squares method, using 25 reflections measured on the diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation with ω-scan mode for 2θ less than 55°. The structure was solved by direct method (MITHRIL method[19]). The non-hydrogen atoms were refined anisotropically and the hydrogens isotropically. The final cycle of full-matrix least-squares refinement was based on 2731 observed reflections [$I > 3.00\sigma(I)$]. The final R value was 0.051.

Acknowledgment. We are very grateful to Prof. Y. Tsuda and Mr. S. Hosoi of this Faculty for helpful discussions on the X-ray analysis of compound **8**.

Supplementary Material Available: ^{13}C NMR spectra for compounds **5d**, **6a**, **6b**, **6d**, **6f**, and **8**, the ^{1}H NMR spectrum of (−)-**5d**, and tables of bond angles and distances for **8** (12 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.

---

(19) Gilmore, C. J. *J. Appl. Cryst.* **1984**, *17*, 42.

Ab Initio Study of the Conrotatory Ring Opening of Phospha- and Azacyclobutenes. 2. Diphospha- and Diazacyclobutenes

Steven M. Bachrach* and Meixiao Liu

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received November 19, 1991

The thermally allowed conrotatory ring opening of 1,2-dihydro-1,3-diphosphate (**1**), *trans*- and *cis*-1,2-dihydro-1,2-diphosphete (**2** and **3**), 1,2-dihydro-1,3-diazete (**4**), and *trans*- and *cis*-1,2-dihydro-1,2-diazete (**5** and **6**) is examined using ab initio calculations. The rings, transition structures, and products were fully optimized at HF/6-31G* with single-point energy calculations performed at MP2. The opening of the dihydrodiphosphetes is endothermic while the opening of the dihydrodiazetes is exothermic. The calculated activation barrier for the opening of **3** and **6** is 19.78 and 24.58 kcal mol^{-1}, respectively. The ring opening of **1**, **2**, **4**, and **5** can occur via two diastereomeric pathways. Inward rotation of the heteroatom lone pair is favored for all four compounds. The lower barriers are: 28.78 kcal mol^{-1} for **1**, 18.00 kcal mol^{-1} for **2**, 27.82 kcal mol^{-1} for **4**, and 22.95 kcal mol^{-1} for **5**. The structural and energetic differences and trends among these compounds are interpreted in terms of ring strain and orbital interactions.

Electrocyclic ring openings of small rings, particularly four-membered rings, have been of significant interest for their synthetic utility and for the theoretical insight they provide about the nature of pericyclic reaction mechanisms.[1,2] The ring opening of heterosubstituted cyclobutenes allows synthetic access to heterosubstituted butadienes. The heteroatom also affords an additional test of the validity of the Woodward–Hoffman rules of electrocyclic reactions and the ability to explore substituent effects on reaction and activation energies.

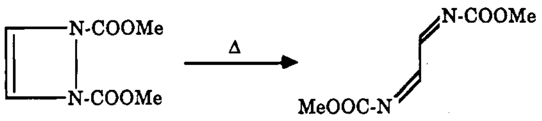
In our previous paper,[3] we examined the ring opening of monoaza- and monophosphacyclobutenes. The MP2/6-31G*//HF/6-31G* activation barriers and the reaction energies for the ring opening of 1,2-dihydrophosphete, 3,4-dihydrophosphete, 1,2-dihydroazete, and 3,4-dihydroazete are listed in Table I. For comparison, the ring opening of cyclobutene is 11.4 kcal mol^{-1} exothermic[4] with a barrier[5,6] of 32.9 kcal mol^{-1}. Substitution with phosphorus leads to an endothermic ring opening, since phosphorus can readily accommodate the bond angles of small rings, while the opening of the azetes is exothermic. The activation barrier for the azetes and 3,4-dihydrophosphete are comparable to cyclobutene, but the opening of 1,2-dihydrophosphete is much smaller. There is also a strong preference in both systems for inward rotation of the heteroatom lone pair, which was explained in terms of favorable interactions of the lone pair with the σ^* orbital of the breaking ring bond. These results suggest that the phosphetes may readily undergo ring opening reactions, particularly when substituted with groups that will stabilize the phosphabutadienes.

