J. Phys. Chem. A **2003,** *107,* 5479−5487

Ab Initio and Density Functional Theory (DFT) Study on [1,5] Sigmatropic Rearrangements in Pyrroles, Phospholes, and Siloles and Their Diels−Alder Reactivities[†,#]

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Received: March 13, 2003; In Final Form: May 6, 2003

CCSD(T) and B3LYP calculations were done on 1*H*-, 2*H*-, and 3*H*-pyrroles, phospholes, and siloles to account for the relative stabilities, activation energies for sigmatropic hydrogen shifts, and Diels−Alder reactivities with two model dienophiles. The computed barrier heights for sigmatropic rearrangements in phospholes account for the observed reversible equilibrium at higher temperatures. Both CCSD(T) and B3LYP calculations support the experimental observation that 1*H*- and 2*H*-phospholes lead to the Diels−Alder adduct of 2*H*-phosphole and validate Mathey's proposal that 1*H*-phosphole (**1P**) converts to 2*H*-phosphole (**2P**) prior to the participation in the Diels−Alder reactions. In contrast to what is observed in phospholes, the sigmatropic shifts in pyrroles and siloles require higher activation energies compared to the Diels−Alder reactions, which indicate no sigmatropic shifts prior to cycloadditions. Distortion energies of dienophiles explain the small discrepancy between the activation energies and exothermicities in the reactions involving ethylene and acetylene. The frontier molecular orbital (FMO) analysis and the extent of charge transfer values from diene to dienophile are also used to assess the Diels−Alder reactivities of all of the dienes considered in this study.

Introduction

Pericyclic reactions, in addition to their diversified synthetic applications, have been one of the most fascinating classes of reactions, which excited theoreticians and experimentalists alike.[1−5] The Diels−Alder reaction and [1,5] sigmatropic shifts are two classes of reactions that fall in this category. The [1,5] sigmatropic shifts in pyrroles and phospholes have been the subject of theoretical and experimental studies.[6−12] Mathey has proposed that 1*H*-phosphole (**1P**) first undergoes a sigmatropic shift and later participates in the Diels−Alder reactions.[9] 1*H*- and 2*H*-substituted phospholes were reported to equilibrate at ambient temperature.[8−12] Similarly, the Diels−Alder reactions involving phospholes with a variety of dienophiles are well-known in the literature.[9−17] Thus, there exist two principal competing pathways for the phospholes, namely, [1,5] sigmatropic shifts and Diels−Alder reactions (the dimerization of phospholes may also be classified under this category). The phospholes, as well as their Diels−Alder adducts, were also shown to participate in novel modes of binding with the transition metal fragments such as FeCp, $Mn(CO)_3$, $Cr(CO)_5$, $Mo(CO)_5$, and $W(CO)_5$.[18] The 7-heteronorbornene and 7-heteronorbornadiene skeletons, which have diversified synthetic applications in phospha-, aza- and sila-chemistries, were usually accessed through the [4+2] cycloadditions between the heterocyclic five-membered ring dienes and a variety of dienophiles.[5] The Diels−Alder products of 2*H*-phospholes with alkenes and alkynes have potential applications in homogeneous catalysis.[12] The interconversions among 1*H*-, 2*H*- and 3*H*-phospholes through sigmatropic shifts also generated considerable experimental and theoretical interests.[5b,8−12]

The 2*H*- and 3*H*-pyrroles were shown to reversibly interconvert through [1,5] sigmatropic shift and the nonreversible interconversion of them resulted to 1*H*-pyrrole.[6] The Diels−Alder adducts of 1*H*-pyrroles have shown to exhibit interesting pharmacological properties.[19] Similarly, the Diels−Alder adducts of 1*H*-pyrroles coordinate with transition metals forming organometallic complexes.[20] Experimental studies indicate that while a reversible equilibrium exists between 2*H*- and 3*H*-siloles at high temperatures, the conversion from 2*H*- to 1*H*-silole seems to take place irreversibly.[21] The Diels−Alder reactions of 1*H*- and 2*H*-siloles with various dienophiles have been reported.[5c,21]

The Diels−Alder reactions of cyclic five-membered rings with acetylene result in norbornadiene systems. The extrusion of bridge in norbornadiene systems by thermolysis was proved to be a successful route to realize the syntheses of benzenes and heterobenzenes.[5c,9,22,23] Several substituted benzenes were obtained by the extrusion of heteroatom bridge from substituted 7-azanorbornadiene, 7-phosphanorbornadiene, and 7-silanorbornadiene.[23] Phosphinines have been synthesized from 1-phosphanorbornadiene.[9] Similarly, silabenzenes have been obtained from 1-silanorbornadiene.[5c]

Previous computational studies on sigmatropic shifts in phospholes and pyrroles were done only at HF and MP2 levels of theory.[8] While the suitability of these methods was not clearly established for modeling the sigmatropic shifts, both HF and MP2 levels were proved to be grossly inadequate in modeling the Diels−Alder reactions.[14a,24] Reliable estimates for the relative barrier heights for the two competing reactions in pyrroles and phospholes will be of considerable help in understanding the mechanistic preferences for the twin pathways in this class of compounds. Isolated computational attempts were made by several groups to study the Diels−Alder reactions and sigmatropic shifts on selected five-membered ring heterocycles at varying levels of theory.[8,14−16,24a] In the present set of

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[†] This paper is dedicated to Professor Goverdhan Mehta on the occasion of his 60th birthday.

[#] IICT communication No. 021211.

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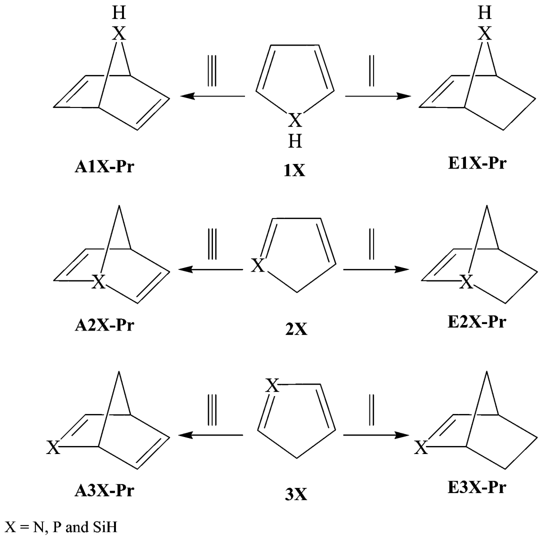
10.1021/jp034642v CCC: $25.00

