Effects of Substituents in the 3-Position on the [2 + 2] Pentadienyl Cation Electrocyclization[1]

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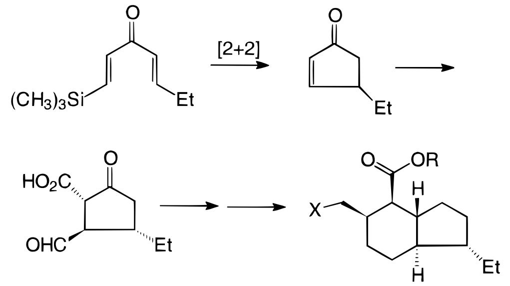
Received February 21, 1997[⊗]

Ab initio molecular orbital calculations at the RHF/3-21G(*), MP2/6-31G**//RHF/3-21G(*), and MP2/6-31G* levels of theory were used to examine the conformational preferences, transition structures, and products of the [2 + 2] electrocyclization reactions of 1,4-pentadienyl systems bearing substituents on carbon 3. The susbstituents examined include resonance-donating and -withdrawing groups: NH_2, OH, SH, H, PH_2, BH_2, and AlH_2. The activation energy for the cyclization (the difference in energy between the most stable acyclic conformation of the various 3-substituted pentadienyl systems and the transition state) decreases in the order shown, as does the energy of cyclization (with the exception of the PH_2 system). These results, as well as the conformational preferences, are explained by a combination of steric and electronic interactions.

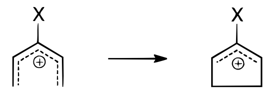
Introduction

The synthetic utility of a reaction is based on a number of factors including ease of the reaction and workup, chemo-, regio-, and stereoselectivity, and the ability to further transform the product. All of these factors must be considered in the design of new reactions and synthetic pathways. In addition, an in-depth understanding of the steric and electronic features and how they affect the reaction mechanism can be invaluable. Toward this end we performed ab initio molecular orbital studies[2] of the Nazarov[3] cyclization, the acid-catalyzed [2 + 2] electrocyclization of divinyl ketones leading to cyclopentenones, due to the importance of the construction of five-membered rings in the synthesis of natural products.[4] While the Nazarov cyclization meets many of the criteria for synthetic utility, one potential problem is that the carbonyl group necessary for the cyclization to occur may not be required in the final synthetic target and can sometimes be difficult to remove or modify. This may be due to the nature of the α,*β*-unsaturated carbonyl or the presence of other functional groups not inert to the subsequent synthetic manipulations. For example, in the development of a synthetic approach to the right wing portion of indanomycin (Scheme 1) removal of the ketone in the presence of other functional groups proved difficult,[5] eventually requiring a six-step process.[6]

Scheme 1



Scheme 2



X=NH_2, PH_2, OH, SH, H, BH_2, AlH_2

One possible solution, amenable to study by computational methods, is to design an analogous reaction which should not suffer from the same functional group manipulation problems. For the Nazarov cyclization, this means replacing the carbonyl oxygen with another functionality that still allows facile electrocyclization but can be easily removed thereafter. We therefore utilized ab initio molecular orbital methods to examine the effect of various heteroatomic functional groups (in their protonated forms necessary for reaction) at carbon 3 of the pentadienyl cation on the [2 + 2] electrocyclization reaction (Scheme 2). While some of these heteroatomic substituents are not synthetically viable, and the remainder are models for more highly substituted functional groups, the set (including oxygen) of six substit-

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

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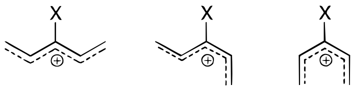
S0022-3263(97)00331-9 CCC: $14.00

Scheme 3



X=NH_2, PH_2, OH, SH, H, BH_2, AlH_2

uents plus hydrogen provides a consistent and comprehendable framework for the understanding and design of novel molecular systems for electrocyclization.