Table I. Reaction and Activation Energies (kcal mol^{-1}) at MP2/6-31G*//HF/6-31G* for the Ring Opening of Cyclobutene and the Dihydroazetes and Dihydrophosphetes[a]

reactant	product	E_a	ΔE
cyclobutene	$H_2C{=}CHCH{=}CH_2$	37.36	−4.96
1,2-dihydrophosphete	anti-$HP{=}CHCH{=}CH_2$	24.59	0.94
	syn-$HP{=}CHCH{=}CH_2$	29.56	0.99
3,4-dihydrophosphete	$H_2C{=}PCH{=}CH_2$	40.76	8.41
1,2-dihydroazete	anti-$HN{=}CHCH{=}CH_2$	29.76	−18.00
	syn-$HN{=}CHCH{=}CH_2$	37.51	−17.36
3,4-dihydroazete	$H_2C{=}NCH{=}CH_2$	37.08	−1.03

[a] See ref 3.

Scheme I



We turn our attention here to the dihydrodiazetes and dihydrodiphosphetes. There have been only three reports[7–9] of the preparation of substituted 1,2-dihydro-

---

(1) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley and Sons: New York, 1985; pp 1002–1013.

(2) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; pp 936–939.

(3) Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 209–215.

(4) Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395–3397.

(5) Carr, R. W., Jr.; Walter, W. D. *J. Phys. Chem.* **1965**, *69*, 1073–1075.

(6) Cooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220–4224.

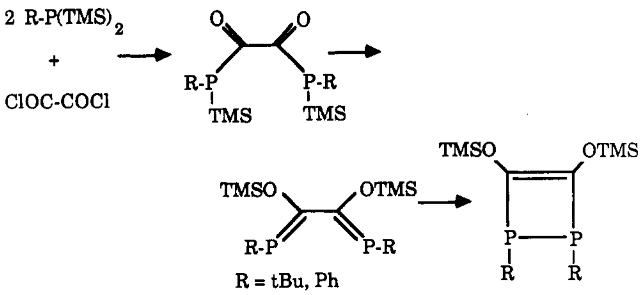
(7) Effenberger, F.; Maier, R. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 416–417.

(8) Nunn, E. E.; Warrener, R. N. *J. Chem. Soc., Chem. Commun.* **1972**, 818–819.

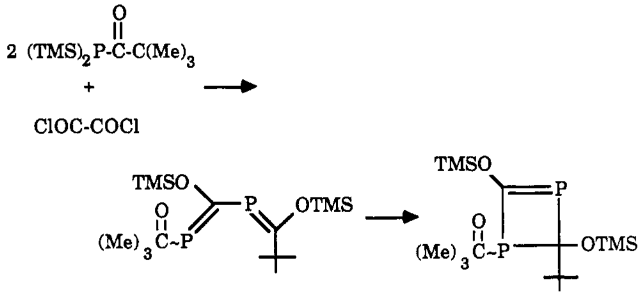
(9) Cheng, C.-C.; Greene, F. D.; Blount, J. F. *J. Org. Chem.* **1984**, *49*, 2917–2922.

0022-3263/92/1957-2040$03.00/0

Scheme II



Scheme III



1,2-diazetes, and all of these compounds are very reactive, resulting in very little structural characterization. Of particular interest here is the work of Nunn and Warrener[8] who reported the ring opening of a dicarboxylate diazete, shown in Scheme I. The vinyl hydrogens of the diazete appear in the normal vinylic region in the ^{1}H NMR, suggesting no aromatic character, even though the system formally has 6 π-electrons. In their extensive review article of four-membered rings containing two nitrogen atoms, Richter and Ulrich[10] report no known 1,2-dihydro-1,3-diazetes as of 1983 and we could find no mention of any in the literature since then.

In contrast to the aza systems, a wide variety of substituted 1,2-dihydro-1,2-diphosphetes are known and fully characterized by X-ray crystallography. Early syntheses of these rings were performed by the pyrolysis of polyphosphines in the presence of alkynes.[11,12] Mathey's group has developed three alternative schemes toward synthesizing substituted 1,2-diphosphetes involving ring contraction of phospholenes,[13] ring expansion of phosphirenes,[14] and selective substituent replacement.[15] Appel has prepared a substituted 1,2-dihydro-1,2-diphosphete via a procedure that suggests a [2 + 2] ring closure of a 1,4-diphospha-1,3-butadiene (Scheme II).[16] This cyclization can be excluded when very bulky substituents are placed on P.[17] While the 1,2-dihydro-1,2-diphosphete formally is a 6 π-electron system, the X-ray structures[13,15,18] of a number of these compounds clearly discount any aromatic character. The P atoms are highly pyramidal, the rings are slightly nonplanar, and the C═C and P—C bond lengths are typical of normal alkenes and phosphaalkanes.