SCHEME 1



calculations, quantitative calculations were carried out on the sigmatropic shifts in siloles and Diels–Alder reactivities of 2*H*- and 3*H*-pyrroles and siloles for the first time, to our knowledge. It is imperative to perform all of the calculations at a uniform level of theory for the comparison of the relative barrier heights for the sigmatropic shifts and Diels–Alder reactions. Considering the importance, we set out to perform computations on the relative stabilities and barrier heights for the sigmatropic shifts and Diels–Alder reactions on pyrrole, phosphole, and silole systems at a quantitatively reliable levels of theory. In the Diels–Alder reactions (Scheme 1), only the concerted pathway is explored, and thus, while the reaction trajectories of **1X** dienes are synchronous, those of **2X** and **3X** dienes are asynchronous by default because of the lack of plane of symmetry. Comparisons were made among the three sets and also attempts were made to explain some of the experimental observations.

Computational Details

All of the dienes considered in this study were fully optimized within the symmetry constraints at B3LYP/6-31G* level. The transition states of [1,5] sigmatropic hydrogen shifts for the conversions among **1X**, **2X**, and **3X** were obtained at the B3LYP/6-31G* level. The Diels–Alder transition-state structures and products of all of the dienes with both ethylene and acetylene were also optimized at the same level. The natures of all of the transition states, reactants, and products were characterized by frequency calculations done at the B3LYP/6-31G* level. Thus, the reactants and products were identified with all real frequencies, and all of the transition states of [1,5] sigmatropic shifts and Diels–Alder reactions possessed one imaginary frequency. The imaginary frequency corresponding to the normal mode for each of the transition-state structures was verified using the MOPLOT program package.[25] Single-point calculations were performed at the CCSD(T)/6-31G* level on B3LYP geometries for all of the reactants, transition states, and products. All of the calculations were done using the Gaussian 98 suite of programs.[26]

Results and Discussion

This section is divided into two parts: the first one deals with the sigmatropic shifts and the latter the Diels–Alder reactions. The equilibrium geometries of various isomers of pyrrole, phosphole, silole, and the sigmatropic transition states, along with the relative energies of isomers and activation barriers for sigmatropic shifts are given in the first section. In the second part, the Diels–Alder reactions were taken up. The percentage of stretching/shortening, frontier molecular orbitals, and reaction and activation energies are discussed. Distortion energy values were used to analyze the differences in the reactivities and the individual contributions from the diene and dienophile. Efforts were made to compare the trends in and between the sigmatropic shifts and the Diels–Alder reactions.

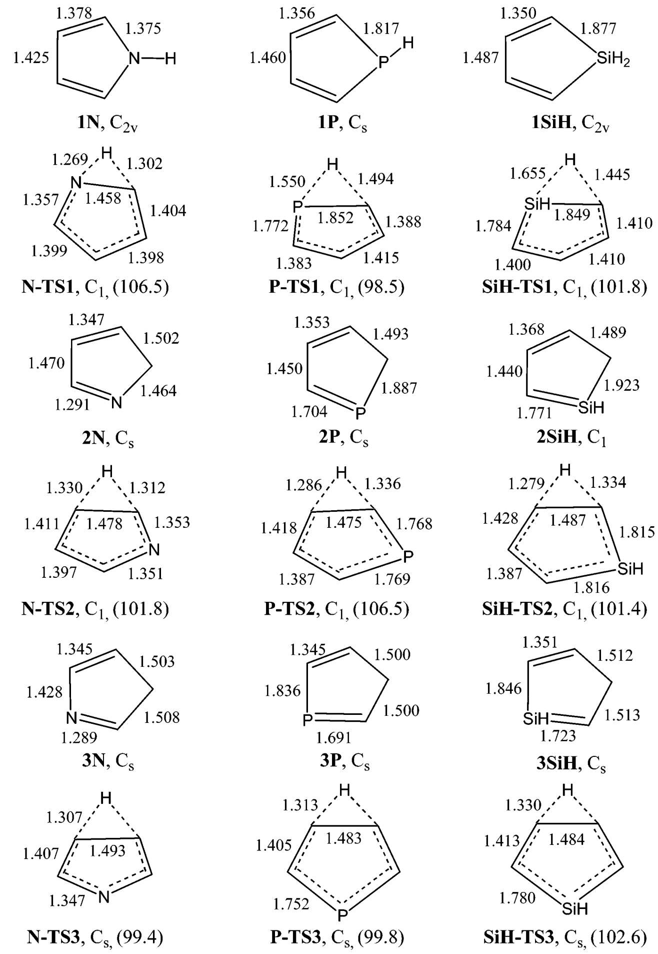


Figure 1. The B3LYP/6-31G* optimized important bond lengths of **1X**, **2X**, and **3X** (X = N, P, and SiH) and the transition states for the conversion of **1X** to **2X**, **2X** to **3X**, and **3X** to **3X** systems through [1,5] sigmatropic hydrogen shift. Angle (in deg) between the plane of the migrating hydrogen atom and the ring plane at the transition state is given in parentheses.

[1,5] Sigmatropic Shifts. *Equilibrium Geometries of Reactants and Transition States.* The geometries of the reactants and the transition states of [1,5] sigmatropic hydrogen shifts are depicted in Figure 1. Except **1P** and **2SiH**, all other dienes are planar. The planar forms of **1P** and **2SiH** are not minima on the potential energy surface. The phosphorus and silicon centers are pyramidal in **1P** and **2SiH**, respectively. In the transition states of [1,5] sigmatropic shifts, all hydrogens with the obvious exception of the migrating hydrogen atom are in the molecular plane except in **SiH-TS2** where the silicon center is pyramidal.

