for the other bradykinin analogues. Only one compound was isolated with a t_R = 15.3 min and an MH$^+$ = 1059, calcd for $C_{48}H_{70}O_{10}N_{18}$ 1058. Amino acid analysis: Arg, 2.37; Gly, 1.00; Phe, 2.37; Ser, 0.90; Ala, 0.36; and Pro, 1.41: ^{13}C NMR (D$_2$O) δ 15.79 (Ala βC), 21.78, 22.98 (Arg γC), 23.03, 23.42 (Pro γC), 25.63 (Arg βC), 26.91, 28.00 (Pro βC), 29.46 (Arg βC), 35.53, 36.03 (Phe βC), 39.15, 39.33 (Arg δC), 41.44 (Gly αC), 46.51, 46.81 (Pro δC), 50.09, 50.19 (Arg αC, Pro^2 αC), 51.58 (Ser βC), 51.57 (Arg αC), 53.56, 53.62 (Phe αC), 55.91 (Ala^3 αC), 59.33, 59.83 (Pro^7 αC, Ser αC), 125.99, 126.02, 127.51, 127.58, 127.94, 128.08, 134.91, 135.02 (Phe Ph), 155.54, 155.57 (Arg δC, CN4), 166.88, 168.43, 168.66, 169.21, 171.32, 171.43, 172.34, 174.05 (C=O).

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Registry No. **1**, 3886-07-5; **2**, 50466-66-5; **3**, 60641-89-6; **4**, 127861-60-3; **5a**, 133641-24-4; *N*-deprotected-**5a**·HBr, 137234-24-3; **5b**, 137234-25-4; **5c**, 137234-32-3; **6a**, 137234-17-4; **6b**, 137234-26-5; **7a**, 133641-25-5; *N*-deprotected-**7a**·HBr, 137234-22-1; **7b**, 137234-27-6; **8a**, 137234-18-5; **8b**, 137234-28-7; **9**, 137234-19-6; *C*-deprotected-**9**, 137234-23-2; **10**, 137234-20-9; **11**, 137234-21-0; **12**, 137259-48-4; **13**, 133641-26-6; **14**, 133697-76-4; **15**, 133641-27-7; Boc-Arg(Tos)-OH, 13836-37-8; Boc-Phe-OH, 13734-34-4; Boc-Gly-OH, 4530-20-5; Boc-Pro-OH, 15761-39-4; Gly-OBzl·TsOH, 1738-76-7; Z-D-Pro-Phe-OBzl, 137234-29-8; Z-Pro-Phe-OBzl, 23707-87-1; Z-D-Pro-Leu-OMe, 137234-30-1; Z-Pro-Leu-OMe, 2873-37-2; Boc-Leu-D-Pro-Phe-OBzl, 137234-31-2; Boc-Leu-Pro-Phe-OBzl, 126868-06-2; Boc-Leu-OH, 13139-15-6.

Ab Initio Study of the Conrotatory Ring Opening of Phospha- and Azacyclobutenes. 1. Monophospha- and Monoazacyclobutenes

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The allowed conrotatory ring-opening reactions of 1,2-dihydrophosphete (**1**), 2,3-dihydrophosphete (**2**), 1,2-dihydroazete (**3**), and 3,4-dihydroazete (**4**) were examined at the HF/6-31G* and MP2/6-31G* levels. Reasonable activation barriers were obtained only with the inclusion of electron correlation; however, geometry optimization at MP2 did not significantly change the geometry from those obtained at the HF level. The opening of the dihydrophosphetes is thermoneutral or slightly endothermic, while the opening of the dihydroazetes is exothermic. The calculated activation barriers for the opening of **2** and **4** are 40.76 and 37.08 kcal mol^{-1}, respectively. The opening of **1** and **3** can occur via two diastereomeric pathways. Inward rotation of the heteroatom lone pair is favored for both systems; the lower barrier is 24.59 kcal mol^{-1} for **1** and 29.76 kcal mol^{-1} for **2**. The differences in these reactions are compared and explained in terms of ring strain and orbital interactions.

The electrocyclic ring opening of cyclobutene to give 1,3-butadiene has garnered a great deal of experimental[1-4] and theoretical[5-14] interest. Orbital symmetry rules demand a thermal conrotatory ring opening.[15] The experimental activation energy[1,2] is 32.9 ± 0.5 kcal mol^{-1}, and the heat of reaction[3] is -11.4 kcal mol^{-1}. Spellmeyer and Houk[13] have surveyed this reaction at a variety of theoretical levels. Calculations at the uncorrelated level overestimate the activation barrier by about 10 kcal mol^{-1}, but inclusion of correlation at the MP2 level lowers the barrier so that is is only a couple of kcal mol^{-1} above the experimental value. Houk and co-workers have also explored the effect of substituent groups on the activation barrier and the stereocontrol of the ring opening.[10,12,16-18]

In comparison, very little work has been published concerning the ring opening of dihydroazetes, due primarily to the instability of this system. Neiman[19] and Snyder[20] have argued, using HMO and semiempirical calculations, that azacyclobutenes should undergo thermal conrotatory ring openings to give 1-aza- and 2-aza-1,3-butadiene. Guillemin, Denis, and Lablache-Combier[21] were