Table II. Total Energies (au) of 1–26

compd	HF/6-31G*	MP2/6-31G*//HF/6-31G*
1	−759.447267	−759.914397
2	−759.451831	−759.907353
3	−759.448464	−759.903250
4	−186.891232	−187.464563
5	−186.837944	−187.416519
6	−186.828589	−187.407632
7	−759.374796	−759.859417
8	−759.385150	−759.868531
9	−759.386050	−759.863999
10	−759.403805	−759.878665
11	−759.395841	−759.871734
12	−186.814087	−187.401496
13	−186.839015	−187.420234
14	−186.764459	−187.365455
15	−186.777129	−187.379941
16	−186.768804	−187.368466
17	−759.425456	−759.894136
18	−759.424981	−759.893410
19	−759.426192	−759.893287
20	−759.426219	−759.893468
21	−759.426395	−759.893586
22	−186.912766	−187.479123
23	−186.914745	−187.480316
24	−186.910354	−187.476891
25	−186.907108	−187.472618
26	−186.915037	−187.481312

Table III. Reaction and Activation Energies (kcal mol^{-1}) at MP2/6-31G*//HF/6-31G*

	E_a		ΔE	
reaction	HF	MP2	HF	MP2
1	45.48	34.50	13.69	12.71
2	38.98	28.78	13.98	13.17
3	41.28	27.21	16.09	8.83
4	30.14	18.00	16.07	8.71
5	33.02	19.78	13.85	6.06
6	48.41	39.58	−13.51	−9.14
7	32.77	27.82	−14.75	−9.89
8	46.11	32.04	−45.44	−37.88
9	38.16	22.95	−43.40	−35.20
10	37.52	24.58	−54.25	−46.23

Only one example of a substituted 1,2-dihydro-1,3-diphosphete is known. The synthesis of this compound is shown in Scheme III, and the mechanism is speculated to involve the electrocyclic ring closure of a 1,3-diphospha-1,3-butadiene.[19] This derivative was isolated, and an X-ray crystal structure was obtained.

In this paper, using ab initio molecular orbital calculations, we investigate the conrotatory ring openings of 1,2-dihydro-1,3-diphosphete (**1**), *trans*- and *cis*-1,2-dihydro-1,2-diphosphete (**2** and **3**), and their nitrogen analogues 1,2-dihydro-1,3-diazete **4** and *trans*- and *cis*-1,2-dihydro-1,2-diazete (**5** and **6**). These reactions are shown in Scheme IV. The structures and stabilities of these strained four-membered rings are examined and are used to explain the vast differences in the known chemistry between the diazetes and diphosphetes. The reaction energies, the activation barriers, and the nature of the transition state for the electrocyclic ring openings are determined. The ring opening of **1**, **2**, **4**, and **6** can occur along two diastereomeric pathways, and we will discuss the energetic preference for one of these pathways.

---

(10) Richter, R.; Ulrich, H. In *Small Ring Heterocycles—Part 2*; Hassner, A., Ed.; John Wiley and Sons: New York, 198; Vol. 42; pp 443–546.

(11) Mahler, W. *J. Am. Chem. Soc.* **1964**, *86*, 2306–2307.

(12) Ecker, A.; Schmidt, U. *Chem. Ber.* **1973**, *106*, 1453–1458.

(13) Charrier, C.; Guilhem, J.; Mathey, F. *J. Org. Chem.* **1981**, *46*, 3–8.

(14) Ricard, L.; Maigrot, N.; Charrier, C.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 548–549.

(15) Charrier, C.; Maigrot, N.; Mathey, F.; Robert, F.; Jeannin, Y. *Organometallics* **1986**, *5*, 623–630.