Relative Energies. The relative energies, zero-point energy corrections, relative enthalpies at B3LYP level, and the enthalpy-corrected relative energy values at CCSD(T) level for the dienes and [1,5] sigmatropic transition states are given in Table 1. In all of the three classes, that is, pyrroles, phospholes, and siloles, **1X** is taken as the reference. Previous studies by Bachrach et al. pointed out that inclusion of electron correlation is important

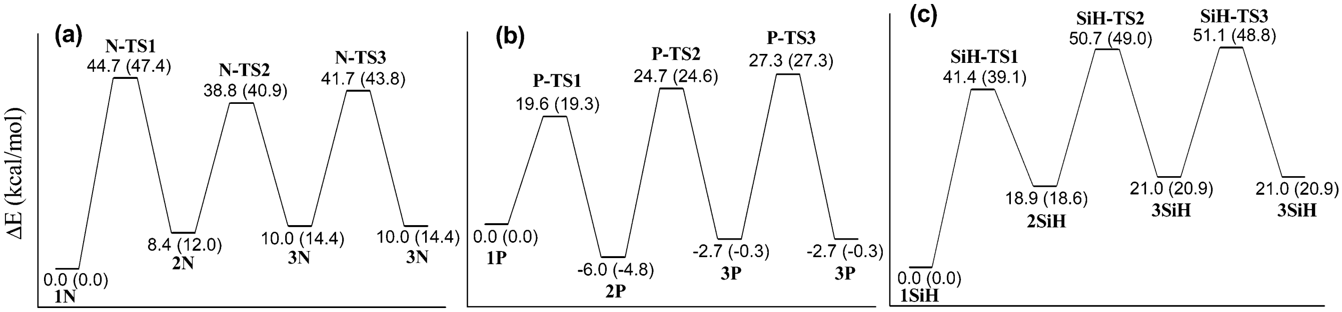


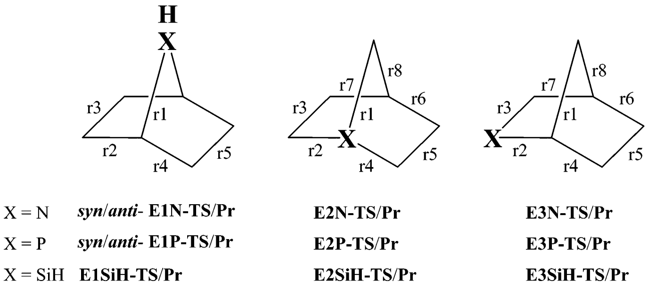
Figure 2. The relative energies at CCSD(T)/6-31G* and B3LYP/6-31G* (in parentheses) levels for the interconversions among **1X**, **2X**, and **3X**: (a) pyrrole system (X = N); (b) phosphole system (X = P); (c) silole system (X = SiH). The CCSD(T)/6-31G* relative energies include thermal correction to enthalpy values obtained at B3LYP/6-31G* level.

TABLE 1: The Relative Energies (Δ*E*), Relative Enthalpies (Δ*H*), and Zero-Point Energy Corrections (ZPE) Obtained at B3LYP/6-31G* and Relative Energies at CCSD(T)/6-31G* Levels for 1X, 2X, and 3X (X = N, P, and SiH) and the Transition States for the Conversions of 1X to 2X, 2X to 3X, and 3X to 3X through [1,5] Sigmatropic Hydrogen Shifts[a]

structure	B3LYP/6-31G* Δ*E*	ZPE	Δ*H*	CCSD(T)/6-31G*[b]
1N	0.0	51.9	0.0	0.0
N-TS1	47.4	48.8	44.1	44.7
2N	12.0	51.3	11.4	8.4
N-TS2	40.9	49.1	37.9	38.8
3N	14.4	51.0	13.5	10.0
N-TS3	43.8	48.9	40.7	41.7
1P	0.0	47.0	0.0	0.0
P-TS1	19.3	45.8	17.9	19.6
2P	−4.8	48.3	−3.4	−6.0
P-TS2	24.6	46.4	23.7	24.7
3P	−0.3	48.3	1.0	−2.7
P-TS3	27.3	46.3	26.3	27.3
1SiH	0.0	51.7	0.0	0.0
SiH-TS1	39.1	50.2	37.4	41.4
2SiH	18.6	52.5	19.6	18.9
SiH-TS2	49.0	50.6	47.7	50.7
3SiH	20.9	52.8	22.0	21.0
SiH-TS3	48.8	50.7	47.6	51.1

[a] All values are given in kcal mol^{-1} [b] Single point calculations were done on B3LYP/6-31G* geometries and the relative energies include the thermal correction to enthalpy values obtained at B3LYP/6-31G* level.

SCHEME 2: The Designation of Bond Lengths and the Nomenclature Used in This Study for the Transition States and Products of the Diels−Alder Reactions of Dienes 1X, 2X, and 3X (X = N, P, and SiH) with Ethylene as Dienophile



in the computations of relative stabilities of phospholes and their sigmatropic rearrangements.[8] The trends obtained at the B3LYP/6-31G* level are virtually identical to CCSD(T) level, and encouragingly, there is a fairly good quantitative agreement. Considering the previous and present theoretical studies, the levels of theory employed in the present study are deemed to be adequate in modeling these reactions. The CCSD(T) values are taken for discussion unless otherwise specified.

In pyrroles, **1N** is 8.4 and 10.0 kcal/mol more stable than **2N** and **3N**, respectively, which may be traced to the aromaticity of the former. Similar trends are observed in siloles, albeit with a larger gap, and thus, **1SiH** is about 19 and 21 kcal/mol more stable than **2SiH** and **3SiH**. The causative factors for the lower stability of **2SiH** and **3SiH** may be due to the presence of unfavorable C=Si bond. However, the relative energy ordering of phospholes is in sharp contrast because **2P** is the most stable among its isomers. Figure 2 depicts the potential energy diagram for [1,5] sigmatropic hydrogen rearrangements in pyrrole, phosphole, and silole systems. Clearly, **2N** and **3N** have comparable energies, and **1N** is significantly lower compared to both, and prominently the barrier heights for the interconversion between **2N** and **3N** are lower than those corresponding to the identity reaction of **3N** and the sigmatropic shifts between **1N** and **2N**. Thus, the computations predict that among the sigmatropic shifts, the most facile rearrangement is between **2N** and **3N**. The disruption of aromaticity in **1N** when converted to **2N** perhaps results in a high activation energy for the rearrangement process. The results obtained for pyrrole system confirm the available experimental reports.[6] Similar to pyrrole system, **2SiH** and **3SiH** are expected to equilibrate on heating. However, the pathway for the irreversible conversion to **1SiH** has the lowest barrier, and thus **2SiH**, once formed, shows greater propensity toward irreversible conversion to **1SiH**, and these results are in accordance with the experimental reports.[5c] In contrast to pyrrole and silole systems, **1P** interconverts to **2P** in an irreversible fashion, which is in agreement with the experimental observations.[9−12] Interestingly, the activation barriers for the identity reactions of all three **3X** systems are around 30 kcal/mol. Thus, the present study indicates that the [1,5] sigmatropic shift is a highly competitive and viable reaction pathway in all three systems considered here.