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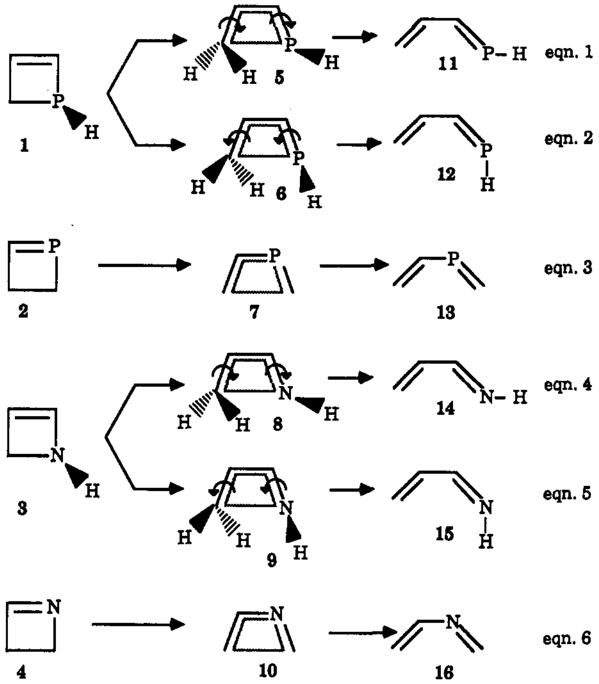
0022-3263/92/1957-0209$03.00/0

Scheme I



the first to report the ring opening of 3,4-dihydroazete. Ring openings of substituted dihydroazetes[22,23] were reported previously.

Unsubstituted dihydrophosphetes are unknown, but Doxsee, Shen, and Knobler[24] prepared a number of substituted 1,2-dihydrophosphetes. Mathey and co-workers[25-28] have prepared a series of substituted dihydrophosphetes that are complexed to metals. No direct ring-opening reaction of a dihydrophosphete has been reported, although Mathey[25,26] has suggested that a complexed dihydrophosphete may be in equilibrium with its complexed phosphabutadiene isomer. The reaction of 1,3,4-triphenyl-1,2-dihydrophosphete with Michael acceptors gave [4 + 2] cycloadducts, but loss of stereochemistry and solvent polarity dependence suggested a zwitterionic intermediate and not the formation of a phosphabutadiene intermediate.[29]

In our[30-33] continuing investigation of phosphaalkenes, we turn our attention here to the ring opening of 1,2-dihydrophosphete (**1**) and 3,4-dihydrophosphete, (**2**) to give the diastereomeric pair of 1-phospha-1,3-butadienes (**11** and **12**) and 2-phospha-1,3-butadiene (**13**), respectively. By using ab initio calculations, we will address the questions regarding the size of the overall energies and the activation energies of these reactions and the nature of the transition structures. The opening of **1** can lead to two isomeric products, with the H attached to P rotating "outward" to give **11** or "inward" to give **12**, using the nomenclature of Houk.[12] The preference for either of these paths will be addressed. We will also compare the phosphorus analogues with their nitrogen systems: 1,2-dihydroazete (**3**), opening to the isomeric pair of 1-aza-1,3-butadienes (**14** and **15**), and 3,4-dihydroazete (**4**), opening to 2-aza-1,3-butadiene (**16**). These electrocyclic ring opening reactions are summarized in Scheme I.

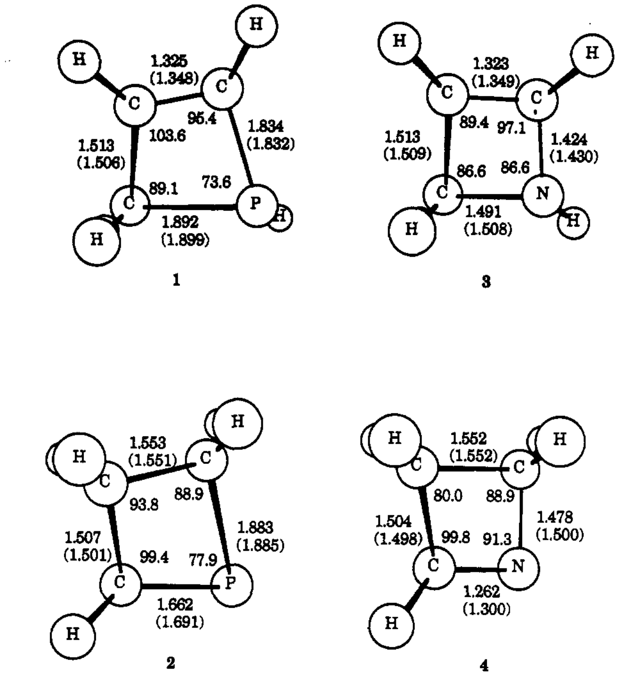


Figure 1. Optimized geometries of **1**–**4**. All distances are in Å and all angles are in deg. Optimized distances at HF/6-31G* are above with the MP2/6-31G* optimized distances below in parentheses.