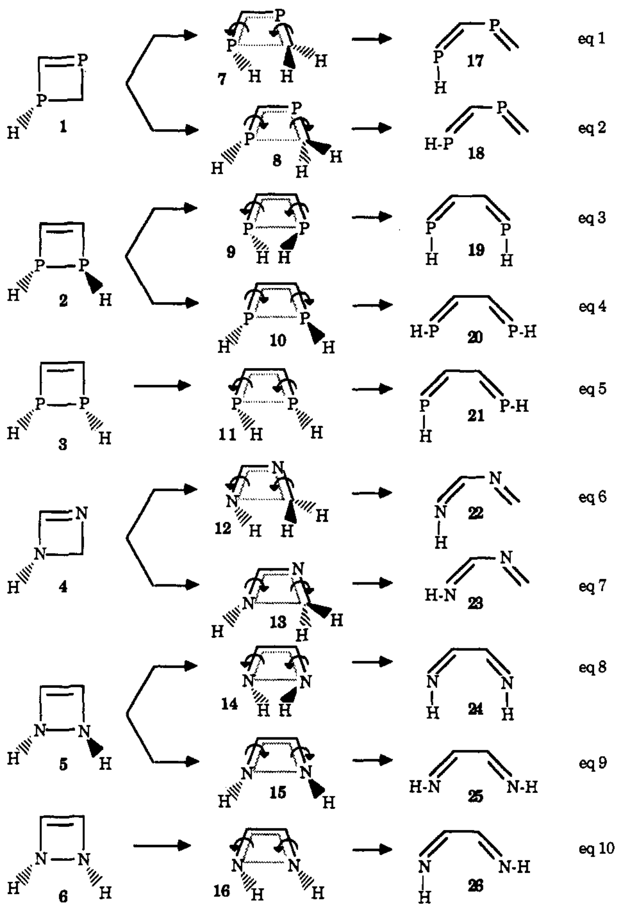
(16) Appel, R.; Barth, V. *Tetrahedron Lett.* **1980**, *21*, 1923–1924.

(17) Appel, R.; Hunerbein, J.; Siabalis, N. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 779–780.

(18) Binger, P.; Wettling, T.; Schneider, R.; Zurmuhlen, F.; Bergstasser, U.; Hoffmann, J.; Maas, G.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 207–210.

(19) Appel, R.; Barth, V.; Knoch, F. *Chem. Ber.* **1983**, *116*, 938–950.

Scheme IV



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.[20] Single point calculations were carried out using second-order Moller–Plesset perturbation theory (MP2) to account for some of the electron correlation. Local minima and transition structures were confirmed using analytical frequencies calculated at HF/6-31G*. The geometries are shown in Figures 1–3 with absolute energies given in Table II and relative energies in Table III.

We have previously shown that the HF/6-31G* method is suitable for obtaining accurate geometries and consistent electron density distributions for a variety of organophosphorus compounds, including strained rings and phosphabutadienes.[21-24] In order to obtain reasonable reaction and activation energies, single-point calculations at the MP2 level are necessary. Spellmeyer and Houk[25] examined the basis set and computational level dependence of the geometry and energies of the ring opening of cyclobutene. They demonstrated that the TS geometry and activation energy are little affected beyond the MP2/6-31G*//HF/6-31G* level. Similar results were reported for the ring opening of oxetene.[26] In our study of monoazetes and monophosphetes, we also found that geometry optimization at the MP2 level did not result in any significant geometric or energetic difference from the MP2/6-31G*//HF/6-31G* calculations.[3]

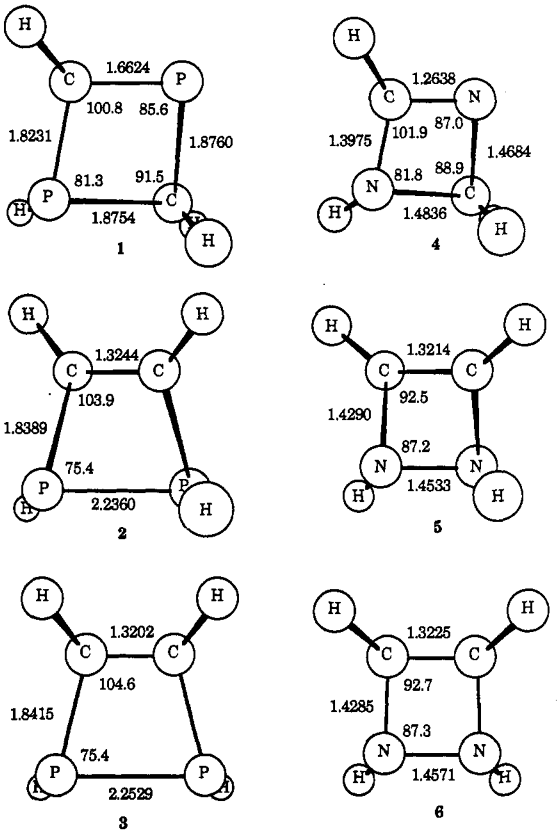


Figure 1. Optimized geometries of 1–6 at HF/6-31G*. All distances are in Å and all angles are in deg.