Diels−Alder Reactions. *Geometries of Transition States and Products.* The principal geometric parameters for the transition states and products of all of the Diels−Alder reactions considered in the study are given in the Supporting Information. The designation of bond lengths and the nomenclature for the transition states and products are depicted in Schemes 2 and 3. The present study considers only the concerted pathway and does not venture into exploring the alternative stepwise mechanism because such a pathway was considered to lie higher in energy.[27] Symmetry considerations make the mechanism of Diels−Alder reactions involving **1X** synchronous, while those involving **2X** and **3X** are nonsynchronous. In case of the transition states and products of **1N** and **1P**, the orientation of a bridged hydrogen results in two conformations, namely, syn and anti, depending on the tilting direction of bridged hydrogen toward or away from the diene, respectively. Both syn and anti

SCHEME 3: The Designation of Bond Lengths and the Nomenclature Used in This Study for the Transition States and Products of the Diels−Alder Reactions of Dienes 1X, 2X, and 3X (X = N, P and SiH) with Acetylene as Dienophile

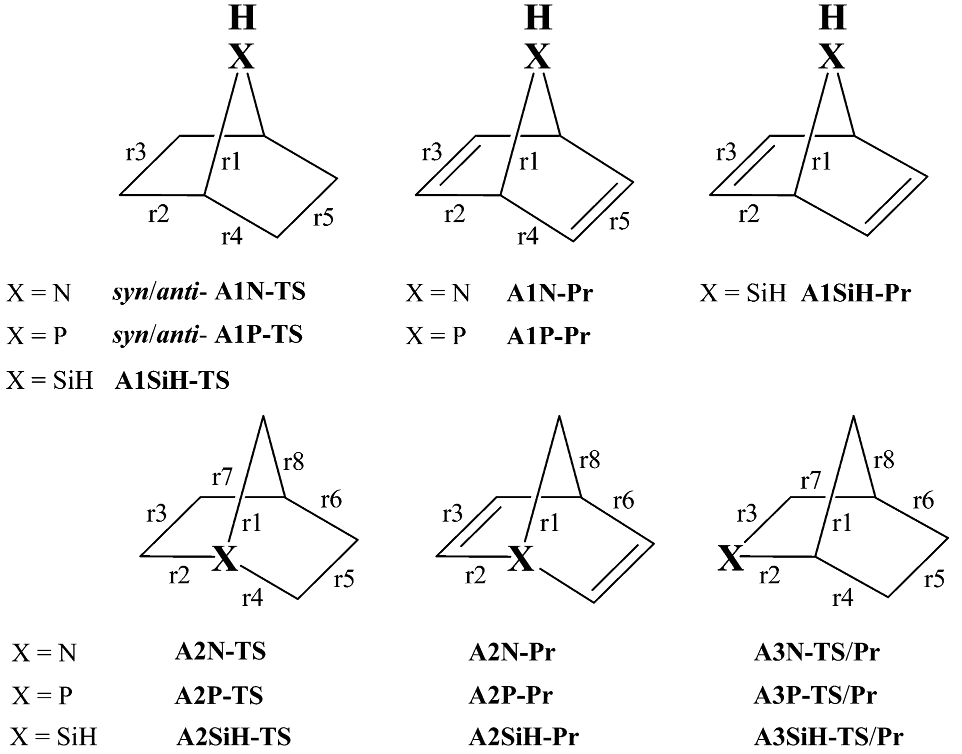


TABLE 2: The Percentages of the Bond Lengths r_2, r_7, and r_5 Stretched and the Bond Length r_3 Shortened at the Transition States of the Diels−Alder Reactions of the Dienes 1X, 2X, and 3X (X = N, P, and SiH) with Both Ethylene and Acetylene as Dienophiles[a]

	ethylene				acetylene			
	% stretching			% shortening	% stretching			% shortening
diene	r_2	r_7	r_5	r_3	r_2	r_7	r_5	r_3
1N	37.8	-	34.6	59.1	29.4	-	37.8	55.6
2N	33.5	38.0	29.2	56.1	26.8	33.5	32.6	52.2
3N	26.6	26.6	23.6	49.3	21.1	22.0	24.8	46.1
1P	26.4 (32.1)[b]	–	27.7 (26.9)[b]	48.8 (52.5)[b]	20.3 (26.9)[b]	–	27.5 (27.5)[b]	44.6 (48.8)[b]
2P	25.0	25.2	22.1	45.0	19.4	19.6	22.1	39.5
3P	31.7	24.4	24.5	46.6	24.9	17.4	25.4	40.3
1SiH	30.4	–	28.0	52.9	23.0	–	25.4	45.8
2SiH	1.9	7.6	9.0	14.1	2.5[c]	5.6	12.3	9.3
3SiH	42.4	18.2	24.7	31.6	35.7	4.5	36.1	9.6

[a] All values were obtained at B3LYP/6-31G* level. [b] The values in parentheses were obtained at the anti transition state. [c] The bond length is shorter at the transition state, and then it is elongated toward the product.

transition-state structures could be located for the diene **1P** with both ethylene and acetylene as dienophiles. All of the attempts in locating a syn transition state for the reactions of **1N** with ethylene, as well as with acetylene, were futile. The putative syn transition state guesses collapse either to the anti transition state or to the syn product. However, both syn and anti products are possible for the reactions of dienes **1P** and **1N** with ethylene, but because of the symmetry of product, only one product results when acetylene is a dienophile. The Diels−Alder reactions of **2X** type with acetylene form the products that possess the plane of symmetry.

The percentage of stretching/shortening of the bonds was calculated as the ratio between the change in bond length from reactant to transition state and the change in bond length from reactant to product, and the values at B3LYP level are given in Table 2. Exceptionally, in the reaction of **2SiH** with acetylene, the r_2 bond length is 2.5% shortened at the transition state, and then it is elongated in the product. Table 2 indicates that the transition states obtained for the dienes **3N**, **2P**, and **2SiH** with ethylene and acetylene are “early” compared to other dienes in pyrroles, phospholes, and siloles, respectively. The diene **1P** in **1X** and SiH-substituted dienes in **2X** and **3X** types form “early” transition states with both dienophiles. The reactions of all of the dienes with acetylene form “early” transition states compared to ethylene as dienophile. The diene **2SiH** forms a very “early” transition state compared to all other dienes considered in the study with both dienophiles.