Table I. Total Energies (au) of 1–16

	HF/6-31G*// HF/6-31G*	MP2/6-31G*// HF/6-31G*	MP2/6-31G*/ /MP2/6-31G*
1	−457.174108	−457.656699	−457.684098
2	−457.172923	−457.6677645	−457.695004
3	−170.878080	−171.420977	−171.440664
4	−170.900956	−171.441030	−171.461334
5	−457.118486	−457.617519	−457.644378
6	−457.109438	−457.609586	−457.636824
7	−457.094659	−457.602692	−457.629724
8	−170.816477	−171.383559	−171.393642
9	−170.800520	−171.361199	−171.381159
10	−170.826394	−171.381935	−171.401653
11	−457.170849	−457.655199	−457.682644
12	−457.170886	−457.655124	−457.682577
13	−457.168145	−457.654248	−457.682151
14	−170.916029	−171.449655	−171.469946
15	−170.914737	−171.448637	−171.469089
16	−170.907804	−171.442679	−171.462903

Computational Methods

All structures were completely optimized at the Hartree–Fock level with the 6-31G* basis set using the standard optimization techniques in GAUSSIAN-90.[34] Single point calculations were carried out at MP2 to account for some of the correlation correction. The

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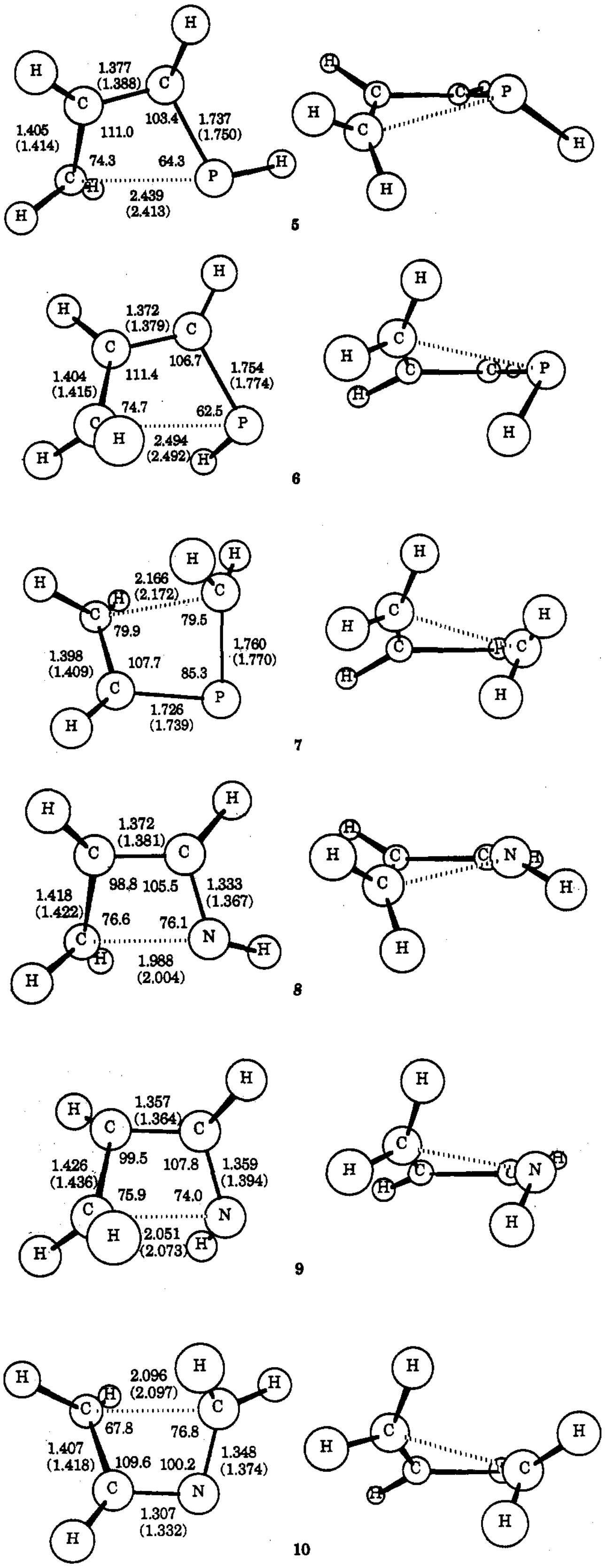

Figure 2. Optimized geometries of the transition structures **5–10**. See Figure 1.

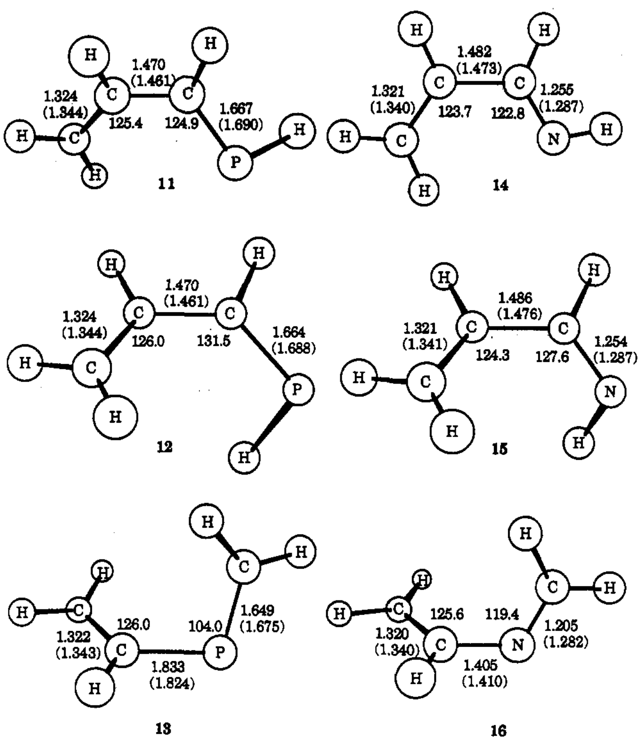

Figure 3. Optimized geometries of **11–16**. See Figure 1.

geometries are shown in Figures 1–3 and the energies are listed in Tables I and II. Local minima and transition structures were confirmed using analytical frequencies calculated at HF/6-31G*. To further test that these transition structures are correct, we followed the intrinsic reaction path[35] for five or six steps (step size of 0.1 amu$^{1/2}$ bohr) in both the forward and reverse directions to ensure that the transition structure connects to the proper reactant and product structures.

