X = **b**, **d** and **f**) are smaller than those of $\mathbf{TS}_{26}$ (X = **a**, **c** and **e**; Table 1) indicating the loss of cyclic delocalization due to protonation of X. The Gibbs reaction energies for protonated **12b**, **12d** and **12f** are less exergonic than those of the non-protonated **12a**, **12c** and **12e** (Figure 1), resulting from the inability to form an aromatic π-electron sextet.

Consequently, the homoaromatic 1,6-reaction of **8** forming **13** becomes more favorable, relative to the 2,6-cyclization, upon protonation of the X heteroatom; Figure 1 indicates that the $\mathbf{TS}_{16}$ barriers are lower than those of $\mathbf{TS}_{26}$ for X = **b**, **d** and **f**. The reaction path $\mathbf{TS}_{16}$ also competes with $\mathbf{TS}_{26}$ in the case of non-protonated X substituents such as **g** and **h**. However, the thermodynamic stabilizations are in favor of all the five-membered cyclic products **12** studied. This is in contrast with the six-membered ring products **13** for which most ΔG(**13**) values are highly endergonic except for **13b** and **13i** (–24.6 and –2.4 kcal mol^{-1}, respectively). Furthermore, the ΔG values of –31.8 and –11.2 kcal mol^{-1} correspond to structures **13d′** and **13f′** resulting from the Claisen-like rearrangement ($\mathbf{TS}_{16'}$) to form the more stable acyclic products **13′** (Scheme 4).

Although the 2,6-cycloaromatizations of **8** exergonically form the five-membered cyclic products **12**, subsequent cyclizations ($\mathbf{TS}_{17''}$) of **12** to yield the bicyclic products **15** are improbable. This is due to the high activation energy barrier [$\Delta G(\mathbf{TS}_{17''})$ = 22–42 kcal mol^{-1}] relative to structures **12** and the short lifetime expected for the biradical products **12**. Berson et al. reported the formation of **15** from **12** (X = O and S) only in low yields at high temperature using flash vacuum pyrolysis.[24] Instead, biradicals **12** typically dimerize at their methylene units (Scheme 2).[21]

Conclusions

By means of systematic computational comparisons of the cyclizations and rearrangements of heteroatom-bridged diallenes **8**, we found that *aromatization* reactions ($\mathbf{TS}_{26}$) are preferred and lead to the formally aromatic hetero-3,4-dimethylenecyclopentadienediyl **12**. The ability of the heteroatom (or group) X to contribute its lone pair of electrons to the π-electron aromatic sextet governs the energy barrier ($\mathbf{TS}_{26}$) but not the reaction energies. As a consequence, protonation of the heteroatom X disrupts the aromatic sextet and results in an increase in the ΔG and $\Delta G^{\ddagger}$ values and gives way to competing 1,6-reaction paths.

Supporting Information (see footnote on the first page of this article): Table of energies, *x*, *y*, *z* coordinates and structural drawings of all optimized species. Additional evaluation regarding the contradiction between the experimental results of the reaction of **8** with X = O and S (barriers of 22.0 and 14.3 kcal/mol, respectively) and the computed values of 15.5 and 21.8 kcal/mol (UBLYP/6-31G*) at different levels of theory (Tables S1 and S2).

Acknowledgments

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