Theoretical Methods

Ab initio calculations were carried out using the Gaussian[7] series of programs on a Cray Y-MP/864. Structures were completely optimized starting from the previously obtained 1,4-pentadien-3-one cation geometries;[2] no symmetry or other constraints were imposed. Restricted Hartree–Fock calculations leading to the stationary points were first performed using the 3-21G(*) split valence basis set, which contains d-type polarization functions on aluminum, phosphorus, and sulfur and were confirmed by frequency calculations.[8] Second order Moeller–Plesset electron correlation corrections[9] were calculated as MP2/6-31G**//RHF/3-21G(*) single points, where the 6-31G** basis set includes d-type polarization functions on all non-hydrogen atoms and p-type polarization functions on hydrogens.[10] Additionally, stationary points were located at the second order Moeller–Plesset level of theory with the 6-31G* split valence basis set in order to compare optimizations performed both with and without correlation corrections.

Results and Discussion

Of the substituents chosen for this study, only systems containing oxygen and hydrogen at position 3 of 1,4-pentadiene moiety are known. However, the α,β-unsaturated thioketone, enimine, and stabilized phosphoranylidene are not unreasonable organic compounds in the synthetic sense. Thus we chose to examine the sulfur-, nitrogen-, and phosphorus-containing compounds in their simplest forms, i.e., with no substituents other than hydrogen. Since these three plus oxygen are all resonance donating, we also chose to examine two resonance withdrawing substituents, boron and aluminum, despite the fact that these can probably never be synthetically useful systems.

Conformational Analysis. All 3-substituted pentadienyl cations exhibit three stable conformations regardless of substituent, named to indicate the orientation of the terminal methylene (CH_2) groups relative to the substituent at the 3-position (Scheme 3).[2] In the syn–syn (SS) conformation X–C–C–C moieties are in an s-cis conformation; in the syn–anti (SA) conformation one terminal methylene is s-cis while the other is s-trans; in the anti–anti (AA) conformation both terminal methylenes are s-trans to the substituent. Note that the terms anti and s-trans are approximations; the dihedral angle relating substituent X and the methylene is not typically 180°.

Table 1. Relative Energies (kcal/mol)

		RHF/3-21G(*)	MP2/6-31G**// RHF/3-21G(*)	MP2/6-31G*
NH_2	SS	1.20	2.48	2.22
	SA	0.08	0.70	0.65
	AA	0.00	0.00	0.00
PH_2	SS	1.14	2.24	2.68
	SA	0.72	2.11	2.12
	AA	0.00	0.00	0.00
OH	SS	0.35	0.94	0.57
	SA	0.00	0.00	0.00
	AA	4.71	0.58	0.47
SH	SS	1.31	1.60	1.38
	SA	0.002	0.67	0.58
	AA	0.00	0.00	0.00
H	SS	0.00	0.00	0.00
	SA	3.52	3.81	3.81
	AA	8.32	7.03	6.64
BH_2	SS	0.00	0.00	0.00
	SA	1.36	1.92	1.94
	AA	2.44	1.52	1.17
AlH_2	SS	0.00	0.00	0.00
	SA	2.20	2.86	2.61
	AA	3.01	2.08	1.16

Nitrogen. The relative energies for the pentadienyl cation conformations with NH_2 in the 3-position are given in Table 1. The order of stability for the three conformations is due to both steric and electronic factors and does not change upon inclusion of electron correlation as either single point calculations or optimization. The most efficient overlap between the filled p orbital of nitrogen with the empty π orbital of the pentadienyl system is expected in the s-trans conformation; it is therefore not surprising that for the strongly resonance electron-donating nitrogen substituent that AA is the most stable conformation followed by SA. There is little difference in energy between SA and AA; the increased stability of the anti substructure relative to the syn is attenuated by the deformation from planarity of the AA conformation due to steric interactions between the hydrogens on C1 and C5. The SS conformation is much less stable than the other two due to the lack of extended s-trans substructures as well as the significant steric repulsion between the amino and terminal methylene hydrogens.

The deformation of the AA conformation from planarity is evident in that the dihedral angles, C1–C2–C3–N and C5–C4–C3–N, are scissored and deviate from the plane by approximately 30°. The terminal methylenes are also twisted slightly so as to rotate the inner hydrogens away from each other. The plane defined by the three atoms of the amino group is also slightly twisted from the mean plane of the molecule in order to maximize overlap of the filled p orbital on nitrogen with the vacant π orbital of the pentadienyl system. The optimized structure at the MP2 level of theory differs little compared to that optimized at the RHF level.