Topological electron density analysis[27] was performed using a locally modified version of PROAIM[28] and the HF wavefunctions. Of particular use for this study is the correlation between the value of the electron density at the bond critical point $\rho(\mathbf{r}_c)$ and bond order $n(\text{X–Y})$.[29] This empirical relationship is given by eq 11, with the appropriate constants for C–C and C–P bonds. This parameter will be used to judge the extent of reaction completed at the transition state.

$$n(\text{X–Y}) = \exp[A(\rho(\mathbf{r}_c) - B)] \tag{11}$$

X–Y	*A*	*B*
C–P[30]	19.628	0.153
C–C[31]	6.458	0.252

Results

Geometries. The geometries of all reactants are shown in Figure 1, the transition structures are presented in Figure 2, and the products are drawn in Figure 3. In our study of the rotational surfaces of phospha- and aza-1,3-butadienes, we discussed the structures of the products **17–26** and need not repeat any details here.[23] It is important to note that, in general, the s-trans conformers are lower in energy than the s-cis-like conformers reported here. However, these conformers are the direct product of the ring-opening reaction; subsequent rotation about the σ-bond will produce the lower energy conformer.

---

(20) GAUSSIAN-90: Frisch, M.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1990.

(21) Bachrach, S. M. *J. Comput. Chem.* **1989**, *10*, 392–406.

(22) Bachrach, S. M. *J. Phys. Chem.* **1989**, *93*, 7780–7784.

(23) Bachrach, S. M.; Liu, M. *J. Am. Chem. Soc.* **1991**, *113*, 7929–7937.

(24) Bachrach, S. M. *J. Org. Chem.* **1991**, *56*, 2205–2209.

(25) Spellmeyer, D. C.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 3412–3416.

(26) Yu, H.; Chan, W.-T.; Goddard, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 7529–7537.

(27) Bader, R. F. W. *Atoms in Molecules—A Quantum Theory*; Oxford University Press: Oxford, 1990.

(28) Biegler-Konig, F. W.; Bader, R. F. W.; Tang, T. H. *J. Comput. Chem.* **1982**, *3*, 317–328.

(29) Bader, R. F. W.; Tang, T. H.; Tal, Y.; Biegler-Konig, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 946–952.

(30) Bachrach, S. M. *THEOCHEM*, in press.

(31) Slee, T. S. In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; p 69.