Frontier Molecular Orbital (FMO) Analysis. HOMO and LUMO energies of all of the dienes, HOMO−LUMO and LUMO−HOMO energy difference between diene and dienophile, and the extent of charge transfer from diene to dienophile at the transition state (q_{CT}) for all of the reactions obtained at B3LYP/6-31G* level are listed in Table 3. Except **1N** and **3SiH**, all other dienes follow inverse electron demand on reaction with both dienophiles. The diene **2SiH** has the lowest FMO energy gap either with ethylene or with acetylene, and this is followed by the diene **2P**. This indicates that **2SiH** and **2P** are expected to have very facile Diels−Alder pathways compared to the rest,

TABLE 3: The Frontier Molecular Orbital Energies (E_{HOMO} and E_{LUMO}, in eV) for All of the Dienes Considered in This Study, FMO energy gap between diene and dienophile (E_N and E_I), and the Extent of Charge Transfer from Diene to Dienophile at the Transition State (q_{CT})[a]

			ethylene			acetylene		
diene	E_{HOMO}	E_{LUMO}	E_N	E_I	q_{CT}	E_N	E_I	q_{CT}
1N	−5.48	1.39	6.00	8.64	0.104	6.91	9.06	0.116
2N	−6.85	−0.87	7.36	6.38	−0.052	8.28	6.80	−0.041
3N	−6.47	−0.83	6.99	6.42	−0.009	7.90	6.84	−0.001
1P	−6.25	−1.02	6.76	6.24	−0.011 (0.007)	7.68	6.66	0.008 (0.027)
2P	−5.91	−1.61	6.43	5.65	0.009	7.34	6.06	0.024
3P	−6.19	−1.4	6.70	5.85	−0.022	7.62	6.27	−0.007
1SiH	−6.26	−1.36	6.77	5.90	−0.013	7.69	6.31	0.010
2SiH	−5.23	−1.77	5.75	5.48	−0.010	6.66	5.90	−0.005
3SiH	−5.35	−0.81	5.86	6.45	0.003	6.78	6.86	0.061

[a] The values given in parentheses are for the anti transition state. All values were obtained at B3LYP/6-31G* level. For ethylene, $E_{HOMO} = -7.26$ eV and $E_{LUMO} = 0.51$ eV. For acetylene, $E_{HOMO} = -7.67$ eV and $E_{LUMO} = 1.43$ eV.

which is in agreement with the computed results, as well as experimental observation.[9,10]

The transfer of electron density from diene to dienophile is given as q_{CT} and the values are depicted in Table 3. Thus, a positive value of q_{CT} indicates that there is electron density transfer from diene to dienophile and vice-versa. However, the electron demand and the direction of charge transfer are not in agreement with each other in several cases, **1P**, **2P**, **1SiH**, etc. Similarly, the frontier orbital energy differences between diene and dienophile is uniformly less for reactions involving ethylene compared to those involving acetylene. While in most cases the reactions with ethylene as a dienophile have lower activation energies, in **3SiH** the result is opposite. These discrepancies point to the limitations in considering only the HOMO and LUMO energies.

Activation and Reaction Energies. The activation energies obtained at B3LYP and CCSD(T) levels and enthalpy, entropy, and Gibbs free energies of activation obtained at B3LYP level for all of the reactions are given in Table 4. Figure 3 depicts the variations in activation energies for the reactions of all of the dienes considered with both dienophiles at B3LYP and CCSD(T) levels. Figure 3 shows that the trends and magnitudes in activation energies at B3LYP and CCSD(T) levels are in good agreement, and in the present study, only CCSD(T) values are taken for discussion throughout unless otherwise specified. Figure 3 also shows that the reactions of dienes require slightly higher activation energy when acetylene is taken as dienophile in general, barring the reaction of **3SiH**, which requires about 1 kcal/mol higher activation energy with ethylene. The activation energy for the reaction of **2SiH** with ethylene is slightly negative at B3LYP level, while all others are positive. The negative activation energies for the gas-phase reactions are similar to the situation in S_N2 reactions, wherein the transition state is preceded by the formation of a reactant cluster.[28] Table 4 indicates that the reactivity of dienes in phospholes decreases in the following order: **2P**, **3P**, **1P** irrespective of the dienophile. The dienes **3N** and **2SiH** require the lowest activation energies among pyrroles and siloles, respectively. The activation energies are comparable for **2N** and **1N** in pyrroles and **1SiH** and **3SiH** in siloles. However, the dienes **3N** and **2P** require lower activation energies by about 9−10 kcal/mol than **2N** and **3P**, respectively. This reactivity zigzags going from the pyrrole to phosphole series, which may be due to change in the ordering of the relative exothermicities, because the products of **3N** are about 22−25 kcal/mol more stable than the products of **2N**, whereas the products of **3P** and **2P** are energetically similar. The diene **2SiH**, enjoying the substantial exothermicities in the Diels−Alder reactions, was computed to be the most reactive. Again the reactivity is directly traced to the reaction exothermicities in siloles. The extremely high reactivity of **2SiH** toward the Diels−Alder reactions is expected to facilitate fast oligomerization rendering the **2SiH** difficult to handle.[5c]

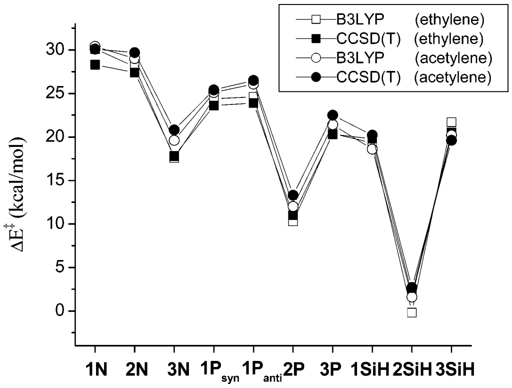


Figure 3. The plot showing the activation energies obtained for the reactions of all of the dienes considered in this study with both ethylene and acetylene as dienophiles at B3LYP/6-31G* and CCSD(T)/6-31G* levels.