The s-trans portion of the SA conformation is more planar than the AA due to the lack of steric interaction between the hydrogens on C1 and C5. However, significant steric interaction now exists between the inner hydrogen of the syn terminal methylene and the hydro-

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gen of the amine group causing the deviation from planarity in the C1−C2−C3−N dihedral angle. The greatest difference between RHF- and MP2-optimized geometries of SA also appears in the s-cis (C1−C2−C3−N) dihedral angle, but this difference is only slightly more than 4°.

The SS conformation suffers from steric repulsion between the amine and terminal methylene hydrogens leading to a nonplanar conformation with terminal methylenes extended outward on opposite sides of the amine functionality. This results in a significant decrease in orbital overlap, hence this is the least stable of the acyclic conformations. The SS geometry also shows the greatest dependence on electron correlation. For example, the dihedral angles of SS open up or become less planar by over 7° when the geometry located at the RHF level is permitted to relax at the MP2 level.

Phosphorus. The relative energies for the pentadienyl cation conformations with PH_2 in the 3-position are given in Table 1. The relative order of stability for the three conformations is the same as the NH_2 system and due mainly to electronic factors (vide supra). The order of stability does not change with inclusion of electron correlation either as single point calculations or optimization, although there is a rather large difference in energy between the AA and the other two conformations at the MP2 level. This is in contrast to the NH_2 system, where the larger energy difference was between the least stable SS and the more stable SA and AA conformations.

These energetic differences between the NH_2 and PH_2 systems are due to the different electron-donating abilities of the substituents to the cationic π system. The AA is the most stable in both systems due to the extended overlap between the electron-donating substituent with the s-trans arms of the pentadienyl cation. In the NH_2 system, the s-trans arm of SA is quite planar and a major stabilizing factor, bringing it closer in energy to the AA, while the SS is nonplanar due to steric effects and thereby destabilizing it relative to the other two. In the PH_2 system, the lone pair of electrons on phosphorus are not donated to the cationic π system as strongly as the nitrogen lone pair (vide infra), therefore the s-trans arm of SA is not as much of a stabilizing factor as in the NH_2 system. The SS conformation is much more planar in the PH_2 system, which causes better orbital overlap and therefore stabilization compared to the SS in the NH_2 system.

The C1−C2−C3−P and C5−C4−C3−P dihedral angles of the AA conformation differ significantly from one another, which is not the case in the NH_2 system. This difference is independent of electron correlation. However, the geometry of the SA conformation changes significantly when optimized at the MP2 level; it becomes much less planar. As previously stated, the SS conformation is much more planar than in the NH_2-substituted system. Two factors work in concert to decrease the steric interactions between the terminal methylene and 3-substituent hydrogens and increase the planarity in the PH_2 SS conformation: the pyramidal phosphorus and the longer C3−P bond (Table 4).

Two other important differences between the PH_2 system and the NH_2 system are (1) in all conformations the phosphorus is pyramidal while the nitrogen is planar; and (2) the PH_2 group rotates 90° upon cyclization while the NH_2 does not. These features, along with the transition structures located for phosphorus inversion in the AA and CP conformation,[2d] can be used to quantify conjugation of the phosphorus lone pair with the π system.[11] The phosphorus inversion barrier in the cyclized product (36.26 kcal/mol at MP2/6-31G**//RHF/3-21G(*)) is the energy required for inversion when there is no conjugation, i.e., the phosphorus lone pair is orthogonal to the π system. The same barrier in the AA conformation (6.29 kcal/mol at MP2/6-31G**//RHF/3-21G(*)) is the energy required for inversion when there is maximum conjugation. The difference between the barrier heights, 29.19 kcal/mol, is the stabilization energy due to conjugation.