Calculations of local minimum structures for a variety of organophosphorus compounds at the HF/6-31G*//HF/6-31G* level have proven to be quite appropriate for the description of the geometry and density distribution.[30] We were concerned about the description of the transition structures at this level. Spellmeyer and Houk's[13] extensive examination on the relationship between the geometry of the TS and energy of the ring opening of cyclobutene with the basis set and degree of electron correlation suggests that little is gained beyond the MP2/6-31G*//HF/6-31G* level. In order to test if correlation affects the geometries in these aza and phospha systems, we completely reoptimized all structures at the MP2/6-31G* level, though we did not perform the frequency analysis at this level. As indicated in Figure 1 and Tables I and II (and supplementary material), only very minor changes result from the optimization at MP2, consistent with the results for the ring opening of cyclobutene.

Topological electron-density analysis, developed by Bader[36] and co-workers, was performed using the HF wavefunctions with a modified version of EXTREME.[37] The particular aspect of the topological method employed here is the correlation of the value of the electron density at bond critical points ($\rho(\mathbf{r}_c)$) with bond order n(X–Y).[38] This empirical relationship is given by eq 7, with constants given for C–C and C–P bonds. This parameter will be used to judge the extent of the reaction completed at the transition state. The numerical ordering of the atoms used when discussing the extent of the reaction will be the numbering scheme of the product.

$$n(\text{X–Y}) = \exp[A^*(\rho(\mathbf{r}_c) - B)] \qquad (7)$$

X–Y	A	B
C–P[39]	19.628	0.153
C–C[40]	6.458	0.252

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Results

Basis Set and Electron Correlation Dependence. The first issue to be addressed is the adequacy of the calculational method in predicting geometries and energies for the systems examined. The reaction energies and activation barriers are unknown for the reactions given in eqs 1–6 in Scheme I. Only a few examples of **1**–**4** and **11**–**16**, most with substituents, are known, and we will discuss below the comparison of the limited experimental geometries with our calculated geometries. The adequacy of the computational method must be judged by comparison to related systems and the degree to which limits have been approached.

We have previously shown that the HF/6-31G* optimized geometries of a variety of phosphaalkanes and phosphaalkenes[30] (including small, strained rings[41,42]) are in very close agreement with the experimental geometries. This basis has also been sufficient to describe the structures of aza-1,3-butadienes[33] and related nitrogen compounds. We believe that the HF/6-31G* level is suitable for obtaining geometries of the ground-state molecules. Optimization at MP2/6-31G* leads to small changes in the structures, usually less than 0.01 Å in any bond distance and 1.5° in any bond or dihedral angle (see Figures 1 and 3 and the supplementary material).

Without any experimental activation energies for eqs 1–6, it is difficult to judge the adequacy of the transition structures **5**–**10**. Spellmeyer and Houk[13] have shown that the activation barrier for the ring opening of cyclobutene is dramatically overestimated at the HF level, but inclusion of correlation reduces the barrier. Various basis set sizes and levels of perturbation theory give slightly different barrier heights, but they are all very close in energy. The implication is that some accounting of correlation is necessary to obtain reasonable activation energies; however, the TS geometry is relatively unaffected by correlation. Yu, Chan, and Goddard[14] have observed essentially the same trend in the ring openings of cyclobutene and oxetene.

We have optimized the structure of all six TSs (**5**–**10**) at HF/6-31G* and MP2/6-31G* and have also performed MP2 single-point calculations at the HF geometry. Examination of Tables I and II clearly indicates conformity with the energy trends described above. The activation barrier decreases in the neighborhood of 10 kcal mol^{-1} with the inclusion of correlation through MP2. It is of interest for our future work (the examination of diaza- and diphosphacyclobutenes) that full optimization at MP2 appears to be unnecessary. Activation barriers and overall reaction energies are relatively unchanged by optimization at MP2. The geometries of reactant, TS, and product are also relatively unaffected by optimization at MP2. Thus, we will usually refer to the MP2/6-31G*//HF/6-31G* results throughout this paper as simply "MP2", recognizing that optimization at MP2 results in little significant change.

Geometries. We have recently reported that calculated structures of the heterosubstituted 1,3-butadienes[33] **11**–**16** and 1,2-dihydrophosphete[42] (**1**) and will not discuss them further here. It should be noted that the s-trans conformers of **11**–**16** are lower in energy than the s-cis conformers presented here; however, the ring opening reaction will lead directly to the s-cis conformers, which can then rotate about the σ-bond to produce the lower energy conformer.