Comparison of the activation barriers for sigmatropic shifts and the Diels−Alder reactions for each of the dienes considered forms the most important part of the present study. For all of

TABLE 4: The Activation Energies (Δ$E^‡$) Obtained at B3LYP/6-31G* and CCSD(T)/6-31G* Levels for the Diels−Alder Reactions of Dienes 1X, 2X, and 3X (X = N, P, and SiH) with Both Ethylene and Acetylene as Dienophiles and the Enthalpy (Δ$H^‡$), Entropy (Δ$S^‡$), and Gibbs Free Energies (Δ$G^‡$) of Activation Obtained at B3LYP/6-31G* Level[a]

	ethylene					acetylene				
	B3LYP/6-31G*				CCSD(T)/ 6-31G*[b]	B3LYP/6-31G*				CCSD(T)/ 6-31G*[b]
diene	Δ$E^‡$	Δ$H^‡$	Δ$S^{‡c}$	Δ$G^‡$	Δ$E^‡$	Δ$E^‡$	Δ$H^‡$	Δ$S^{‡c}$	Δ$G^‡$	Δ$E^‡$
1N	30.1	31.1	−12.3	43.3	28.3	30.4	31.1	−11.2	42.2	30.1
2N	28.1	29.2	−12.7	41.9	27.4	29.0	29.7	−11.5	41.2	29.7
3N	17.6	18.8	−12.5	31.4	17.8	19.6	20.3	−11.4	31.7	20.8
1P	24.4 (24.6)	25.3 (25.5)	−12.5 (−12.6)	37.7 (38.1)	23.6 (23.9)	25.1 (26.1)	25.5 (26.6)	−11.3 (−11.4)	36.8 (38.0)	25.4 (26.5)
2P	10.3	11.4	−12.4	23.8	11.0	12.0	12.6	−11.2	23.8	13.3
3P	20.4	21.5	−12.4	33.9	20.3	21.4	22.1	−11.1	33.2	22.5
1SiH	19.3	20.3	−12.2	32.5	19.8	18.6	19.0	−11.1	30.1	20.2
2SiH	−0.2	0.5	−11.3	11.8	1.9	1.6	1.9	−10.2	12.0	2.7
3SiH	21.7	22.7	−12.1	34.8	20.5	20.2	20.7	−10.5	31.2	19.6

[a] The values obtained for the anti transitions states of **1P** are given in parentheses. All values are in kcal mol^{-1}. [b] Single-point calculations were done on B3LYP/6-31G* geometries. [c] The entropy is multiplied by 298.15 K/1000 to convert into kcal/mol.

TABLE 5: The Reaction Energies (ΔE_r) Obtained at B3LYP/6-31G* and CCSD(T)/6-31G* Levels for the Diels−Alder Reactions of Dienes 1X, 2X, and 3X (X = N, P, and SiH) with Both Ethylene and Acetylene as Dienophiles and the Enthalpy (ΔH_r), Entropy (ΔS_r), and Gibbs Free Energies (ΔG_r) of Reaction Obtained at B3LYP/6-31G* Level[a]

	ethylene					acetylene				
	B3LYP/6-31G*				CCSD(T)/6-31G*[b]	B3LYP/6-31G*				CCSD(T)/6-31G*[b]
diene	ΔE_r	ΔH_r	ΔS_r[c]	ΔG_r	ΔE_r	ΔE_r	ΔH_r	ΔS_r[c]	ΔG_r	ΔE_r
1N	−0.6 (1.5)	2.9 (4.8)	−13.2 (−13.2)	16.1 (18.0)	−9.8 (−7.7)	−3.4	−0.2	−12.4	12.2	−10.0
2N	−6.2	−2.4	−13.7	11.3	−12.4	−11.0	−7.6	−12.9	5.3	−14.8
3N	−28.6	−24.2	−13.7	−10.5	−34.8	−36.7	−32.5	−13.0	−19.6	−39.9
1P	−19.3 (−21.5)	−15.5 (−17.6)	−13.7 (−13.7)	−1.8 (−3.9)	−26.4 (−28.4)	−30.7	−27.0	−12.9	−14.1	−34.6
2P	−27.7	−24.3	−13.5	−10.8	−32.7	−38.4	−34.9	−12.9	−22.0	−40.9
3P	−27.0	−22.7	−13.7	−9.0	−33.6	−38.4	−34.1	−13.0	−21.1	−42.0
1SiH	−24.7	−21.1	−13.3	−7.8	−30.2	−42.0	−38.5	−13.0	−25.5	−43.9
2SiH	−51.4	−47.8	−13.8	−34.0	−56.0	−64.4	−60.4	−13.3	−47.1	−66.1
3SiH	−23.2	−19.2	−13.6	−5.6	−30.5	−33.6	−29.6	−12.8	−16.8	−37.9

[a] The values given in parentheses are for the anti products. All values are in kcal mol^{-1}. [b] Single-point calculations were done on B3LYP/6-31G* geometries. [c] The entropy is multiplied by 298.15 K/1000 to convert into kcal/mol.

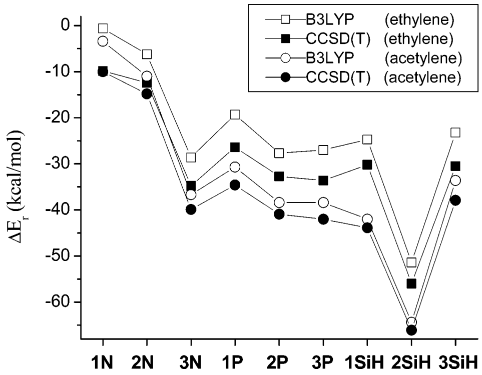


Figure 4. The plot showing the reaction energies obtained for the reactions of all of the dienes considered in this study with both ethylene and acetylene as dienophiles at B3LYP/6-31G* and CCSD(T)/6-31G* levels. Only the syn product energies were considered.

the dienes considered, except for **1P**, the Diels−Alder reactions are more facile. While the differences between the activation barriers are much higher for **2P**, pyrrole, and silole systems, it is marginal for **3P**. Thus, phospholes in general are predicted to interconvert to **2P**, which is the most active diene among its isomers. However, pyrroles and siloles have clearly a strong preference for the Diels−Alder reactions compared to sigmatropic shifts. In the absence of dienophiles, these systems may dimerize.[29]

Table 5 lists the reaction energies obtained at B3LYP and CCSD(T) levels and the enthalpy, entropy, and Gibbs free energies of reactions at B3LYP level for all of the reactions considered. The variations in reaction energies for the reactions of all of the dienes with both dienophiles at B3LYP and CCSD(T) levels are illustrated in Figure 4. While there is an excellent agreement between B3LYP and CCSD(T) levels regarding the barrier heights, reaction exothermicities are consistently underestimated at B3LYP level compared to CCSD(T) values. The inadequacy of the B3LYP level in modeling the reaction exothermicities is well-known.[14] The discrepancy in the reaction energies is higher in cases where ethylene is a dienophile compared to acetylene. However, the trends obtained are identical at both levels. Figure 4 reveals that in the case of every diene, the reactions with acetylene are more exothermic compared to those with ethylene as dienophile. The reactions of dienes **2SiH** and **1N** are computed to be the most and the least exothermic, respectively, among all of the dienes considered with both dienophiles. The reaction exothermicities are comparable for the three phospholes. However, among the pyrrole isomers, products of **3N** are the most stable. The high exothermicity of **2SiH** reactions may be traced to the fact that while the reactant diene suffers from the presence of an unstable C=Si, in the product it is replaced by a single bond and the product simultaneously forms a stable C=C.