Table 2. Energy of Activation (kcal/mol)

	RHF/3-21G(*)	MP2/6-31G**// RHF/3-21G(*)	MP2/6-31G*
NH_2	36.26	22.58	23.29
OH	30.67	15.56	15.94
SH	20.24	12.05	12.02
H	18.26	6.76	7.94
PH_2	13.93	5.10	5.92
BH_2	12.78	1.14	2.46
AlH_2	11.77	0.04	1.48

Table 3. Energy of Cyclization (kcal/mol)

	RHF/3-21G(*)	MP2/6-31G**// RHF/3-21G(*)	MP2/6-31G*
NH_2	16.15	6.97	6.80
OH	5.59	−3.19	−3.83
SH	−8.67	−5.36	−8.14
H	−15.40	−19.92	−20.33
PH_2	−17.33	−17.19	−17.42
BH_2	−21.89	−24.88	−25.08
AlH_2	−21.94	−26.88	−27.41

Table 4. C3−X Bond Lengths in Angstroms

		SS	SA	AA	TS	CP
NH_2	RHF/3-21G(*)	1.296	1.296	1.297	1.338	1.385
	MP2/6-31G*	1.310	1.311	1.313	1.337	1.345
PH_2	RHF/3-21G(*)	1.834	1.822	1.809	1.835	1.848
	MP2/6-31G*	1.813	1.775	1.780	1.826	1.866
OH	RHF/3-21G(*)	1.303	1.303	1.298	1.331	1.349
	MP2/6-31G*	1.305	1.305	1.304	1.325	1.333
SH	RHF/3-21G(*)	1.698	1.692	1.689	1.738	1.771
	MP2/6-31G*	1.688	1.685	1.688	1.726	1.748
H	RHF/3-21G(*)	1.077	1.077	1.077	1.071	1.067
	MP2/6-31G*	1.092	1.092	1.091	1.088	1.084
BH_2	RHF/3-21G(*)	1.584	1.579	1.574	1.579	1.569
	MP2/6-31G*	1.576	1.569	1.566	1.570	1.579
AlH_2	RHF/3-21G(*)	2.077	2.076	2.067	2.029	2.001
	MP2/6-31G*	2.074	2.069	2.053	2.039	2.023

Oxygen.[2] The relative energies for the pentadienyl cation conformations with OH in the 3-position are given in Table 1. The energetic order of the three conformations changes upon inclusion of electron correlation; however, both single point calculations and optimization with electron correlation yield the same trend. The SA conformation lacks the destabilizing steric interactions observed between the group VA substituents and the terminal methylene hydrogen; the lone hydroxyl hydrogen is on the anti side. This allows the SA conformation to be more planar, resulting in better orbital overlap. Along with the extended conjugation of the s-trans portion, these features make SA the most stable conformation at all levels of theory.

The higher energy of the AA conformation is directly attributable to the loss of planarity of the s-trans enone moieties due to steric interaction between the two inner hydrogens on C1 and C5. The geometry is independent

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Table 5. Central C2−C3−C4 Angle (deg)

		SS	SA	AA	TS	CP
NH_2	RHF/3-21G(*)	117.24	121.10	123.03	108.57	106.41
	MP2/6-31G*	120.04	122.84	124.02	109.16	105.63
PH_2	RHF/3-21G(*)	115.41	121.50	122.30	110.48	107.07
	MP2/6-31G*	114.86	121.02	120.62	110.46	105.49
OH	RHF/3-21G(*)	119.88	124.59	125.48	111.07	108.28
	MP2/6-31G*	120.90	124.85	125.77	111.75	107.34
SH	RHF/3-21G(*)	115.57	121.56	122.79	110.52	108.02
	MP2/6-31G*	118.13	121.60	122.14	110.13	105.91
H	RHF/3-21G(*)	124.12	127.82	126.42	113.21	108.64
	MP2/6-31G*	124.48	127.68	123.01	115.13	107.36
BH_2	RHF/3-21G(*)	118.46	123.79	123.03	111.33	106.94
	MP2/6-31G*	118.25	122.89	119.73	112.68	105.31
AlH_2	RHF/3-21G(*)	115.42	121.60	120.96	109.98	105.60
	MP2/6-31G*	114.70	119.96	116.47	112.03	104.07

of electron correlation. On the other hand, the SS conformational geometry depends on electron correlation, as is evident from the s-cis dihedral angle on the same side as the hydroxyl hydrogen. In either case, planar at the RHF level or nonplanar at the MP2 level, the s-cis enones result in less than optimal orbital overlap.