Table II. Relative Energies (kcal mol^{-1}) of 1–16

	1	**5**	**11**
HF/6-31G*//HF/6-31G*	0.00	34.90	2.05
MP2/6-31G*//HF/6-31G*	0.00	24.59	0.94
MP2/6-31G*//MP2/6-31G*	0.00	24.92	0.91
		6	**12**
HF/6-31G*//HF/6-31G*		40.58	2.02
MP2/6-31G*//HF/6-31G*		29.56	0.99
MP2/6-31G*//MP2/6-31G*		29.66	0.95
	2	**7**	**13**
HF/6-31G*//HF/6-31G*	0.00	49.11	3.00
MP2/6-31G*//6-31G*	0.00	40.76	8.41
MP2/6-31G*//MP2/6-31G*	0.00	40.96	8.07
	3	**8**	**14**
HF/6-31G*//HF/6-31G*	0.00	38.66	−24.81
MP2/6-31G*//HF/6-31G*	0.00	29.76	−18.00
MP2/6-31G*//MP2/6-31G*	0.00	29.51	−18.37
		9	**15**
HF/6-31G*//HF/6-31G*		48.67	−23.00
MP2/6-31G*//HF/6-31G*		37.51	−17.36
MP2/6-31G*//MP2/6-31G*		37.34	−17.84
	4	**19**	**16**
HF/6-31G*//HF/6-31G*	0.00	46.79	−4.30
MP2/6-31G*//HF/6-31G*	0.00	37.08	−1.03
MP2/6-31G*//MP2/6-31G*	0.00	37.45	−0.98

Neither the parent 3,4-dihydrophosphete nor any substituted version has been prepared. The optimized structure of the parent **2** is shown in Figure 1. The molecule is planar, unlike **1** which is puckered about 4–5°. The C=P distance is 1.662 Å, which is typical for phosphaalkenes.[30] The P–C distance is 1.883 Å, which, like the P–C2 bond in **1**, is longer than normal P–C bond lengths (1.85–1.86 Å). The C–C distance is quite long, 1.553 Å. These longer bonds aid in accommodating the strain of the four-membered ring.

1,2-Dihydroazete **3** has not been prepared; its optimized structure is shown in Figure 2. The ring is puckered by about 4°. The structure is quite similar to that of **1**: both are puckered, the bond across the ring from the C=C is abnormally long, and the C=C bond length is standard. 3,4-Dihydroazete (**4**) has been prepared,[21] and its ^{1}H NMR,[21] IR,[43] PE,[44] and microwave spectra[45] have been recorded. While no experimental structure determination has been published, the MNDO[44] and 4-31G(N*)[45] calculated geometries are consistent with the IR and microwave spectra. The HF/6-31G* structures is similar to the 4-31G(N*) structure, with all ring bonds 0.002–0.011 Å smaller in the former. Similar to **2**, **4** is planar and the C–C bond across the ring from the double bond is abnormally long. In fact, the carbon portions of **2** and **4** are very similar, having nearly identical bond lengths and angles about C2 and C4.

The transition structures for the ring opening of **1**–**4** are shown in Figure 2. We explored only the formally allowed conrotatory ring opening. For **1** and **3**, two different conrotatory paths can occur, leading through diastereomeric transition states to the diastereomeric butadienes. TS **5** leads to the *E*-phosphabutadiene **11** while **6** leads to the *Z*-phosphabutadiene **12**. Similarly, **8** leads to the *E*-azabutadiene **14** and **9** leads to the *Z*-azabutadiene **15**. The opening of **2** progresses through the TS **7** to 2-phos-

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Table III. Extent of Reaction at the Transition State

	$r(1\text{-}2)$	$r(2\text{-}3)$	$r(3\text{-}4)$	$r(1\text{-}4)$
	Based on Bond Distances			
5	58.08	35.86	57.14	38.90
6	47.06	32.41	57.67	39.30
7	52.56	37.43	58.92	36.64
8	53.85	30.82	49.48	35.40
9	38.24	20.86	45.31	35.71
10	47.62	31.47	52.72	38.66
	Based on $\rho(\mathbf{r}_c)$			
5	63.42	42.30	63.97	65.44
6	54.76	34.64	64.94	67.45
7	37.90	48.70	58.96	74.22
8	50.91	35.14	47.05	73.92
9	37.67	21.85	44.38	71.06
10	63.73	35.16	55.57	71.66

phabutadiene while **10** is the TS for the opening of 4 to give 2-azabutadiene. All TSs were fully optimized and confirmed by the presence of one and only one imaginary frequency. The intrinsic reaction pathway was followed for five or six steps in both the forward and reverse direction to confirm that these TSs connect to the proper reactant and product. Optimization at MP2 resulted in generally very small changes from the HF geometry for all six TSs.

Relative to their respective reactants, all TSs show the same geometric trends. The 1–4 bond stretches considerably, while the 1–2 and 3–4 bonds contract. The angles about atoms 2 and 3 widen as the ring opens up. The TSs clearly display the conrotatory opening (particularly in the side views shown in Figure 2). The imaginary frequency involves primarily further conrotatory motion coupled with further separation of atoms 1 and 4.

The relative position of the TS along the bond path can be estimated using eq 8, where x is a bond length or the value of the electron density at the bond critical point, $\rho(\mathbf{r}_c)$. The ratio obtained from eq 8 indicates how much

$$\frac{x_{\text{reactant}} - x_{\text{TS}}}{x_{\text{reactant}} - x_{\text{product}}}(100) \qquad (8)$$

progress has occurred in converting the variable of interest from reactant to product. Values of this "progress ratio" are listed in Table III. Since bond length and $\rho(\mathbf{r}_c)$ correlate well,[30,38] the values obtained using the two methods are very similar. This correlation does not hold for breaking bonds, i.e., bond orders less than 1, where an exponential relationship holds. Therefore, the extent of reaction based on $\rho(\mathbf{r}_c)$ for $r(1\text{-}4)$ will be excessive. One observation immediately apparent is that these reactions are not synchronous; the bonds created are not formed to the same extent as the bonds are broken.