As expected, the reaction of the most stable isomer **1N** with both dienophiles requires high activation energy and is the least exothermic compared to the reactions involving the dienes **2N** and **3N**. The computations fully support Mathey's mechanistic proposal that in the Diels−Alder reactions involving 1*H*-phosphole (**1P**), the [1,5] sigmatropic shifts proceed and therefore the cycloaddition occurs only between the 2*H*-phosphole (**2P**) and the dienophile.[9] The activation barriers obtained for the Diels−Alder reactions of **1P** are higher than the barrier for the conversion of **1P** to **2P**, which further establishes Mathey's proposal and supports Bachrach's computational studies carried out at MP2 and HF levels of theory.[8,9] However, the inadequacies of the HF and MP2 methods in modeling pericyclic reactions were known in the literature, and therefore, one gets circumspect about the reliability of these results.[14a,24,27a] Thus, the present study provides the first quantitatively reliable data on sigmatropic shifts in these systems and importantly compares and contrasts with the Diels−Alder reactivities.

Table 4 indicates that, in general, the entropy of activation obtained for the reaction of diene with ethylene is more negative compared to the reaction of the corresponding diene with acetylene by about 1−2 kcal/mol. Similarly, the reaction entropies are also more negative for ethylene reactions than for acetylene reactions (Table 5). The substantial negative entropies of activation are a feature of cycloaddition reactions, and the high-pressure techniques will be of use in effecting the Diels−Alder reactions, which are otherwise unreactive under normal conditions.[30] The entropies and free energies of activations obtained, after the zero-point energy and enthalpy corrections, indicate that all other dienes considered in the study are more reactive than pyrrole. The foregoing discussion strengthens the general belief that the cycloaddition reactions are highly attractive synthetic strategies to access novel polycyclic compounds.

Distortion Energies. The distortion energy is the energy difference between the reactant's energy at the transition state and the equilibrium geometry (Table 6). The interaction energies are obtained by subtracting the total distortion energies from the activation energies. The distortion energy data provide the reasons for obtaining the lowest activation energy barriers for

TABLE 6: The Reactant and Total Distortion Energies, the Interaction Energies (IE), and the Activation Energies ($\Delta E^\ddagger$) Obtained for the Diels−Alder Reactions of Dienes 1X, 2X, and 3X (X = N, P, and SiH) with Both Ethylene and Acetylene as Dienophiles[a]

	ethylene					acetylene				
	distortion energy					distortion energy				
	diene	ethylene	total	IE	$\Delta E^\ddagger$	diene	acetylene	total	IE	$\Delta E^\ddagger$
1N	24.4	13.7	38.1	−8.0	30.1	23.8	16.9	40.7	−10.3	30.4
2N	22.1	10.0	32.1	−4.0	28.1	22.4	11.7	34.1	−5.1	29.0
3N	16.2	6.7	22.9	−5.3	17.6	15.6	9.3	24.9	−5.3	19.6
1P	20.7 (17.6)	8.9 (8.7)	29.6 (26.3)	−5.2 (−1.7)	24.4 (24.6)	18.7 (16.9)	10.8 (11.3)	29.5 (28.2)	−4.4 (−2.1)	25.1 (26.1)
2P	10.6	6.1	16.7	−6.4	10.3	9.7	8.6	18.3	−6.3	12.0
3P	16.0	7.2	23.2	−2.8	20.4	14.7	9.3	24.0	−2.6	21.4
1SiH	14.9	9.1	24.0	−4.7	19.3	12.2	10.2	22.4	−3.8	18.6
2SiH	2.0	1.1	3.1	−2.4	0.7	2.2	2.8	5.0	−3.4	1.6
3SiH	15.9	7.6	23.5	−1.8	21.7	9.8	10.8	20.6	−0.4	20.2

[a] The values in parentheses are for the anti form. All of the values are obtained at B3LYP/6-31G* level and are in kcal mol^{-1}.