Sulfur. The relative energies for the pentadienyl cation conformations with SH in the 3-position are given in Table 1. The trend does not change upon inclusion of electron correlation as either single points or optimization. As with the two group VA functional groups, there are significant differences between systems with second and third row group VIA elements. Thus, the order of stability for the thiol is AA > SA > SS compared to SA > AA > SS for the OH system. These differences appear to be steric in origin; the larger sulfur leads to a preference for the anti over the syn conformation at all levels of theory. The C2−C3−C4 angle (Table 5) is smaller in the SH-substituted system than in the OH-substituted system for all three conformers.

The AA geometry is only slightly changed by electron correlation while both the SA and SS conformers vary more as a function of electron correlation. However, unlike the OH-substituted system, the change in geometries upon inclusion of electron correlation is independent of the thiol hydrogen position. This is evident in SS where both dihedral angles change to the same extent and in SA where the s-trans dihedral angle is most affected by the inclusion of electron correlation during optimization.

In the SH-substituted system there is a larger energy difference between the nearly equienergetic AA and SA conformations and the SS conformation, whereas in the OH-substituted system the larger difference is between the SA conformation and the nearly equienergetic AA and SS conformations. This shift is due to the decreased stability of the thiol SA conformation, most likely due to less favorable orbital overlap of the sulfur 3p orbitals with the cationic π system as compared to the oxygen 2p orbitals. Therefore, SA is less stable than AA in the thiol system, while SS is least stable due to the absence of extended overlap between the sulfur and the s-trans moiety.

Hydrogen. In previous studies of the pentadienyl cation symmetry constraints were imposed.[12] In order to allow for direct comparison in this study, the pentadienyl system was reinvestigated without imposing symmetry; however, our results do not differ significantly from the symmetry-constrained results. The acyclic conformations are virtually invarient upon optimization with or without electron correlation correction; both the SS and SA geometries are planar. The SS conformation is, as expected, the most stable conformation followed by SA and finally AA at all levels of theory.

Boron. The relative energies for the pentadienyl cation with BH_2 in the 3-position are given in Table 1. The order of stability of the three conformations changes with the inclusion of electron correlation; however, both single point calculations and optimization with electron correlation yield the same trend where SS is the most stable, followed by AA and SA. This reversal in order of stability from the resonance-donating systems discussed above is due to the lack of any electron donation through resonance by the BH_2 to the pentadienyl π system. The empty p orbital on boron is orthogonal to the cation π system in all conformations. This also places the two hydrogens on boron perpendicular to the plane of the pentadienyl system, thus reducing steric interactions.

The pentadienyl portion of the BH_2-substituted SS conformational geometry is planar both with or without electron correlation correction included during optimization. The geometry of the SA conformation depends upon the inclusion of electron correlation during the optimization, while the AA geometry does not. It is not readily apparent why AA is more stable than SA. One would expect AA to be less stable due to nonplanarity in the pentadienyl π system that decreases orbital overlap. However, this is not the case in either the single point calculations or the MP2 optimizations.

Aluminum. The relative energies for the pentadienyl cation cyclization with AlH_2 in the 3-position are given in Table 1. The order of stability for the conformations parallels that of the BH_2 system. Again, the order of stability changes with the inclusion of electron correlation correction at both the single point level and optimization; however, the conformational geometries are relatively invariant to the electron correlation correction in the optimization.

The SS conformation is the most stable conformation at all levels of theory, most likely due to better orbital overlap because of planarity. Unlike the BH_2 system, the AlH_2 group is coplanar with the pentadienyl system, yet there are no steric interactions between the hydrogens on aluminum and the terminal methylene groups due to the long carbon−aluminum bond length (Table 4). The long C−Al bond and the difference in energy between the aluminum 3p and the pentadienyl π molecular orbital precludes efficient overlap and thus electronic destabilization.

The s-cis arm of the SA conformation is relatively planar, even when optimized at the MP2 level, while the s-trans arm is more than 20° out of the plane in the MP2 optimized geometry. The AA conformation is nonplanar as with all substituents and shows little dependence on electron correlation correction in the optimization. Here, even more so than in the BH_2 system, SA is less stable than AA, although it is again not obvious as to why this is the case.