The topological method defines the bond path network as the union of all bond paths in a molecule. The bond path[46] is the ridge of maximum density between two neighboring atoms that share a common surface. The bond path traces the gradient of the electron density from the bond critical point toward the two neighboring atoms. The bond path network is usually in a 1:1 correspondence with chemical bond networks. The bond path networks for the TSs **5**–**10** are all isomorphic with one another, as well as with the reactant rings **1**–**4**. One example is shown in Figure 4, which is the network for **5**. The ring structure is still present; a bond path persists connecting P with C4 and the ring critical point[47] is present. The electron-density distributions in the TSs are therefore reactant-like.

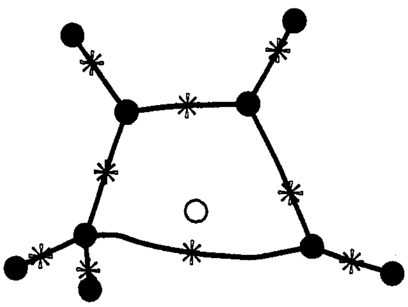

Figure 4. Topological bond path network of **5**. Bond and ring critical points are denoted by (*) and (o), respectively.

The diastereomeric TSs **5** and **6** differ in the direction of rotation taken by the H connected to P; outward rotation from **1** leads to **5** while inward rotation leads to **6**. On first sight it may appear that **6** is more sterically congested than **5**; however, in **5** the P lone pair most rotate inward, while outward rotation of the lone pair occurs in **6**. The main geometric differences between **5** and **6** are (1) the P-C4 distance is 0.055 Å longer in **6** and (2) the P–C2 bond is 0.017 Å shorter in **5**. However, from Table III, **5** is further along the reaction path than **6**, since the extent of reaction measured at the P–C2 and C2–C3 bonds is larger in **5** than in **6**, while the extent of reaction for the other two bonds is similar. Estimated bond orders, using eq 7, for the P–C2, C2–C3, and C3–C4 bonds in **5** are 1.52, 1.66, and 1.52, respectively, and 1.44, 1.70, and 1.54 in **6**. **5** is lower in energy than **6**, consistent with the geometric factors suggesting that **5** is an "earlier" TS than **6**.

The diastereomeric TSs **8** and **9** are the N analogues of **5** and **6**. The differences between the diastereomers are similar for the pairs. The outward rotation path, leading through **5** and **8**, has a lower barrier and an earlier TS than the outward path. The extent of reaction for the N–C2 bond and C2–C3 bonds is greater in **8** than in **9**, while the other two bonds have altered to essentially the same extent. The estimated bond orders in **8** for the C2–C3 and C3–C4 bonds are 1.70 and 1.44 and are 1.82 and 1.41 in **9**.

TS **7** displays the conrotatory opening of **2** with the P–C1 distance only 0.034 Å longer than the P–C3 distance. The dihedral angle formed by the heavy atoms is 26.3°, slightly more than halfway toward the dihedral angle in **13**. Based on eq 8, the P–C3 π-bond breaking lags behind the formation of the new π-bonds. The nitrogen analogue, TS **10**, displays similar features. Its dihedral angle is 25.16°, which is less than half the dihedral angle in **16**.

Energies. The total energies of **1**–**16** at the three calculational levels are listed in Table III. Activation energies for eqs 1–6 are listed in Table II.

A number of comparisons are of interest. Equations 1 and 2, which lead to diastereomers, have essentially identical reaction energies, being 1 kcal mol^{-1} *endothermic*. The energy of eq 3 is 8.41 kcal mol^{-1} *endothermic*. These energies should be compared with the ring opening of cyclobutene which is 7.8 kcal mol^{-4} *exothermic* (at MP2/6-31G*). The ring opening of **3** is strongly exothermic by approximately 18 kcal mol^{-1}, while the energy for ring opening of **4** is −1.03 kcal mol^{-1}. P substitution significantly stabilizes the four-membered ring.

Ring opening with H rotating outward is more favorable than inward rotation for both **1** and **3**. The activation barrier difference is 4.97 kcal mol^{-1} in the P system and 7.75 kcal mol^{-1} in the N system. The lower barrier for opening of **3** is 5.17 kcal mol^{-1} larger than the lower barrier for opening of **1**, though all four barriers are lower than

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[46] Runtz, G. R.; Bader, R. F. W.; Messer, R. R. *Can. J. Chem.* **1977**, *55*, 3040–3045.

[47] Bader, R. F. W.; Anderson, S. G.; Duke, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1389–1395.

the calculated barrier for the opening of cyclobutene (37.6 kcal mol^{-1} at MP2/6-31G*[13]).

The barrier for opening of **2** is 40.76 kcal mol^{-1}, much larger than the barrier for opening of **1** or cyclobutene. The activation barrier for the opening of **4** is 37.08 kcal mol^{-1}, slightly less than the barrier of eq 5.

Discussion

The ring opening of cyclobutene is −11.4 kcal mol^{-1}, and much of the driving force behind this reaction is the release of the ring strain of cyclobutene, estimated[48] at 29.8 kcal mol^{-1}. In contrast, the ring opening of **1** is nearly thermoneutral and the energy of the ring opening of **2** is +8.41 kcal mol^{-1}, implying that replacement of C with P stabilizes the cyclobutene ring. Bond angles about P are much smaller than about C, enabling P to better accommodate the small angles of strained ring systems.[41,42]

The energy for the ring opening of the dihydroazetes **3** and **4** are sharply different from their P analogues: the energy is about −18 kcal mol^{-1} for **3** and −1.03 kcal mol^{-1} for **4**. The more exothermic ring opening of the nitrogen rings relative to the P systems is due to the reduced ring strain energy of **1** and **2**.