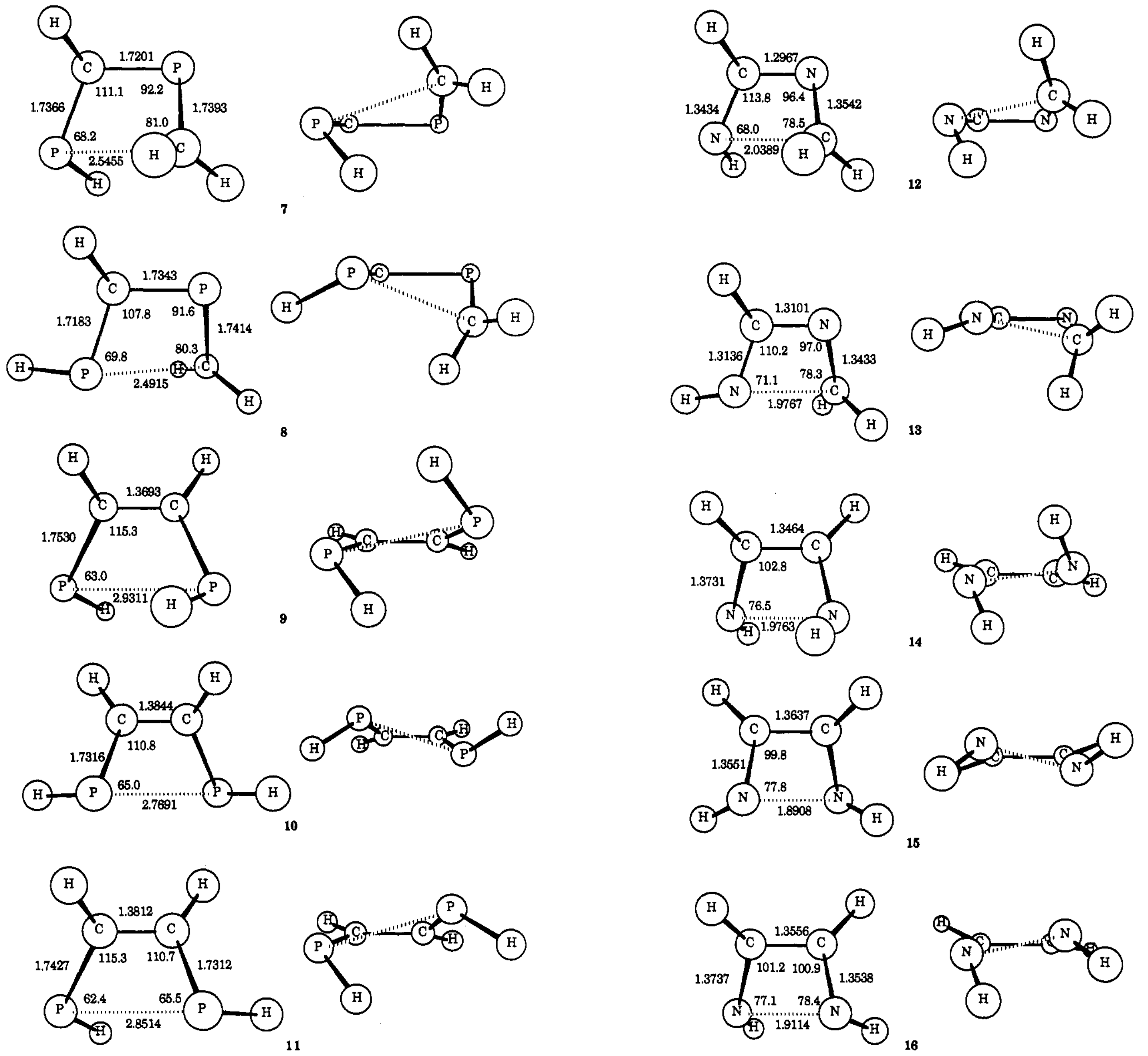
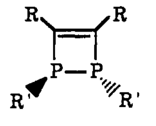


Figure 2. Optimized geometries of the transition structures 7–16. See Figure 1.

While 1 is an unknown compound, a substituted 1,2-dihydro-1,3-diphosphete has been prepared (see Scheme III) and its X-ray structure determined.[19] The P3=C4, P1—C2, C2—P3, and P1—C4 distances are 1.679, 1.890, 1.912, and 1.792 Å, respectively. Comparison to the calculated structure of 1 is hazardous due to the differences in substituents and phases. Nevertheless, the calculated distances are reasonably close, and the ring angles all agree with 3.5°. The ring is puckered; the P1—C1—P2—C2 dihedral angle is 6.9° in 1 and 7.2° in the crystal structure. The P3=C4 distance is typical for phosphaalkenes while the P1—C2 and C2—P3 distances are slightly longer than typical C—P bond lengths.

A number of substituted derivatives of 1,2-dihydro-1,2-diphosphete are known.[11-16,18,32,33] The X-ray crystal structures of three derivatives[13,15,18] have been solved and are summarized in Table IV. All three of these compounds have the P substituents arranged trans, and other derivatives have been assumed to possess the same stereochemistry. Thus, there are no known derivatives of 3, only of 2. The agreement between the geometric parameters of 2 and the experimental values listed in Table IV is excellent. The calculated structure is somewhat less puckered than the derivatives; its corresponding dihedral angle is only 11.0°. Larger substituents at C will tend to cause a larger puckering, which is consistent with the results. The geometries of 2 and 3 are very similar, except

Table IV. X-ray Crystal Structure Data for Derivatives of 2[a]



2a: R=R'=Ph
2b: R=t-Bu, R'=Ph
2c: R=t-Bu, R'=I

compd	P—P	P—C	C=C	P—C—C	C—P—P	dihedral[b]
2a[c]	2.248	1.830	1.358	102.1	74.7	23.6
2b[d]	2.214	1.847	1.357	102.8	76.2	13.1
2c[e]	2.192	1.827	1.334	102.1	75.5	20.3

[a] All distances are in Å and all angles are in deg. [b] Dihedral angle defined as P—C—C—P. [c] See ref 13. [d] See ref 15. [e] See ref 18.