Electrocyclization. We define the activation energy ($\Delta E^{\ddagger}$) for the electrocyclization reaction as the difference in energy between the most stable acyclic conformation of the various 3-substituted pentadienyl systems and the transition state (Table 2). Systems bearing resonance-donating substituents exhibit a larger $\Delta E^{\ddagger}$, while resonance-withdrawing substituents lead to lower values. This follows from the observation that positive charge is transferred from carbons 1, 3, and 5 to carbons 2 and 4

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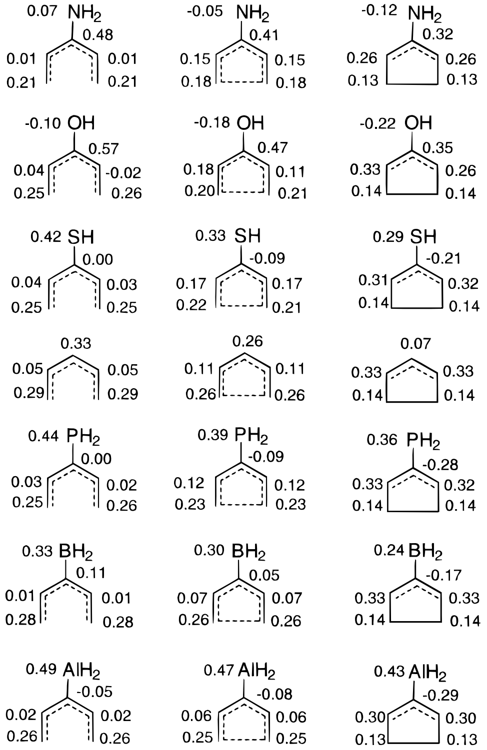
Scheme 4



during the electrocyclization reaction.[2b] Scheme 4 shows the charge at each position for the three stationary points (AA, TS, CP) for the substituted systems along the reaction coordinate. These values are taken from the MP2/6-31G* Mulliken population analysis and are the sum of each heavy atom and all its attached hydrogens.[13] Resonance-donating substituents tend to stabilize the reactants (larger positive charge on carbon 3) relative to the transition state leading to a larger $\Delta E^{\ddagger}$; resonance-withdrawing substituents destabilize the reactants relative to the transition state thereby decreasing $\Delta E^{\ddagger}$.

The $\Delta E^{\ddagger}$ decreases in the order of $NH_2 > OH > SH > H > PH_2 > BH_2 > AlH_2$. While electron correlation does, as expected, lower the $\Delta E^{\ddagger}$, the trend remains the same at all levels of theory. Both NH_2 and OH contain 2p electrons which strongly donate into the pentadienyl cationic π system, thereby stabilizing the starting material relative to the transition state and leading to the highest energy of activation. The filled 3p orbitals of sulfur and phosphorus do not donate into the pentadienyl π system as strongly; the $\Delta E^{\ddagger}$ for these systems is lower when compared to the OH and NH_2 systems. The pentadienyl cation (substituent = H) surprisingly exhibits a higher energy of activation than the PH_2-substituted system (vide infra). Finally, BH_2 and AlH_2, both resonance-withdrawing substituents, exhibit the lowest $\Delta E^{\ddagger}$.

The length of the forming σ bond between carbons 1 and 5 in the transition state provides an indication of the early or late nature of the transition state (Table 6). In similar systems undergoing the same type of reaction, those with the highest energy of activation are expected to have transition states which are later and more product-like, i.e., shorter C1−C5 distances, while those with lower $\Delta E^{\ddagger}$ are expected to have transition states which are earlier and more reactant-like, i.e., longer C1−C5 distances. The data in Table 6 follows the same trend as the $\Delta E^{\ddagger}$ with one exception: the PH_2-substituted system exhibits a shorter C1 to C5 distance, i.e., a later transition state, than the H substituted system even though the $\Delta E^{\ddagger}$ for the PH_2 system is lower. Presumably, the steric bulk of the PH_2 relative to H causes compression of the central C2−C3−C4 angle (Table 5), thereby bringing the pentadienyl termini closer together.