The relative stabilities of **3** and **4**, the latter is 12.6 kcal mol^{-1} more stable, can be understood in very simple terms. The difference between these two isomers is the presence of a C=N (147 kcal mol^{-1}) and one more C–C bond (83 kcal mol^{-1}) in **4** and a C=C (144 kcal mol^{-1}) and one more C–N bond (73 kcal mol^{-1}) in **3**. Assuming the additivity of bond energies and similar ring strain energies, **4** is, using this admittedly crude method, 13 kcal mol^{-1} more stable than **3**.

The difference in the reaction energies for the opening of **1** and **2** is due to the relative stabilities of these dihydrophosphetes, since the isomeric products are nearly isoenergetic. **2** lies 6.87 kcal mol^{-1} below **1**. We cannot apply the bond additivity argument since the energy of the P=C bond is not known; however, any reasonable estimate will lead to **2** being more stable, due to the weak P–C bond (63 kcal mol^{-1}). One other factor favoring **2** is that in **1** two formally sp^2-hybridized carbon atoms must adapt to the small angle of the ring, while in **2** one of the carbons is replaced with P which needs less rehybridization to adapt to the ring geometry.

The barriers for reaction 1 and 2 are less than 30 kcal mol^{-1}, which is less than the calculated barrier for the opening of cyclobutene. The experimental observation of the ring opening of **1** should be realizable, but since the reaction is thermoneutral, substituent groups that can stabilize phosphabutadienes will be desirable to drive the equilibrium to product. Substituents attached to the ring, such as phenyl and mesityl groups, should prove suitable by conjugating with the butadiene product and causing steric crowding which will destabilize the ring. Phenyl groups are likely to lower the reaction barrier as well.[49]

The activation barrier for the opening of **4** is very close to the barrier for the opening of cyclobutene. The barrier for the opening of **2** is slightly larger, probably reflective of the endothermic nature of the reaction.

Since the transition states for the six reactions have no symmetry elements, the reaction will not be synchronous, though all six are concerted and proceed via a conrotatory path. For all the ring openings examined here, the double bonds between atoms 1 and 2 and between atoms 3 and 4 have formed to a similar extent, around 50%, while the breaking double bond between atoms 2 and 3 lags behind, having proceeded only about 30%. According to the distance-based extent criterion, the 1–4 bond has cleaved only 40%, though the density-based method suggests about 70% cleavage. For the most part, the density and distance criteria parallel each other. Problems arise in judging bonds that cleave to separate atoms using the density criteria, since the density between unbound atoms is arbitrarily set to zero. Using eq 7, the bond order for the 1–4 interaction in TSs **5**–**7** is between 0.1–0.3, suggesting that the distance method is fairly reflective of the nature of the TS.

Since two bonds have progressed just past 50% and the other two only 30–40%, the TSs can be considered early. The topological bond path network for the TSs indicates that the ring structure still persists, and, therefore, the TSs are reactant-like.

One last issue to address is the difference in the activation barrier for the inward and outward conrotatory pathways for the opening of **1** and **3**. For both systems, the path with the H attached to the heteroatom rotating outward has the lower activation barrier. This requires the lone pair electrons to rotate inward. Following on Houk and co-workers' MO arguments concerning the substituent effects on the preferred path for opening of cyclobutene,[10,12,16–18] the important frontier orbital interaction is the cleavage of the 1–4 σ bond by occupation of the σ^* orbital. Lowering the σ^* orbital will lower the TS energy. When the lone pair rotates inward, it can effectively overlap with the σ^* orbital; however, outward rotation moves the lone pair orbital away from the 1–4 σ^* orbital. Inward rotation lowers the σ^* orbital and lowers the energy of the TS; outward rotation allows for little stabilization of the σ^* orbital.

In the N case, where the lone pair has large p character and is directed away from the nucleus, outward rotation (reaction 5) of the lone pair leads to no effective stabilization of the σ^* orbital and the activation barrier is similar to the barrier for opening of cyclobutene. The P lone pair has significant s character and is close to the nucleus. Thus, outward rotation will still lead to some small interaction and stabilization of the σ^* orbital, though certainly less than inward rotation. Thus, both pathways for opening of **1** are lower than the opening of **3**.

Conclusions

The ring opening of dihydrophosphetes and dihydroazetes were examined at the HF/6-31G* and MP2/6-31G* levels. Inclusion of electron correlation is necessary to obtain reasonable activation energies, but full optimization at this correlated level does not significantly alter the geometry of any reactant, transition structure, or product from the HF geometry. The opening of the dihydrophosphetes is thermoneutral or slightly endothermic, supporting Mathey's[25,26] conjecture of the ring and open chain isomers existing in equilibrium. The ring opening of the dihydroazetes is exothermic, and isolation of these species will be difficult. The dihydrophosphetes are stabilized by the P substitution which can readily accommodate the small ring angle.

While these reactions are concerted, they are decidedly asynchronous. Distance or electron-density criteria for estimation of the extent of reaction at the TSs clearly indicate that the new π-bonds form before the other bonds break. The TSs can be characterized as early.