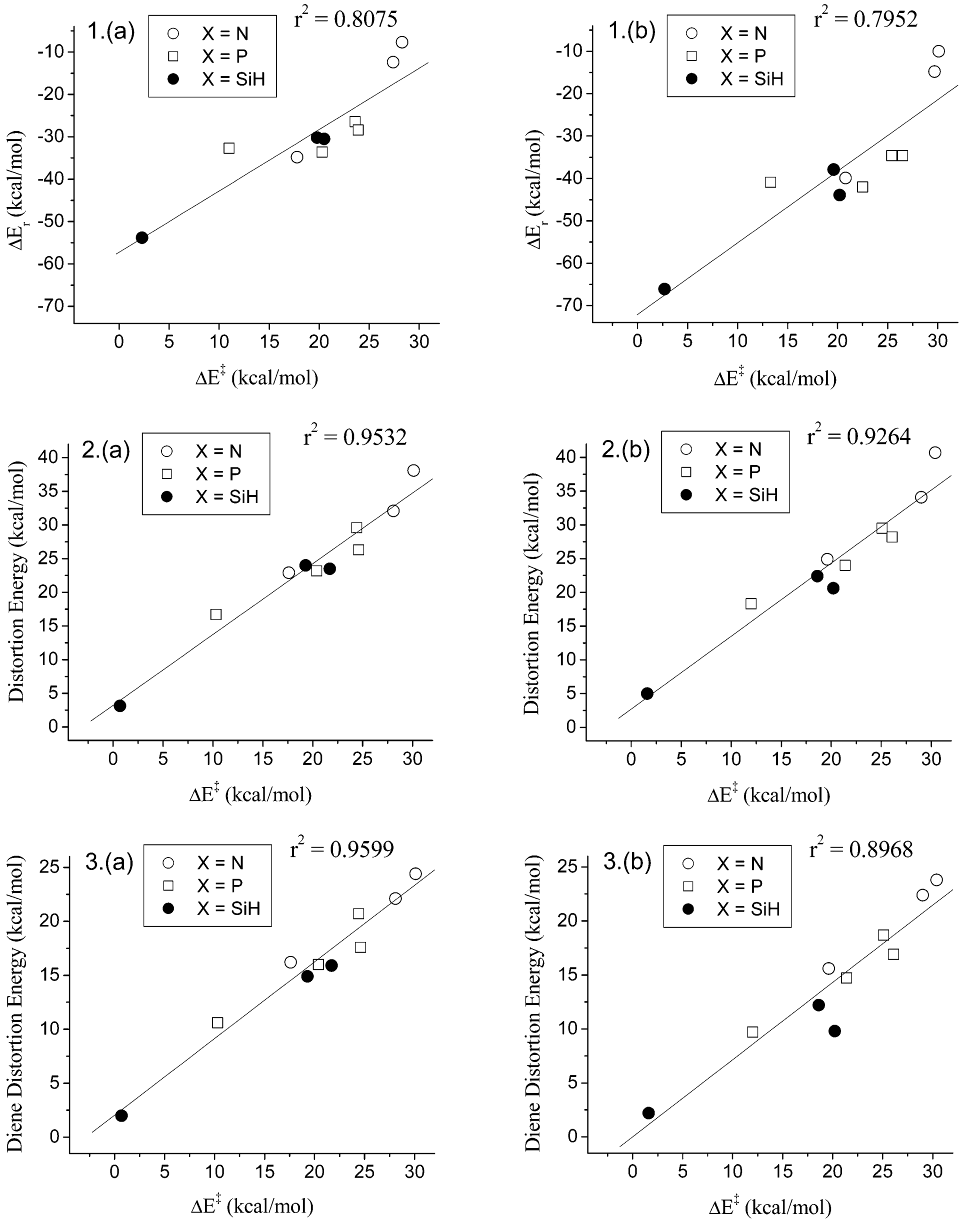


Figure 5. The correlation between activation energies and (1) reaction energies, (2) distortion energies, and (3) diene distortion energies for the reactions of **1X**, **2X**, and **3X** (X = N, P, and SiH) with (a) ethylene and (b) acetylene as dienophiles.

3N, **2P**, and **2SiH** in their respective classes. In general, acetylene shows consistently higher distortion energy compared to ethylene, which may be traced to a higher π-bond strength of the former. Interestingly, comparing activation and reaction energies between the reactions with ethylene and acetylene as dienophiles shows conflicting trends. While all of the reactions with acetylene as dienophile are more exothermic, unexpectedly these reactions (except the reaction of **3SiH** with acetylene) show higher activation barrier compared to reactions involving ethylene as dienophile (Tables 4 and 5). However, a careful comparison of distortion energies for the two dienophiles provides a hint to understand this discrepancy. Thus, in reactions involving ethylene and acetylene as dienophiles, the diene portions have very similar distortion energies. In contrast, in the dienophile part, the distortion energies of acetylene are consistently higher compared to those of ethylene. Thus, the strain at the transition state is higher for reactions in which acetylene is a dienophile. The variation in distortion energies is marked among dienes compared to dienophiles, and thus the dienes showing higher distortion energies possess higher activation energies. The interaction energies are quite comparable indicating that the transition-state bonding is to a similar extent for both ethylene and acetylene.

Figure 5 illustrates the correlation of activation energies with the reaction energies and distortion energies, as well as with the distortion energies of dienes. Excellent correlation was obtained between the distortion energies and activation energies. Although a linear correlation is obtained with the total distortion energy, the diene distortion energy alone seems to be sufficient to ascertain the activation energies.

Conclusions

CCSD(T) and B3LYP calculations on 1*H*-, 2*H*-, and 3*H*-pyrroles, phospholes, and siloles, the sigmatropic rearrangements among them, and the Diels−Alder reactivities considering ethylene and acetylene as dienophiles were reported in the present study. The systematic computational study accounts for some experimental observations. The results indicate that **1P** and **3P** interconvert to **2P** through sigmatropic shifts prior to undergoing Diels−Alder reactions. Thus, only the products of 2*H*-phospole are expected to be obtained irrespective of the starting diene, which is in agreement with the experimental results and supports Mathey's mechanistic proposal.[9−11] However, the situation is not similar in pyrroles and siloles, where in most cases the barrier for the Diels−Alder reactions are usually lower compared to the sigmatropic shifts. The relative stabilities of the three isomers also show interesting variations as a function of the heteroatom substituent, which are partly responsible for the computed reactivity zigzags.

The Diels−Alder activation barriers range from 2 to 30 kcal/mol for the reactions considered in the study, and the high exothermicity of **2SiH** reaction seems to be responsible for a negligibly small activation barrier. Good linear correlation is obtained between the reaction exothermicities and activation energies. However, the correlation between the distortion energies (especially of diene) with the activation energies is much better. The activation energies and free energies of activation are generally lower for ethylene as dienophile, which is in agreement with an earlier study on five-membered heterocyclic rings with ethylene and acetylene as dienophiles.[14b] The present study, thus, indicates that Diels−Alder reaction is one of the most important and a viable pathway for constructing polycyclic networks possessing heteroatom starting from phospholes, siloles, and pyrroles. The fine-tuning of the activation energy, and the ultimate feasibility of the reaction, may be achieved by selectively choosing the alterations, which increase the reaction exothermicities. Consistently lower magnitude of entropies of activation are observed when acetylene is the dienophile compared to when ethylene is. The significantly negative entropies of activations indicate that high-pressure techniques will be of immense use to achieve the feasibility of reactions, which are futile under normal conditions.[30] Thus, the experimental efforts in this direction, especially with pyrroles, are worth exploring.

Acknowledgment. T.C.D. thanks CSIR, New Delhi, for a research fellowship. Dr. K. V. Raghavan, Director, IICT, and Dr. J. S. Yadav are thanked for their interest and support.

Supporting Information Available: The tables of the bond lengths of the transition states and products of all the Diels−Alder reactions considered and the B3LYP/6-31G* optimized Cartesian coordinates along with the total energies obtained at B3LYP and CCSD(T) levels for all the stationary points obtained in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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