Table 6. C_1-C_5 Interatomic (forming bond) Distance in the Transition State (Å)

	RHF/3-21G(*)	MP2/6-31G*
NH_2	2.007	2.052
OH	2.087	2.140
SH	2.147	2.166
PH_2	2.212	2.287
H	2.268	2.455
BH_2	2.289	2.475
AlH_2	2.284	2.541

We define the energy of cyclization, ΔE_{cyc} (Table 3), as the difference in energy between the most stable acyclic conformation and the cyclized product. The trend exhibited by the ΔE_{cyc} is independent of electron correlation correction except for the reversal of the PH_2- and H-substituted systems at the MP2 level. If the C1 to C5 forming bond distance is used to predict the early/late nature of the transition state, these cyclization reactions obey the Hammond postulate. That is, ΔE_{cyc} is less exothermic when the transition state occurs late (the substituent is electron donating) and more exothermic when the transition state occurs early (the substituent is electron withdrawing) along the reaction coordinate. We would therefore expect amino-substituted system to undergo cycloreversion reactions while all others should undergo cyclization with the resonance-withdrawing systems most facile.

An interesting phenomenon occurs during the electrocyclization of the BH_2-substituted system. The empty p orbital on the boron begins perpendicular to the π system in each of the three acyclic conformations. During cyclization, the BH_2 group rotates about the carbon−boron bond so that the empty p orbital on boron is parallel to the π system in the cyclized product. This is readily explained using frontier molecular orbital theory. In the acyclic systems, there is a node in the highest occupied molecular orbital (HOMO) of the pentadienyl cation π system at C3, while the lowest unoccupied molecular orbital (LUMO) of BH_2 is the empty 2p orbital. The absence of a stabilizing HOMO−LUMO interaction, coupled with steric interactions, allows the perpendicular BH_2 group to be lower in energy than the coplanar arrangement. In the cyclized product, the LUMO is still the empty 2p orbital on boron but the HOMO is now the π bonding molecular orbital of an allyl system, which contains no nodes. This stabilizing HOMO−LUMO interaction favors the BH_2 group coplanar with the cyclopentenyl ring. The functional group rotation is not observed in the AlH_2-substituted system, i.e., the AlH_2 group is coplanar with the carbon backbone throughout the reaction. We attribute this to the lack of destabilizing steric interactions between the AlH_2 and the pentadienyl hydrogens due to the longer Al−C bond as compared to the B−C bond. Also, any destabilization in the starting material due to the HOMO−LUMO interaction is minor, since the LUMO (empty 3p orbital on Al) is much higher in energy than the HOMO of the pentadienyl cation as compared to the BH_2-substituted system.

Also of interest is the rotation of the PH_2 group around

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(13) Charges for the RHF/3-21G(*)-optimized geometries and MP2/6-31G** single points differ; however, the trend remains the same at all levels.

the C−P bond during cyclization at both levels of optimization, RHF and MP2. This rotation is opposite that of the BH_2 rotation. However, note that the phosphorus is pyramidal and the use of "perpendicular" to describe the position of the filled p orbital in relation to the pentadienyl π system is approximate, as is the use of "coplaner" to describe the PH_2 orientation relative to the pentadienyl chain in the ensuing discussion.

The PH_2 group is "coplanar" to the pentadienyl chain in the acyclic conformations but rotates during the reaction so that the filled p orbital is "perpendicular" to the pentadienyl π system in the cyclized product. It was first thought that this, too, could be explained on the basis of frontier molecular orbital theory, where the filled p orbital is the HOMO and the LUMO is that of the pentadienyl π system. The pentadienyl LUMO contains two nodes at C2 and C4, with p-π orbitals on C1, C3, and C5, where the HOMO (p orbital on phosphorus) can interact with the orbital on C3. The HOMO−LUMO interaction in the cyclized product is now the LUMO of the allyl π system, and the HOMO remains the filled p orbital of phosphorus. There is a node in the LUMO of the pentadienyl π system at C3. Without this stabilizing HOMO−LUMO interaction, the phosphorus rotates so that the filled p orbital is "perpendicular" to the allyl π system, and the phosphorus hydrogens are on either side of the cyclopentenyl ring. If this explanation were correct, then it must hold for the NH_2-substituted system and it does not. The NH_2 group remains planar and in full conjugation with the pentadienyl π system throughout the reaction. We are therefore unable to explain this phenomenon at this time.