The calculated activation barriers for the allowed conrotatory ring openings are 25–30 kcal mol^{-1} for 1,2-dihydrophosphete (**1**), 41 kcal mol^{-1} for 2,3-dihydrophosphete

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[48] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley and Sons: New York, 1976.

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(**2**), 30–37 kcal mol^{-1} for 1,2-dihydroazete (**3**), and 37 kcal mol^{-1} for 3,4-dihydroazete (**4**). Two diastereomeric pathways are allowed for the opening of **1** and **3**. The favored pathway involves the heteroatom lone pair rotating inward. This rotation allows for stabilization of the C–P or C–N σ^* orbital through overlap with the lone pair and thereby stabilizes the TS. Experimental verification of these results awaits the synthesis of stable dihydrophosphetes with pendent groups that can stabilize the product phosphabutadiene.

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Registry No. **1**, 132515-09-4; **2**, 125033-70-7; **3**, 6788-71-2; **4**, 6788-85-8; **11**, 137465-59-9; **12**, 137465-60-2; **13**, 122682-85-3; **14**, 73311-40-7; **15**, 80861-03-6; **16**, 38239-27-9.

Supplementary Material Available: Optimized geometries in the form of *Z* matrices for all structures at the HF/6-31G* and MP2/6-31G* levels (10 pages). This material is contained in many 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.

Incipient Nucleophilic Attack as a Probe for the Electronic Structure of Diazonium Ions. An Analysis of Neighboring-Group Interactions in β-(Carboxyvinyl)diazonium Ions

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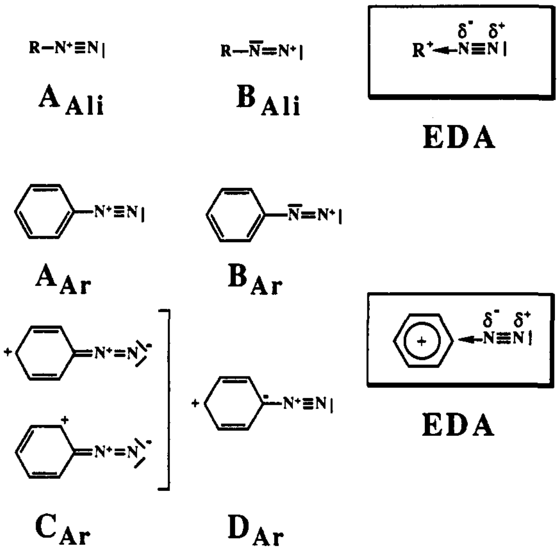
Crystal structures of diazonium ions with nucleophilic neighboring groups exhibit distortions that have commonly been interpreted by postulating an "incipient nucleophilic attack" of the proximate nucleophile on N_α. We have recently challenged the assumption that the charge distribution is correctly represented by the most important Lewis structure $R{-}N^+{\equiv}N$ and propose here an alternative explanation of these structural features thereby providing a crucial link between the theoretically derived bonding model and experimental data. The rotamers of 3-diazonium propenoic acid and their zwitterions are examined in this context. The role of the atomic first moments for a correct appreciation of the anisotropy of the electron density distribution within the atomic basins and for an adequate description of electrostatic interaction between neighboring groups is discussed. A method is described for the evaluation of neighboring group interactions based on integrated atomic charges, first moments and quadrupole moments. It is found that the electrostatic interactions of the neighboring groups in the cis isomers correlate with the nucleophilicity of the proximate nucleophile and that the differences in the neighboring group interactions of geometrical isomers correlate with the cis preference energies.

Introduction

Diazonium ions are important reactive intermediates, and several resonance forms have been employed to discuss a variety of their properties.[2] The most popular resonance from—and the one commonly found in textbooks—is the resonance form A (Chart I) in which N_α is *formally* assigned a positive charge. The resonance form B may be conveniently used to explain azo coupling and like reactions in which N_β acts as the electrophilic center. While the resonance forms A and B usually are considered to suffice for the description of aliphatic diazonium ions, several others are discussed additionally for aromatic diazonium ions. The various resonance forms that result from π-electron pair pushing from the phenyl ring to the N_2 group are collectively referred to as resonance forms C_{Ar} in the scheme. The resonance form D_{Ar} resembles A but takes into account a polarization of the π density of the ring and D_{Ar} has been regarded as a major contributor to the ground-state electronic structure.[3,4]

Chart I



These resonance forms either assign a formal positive charge to the N_2 group (A, B, D) or none (C), and, with the exception of B, they assign the formal positive charge to N_α. Considering the qualitative rules regarding the relative contributions of the resonance forms, the resonance form A (and D) is appropriate indeed for the description of the diazonium ions. We have recently shown however that the *formal* charges of these resonance forms

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[1] (a) Part of the projected dissertation of Christopher J. Horan. (b) Presented in part at the 25th ACS Midwest Regional Meeting, Manhattan, KS, Nov 8, 1990 and at the American Chemical Society National Meeting, Atlanta, GA, April 14, 1991.

[2] For reviews on diazonium ions, see: (a) Zollinger, H. *Acc. Chem. Res.* **1973**, *6*, 335. (b) Zollinger, H. *Azo and Diazo Chemistry*; Wiley Interscience, New York, 1961. (c) Patai, S., Ed. *The Chemistry of the Diazonium and Diazo Groups*; Wiley Interscience, New York, 1978. (d) Laali, K., Olah, G. A. *Rev. Chem. Intermed.* **1985**, *6*, 237.

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