Finally, there is rotation about the carbon−sulfur bond during the electrocyclization of the SH-substituted system in the RHF optimization but not in the MP2 optimizations. In the RHF optimizations, the hydrogen bonded to sulfur remains in the same plane as the carbon chain for all acyclic conformations. This undergoes rotation during the reaction so that the hydrogen−sulfur bond is perpendicular to the carbon ring in the cyclized product. This rotation does not occur in the OH-substituted system at either level of optimization.

The rotation at the RHF/3-21G(*) level exhibited by the SH system but not OH system is not due to the d-type functions on sulfur. The cyclized product of the SH-substituted system was optimized at the RHF level with the 3-21G basis, which does not contain d-type functions on sulfur, and produced the same result, i.e., the sulfur−hydrogen bond remained perpendicular to the carbon ring. Optimization of the cyclized product for both the OH- and SH-substituted systems at the RHF/6-31G* level, where d-type functions for both oxygen and sulfur are included, had the same result, i.e., the sulfur−hydrogen bond remained perpendicular while the oxygen−hydrogen bond remained parallel to the carbon ring. Therefore, this difference between the two systems is not a basis set effect. However, optimization of both systems at the MP2 level showed no rotation of the substituent.

Conclusions

All 3-substituted pentadienyl cations exhibit three stable conformations, regardless of substituent, named to indicate the orientation of the terminal methylene (CH_2) groups relative to the substituent at the 3-position. The order of stability of the conformations is for the most part insensitive to the bases set or method used for optimization, although the relative energies vary as one includes electron correlation. At the MP2/6-31G* level, the AA conformation is most stable for the most strongly electron-donating NH_2, PH_2, and SH groups, followed by SA and SS. For OH, the order of stability is SA > AA > SA. For H and the electron-withdrawing BH_2 and AlH_2 groups, the SS conformation is most stable. When H is the substituent, SA is more stable than AA; the opposite is observed for BH_2 and AlH_2.

Systems bearing resonance-donating substitutents exhibit a larger $\Delta E^\ddagger$, while resonance-withdrawing substituents lead to lower values. This follows from the observation that positive charge is transferred from carbons 1, 3, and 5 to carbons 2 and 4 during the electrocyclization reaction.[2b] Resonance-donating substitutents tend to stabilize the reactants (larger positive charge on carbon 3) relative to the transition state leading to a larger $\Delta E^\ddagger$; resonance-withdrawing substituents destabilize the reactants relative to the transition state thereby decreasing $\Delta E^\ddagger$. The $\Delta E^\ddagger$ decreases in the order of $NH_2 > OH > SH > H > PH_2 > BH_2 > AlH_2$. While electron correlation does, as expected, lower the $\Delta E^\ddagger$, the trend remains the same at all levels of theory.

The trend exhibited by the ΔE_{cyc} is independent of electron correlation correction except for the reversal of the PH_2- and H-substituted systems at the MP2 level. If the C1 to C5 forming bond distance is used to predict the early/late nature of the transition state, these cyclization reactions obey the Hammond postulate. That is, ΔE_{cyc} is less exothermic when the transition state occurs late (the substituent is electron donating) and more exothermic when the transition state occurs early (the substituent is electron withdrawing) along the reaction coordinate.

Both the BH_2 and the PH_2 substituents exhibit interesting but opposite rotational characteristics during the cylization reaction. That is, the boron empty p orbital is perpendicular to the π system of the starting material and parallel to the π system of the cyclized product, while the phosphorus filled p orbital begins parallel and ends up perpendicular. These behaviors occur at all levels of theory. There is, at the RHF level only, rotation about the carbon−sulfur bond during the electrocyclization of the SH system.

Supporting Information Available: Cartesian coordinates, total energies, and dihedral angles for all structures optimized at the RHF/3-21G(*) and MP2/6-31G* levels (36 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9703313