---

(32) Charrier, C.; Mathey, F.; Robert, F.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 1707–1708.

(33) Maigrot, N.; Charrier, C.; Ricard, L.; Mathey, F. *Polyhedron* **1990**, 9, 1363–1367.

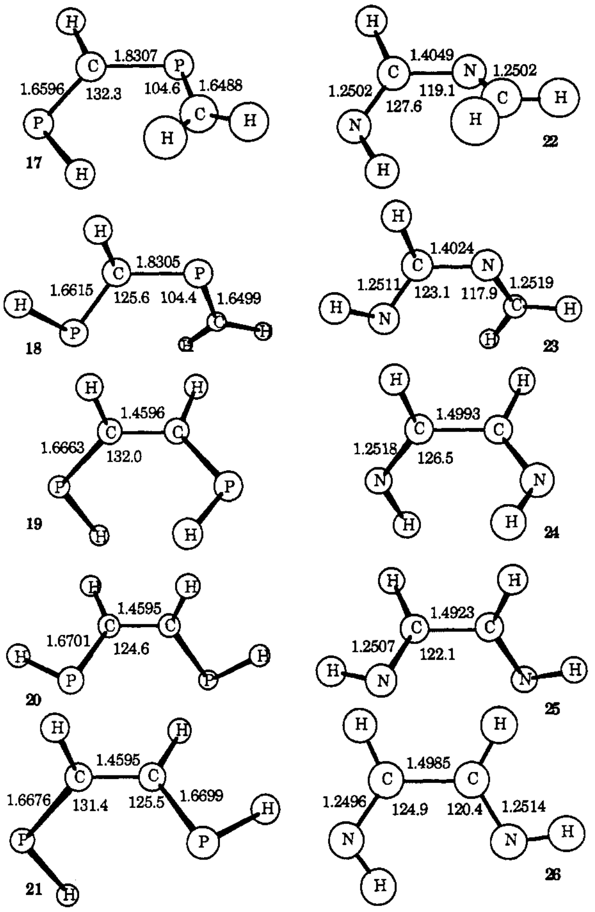


Figure 3. Optimized geometries of **17–26**. See Figure 1.

for the longer P–P bond in the latter. The trans structure minimizes the P lone-pair–lone-pair repulsions, which leads to a shorter P–P bond. Also, due to **3** having C_s symmetry, the ring is not puckered.

There are no literature reports concerning 1,2-dihydro-1,3-diazetes. The structure of **4** is shown in Figure 1. The molecule is slightly puckered, and its most notable feature is the short N1–C4 distance (1.3975 Å). Otherwise, the bond distances and angles are very similar to the comparable bonds and angles in the dihydromonoazetes.[3]

Table V. Extent of Reaction at the Transition State

compd	$r(1\text{-}2)$	$r(2\text{-}3)$	$r(3\text{-}4)$	$r(1\text{-}4)$
	Based on Distances			
7	52.91	34.28	60.17	39.47
8	64.85	42.77	59.53	39.99
9	49.77	33.21	49.77	45.32
10	63.57	44.41	63.57	42.66
11	56.81	43.79	64.28	43.76
12	36.73	23.32	52.34	37.77
13	57.31	33.41	57.78	38.62
14	31.55	14.05	31.55	33.01
15	41.45	24.75	41.45	30.55
16	30.63	18.81	42.18	32.68
	Based on $\rho(\mathbf{r}_c)$			
7	63.12	36.58	52.67	72.92
8	73.75	46.82	47.83	69.35
9	56.23	33.46	56.23	76.48
10	70.86	46.25	70.86	68.43
11	64.79	44.06	69.82	72.63
12	44.30	25.51	61.22	71.50
13	57.47	37.00	72.35	71.58
14	28.13	11.78	28.13	70.39
15	33.87	27.57	33.87	66.00
16	37.62	19.72	22.35	67.52

The three literature reports of substituted 1,2-dihydro-1,2-diazetes all find a highly unstable compound. The only structural characterization is the ^{1}H NMR spectrum for the diazete shown in Scheme I. The vinylic hydrogen appears at δ 6.57 ppm which indicates no diamagnetic ring current. A number of theoretical investigations of **5** and **6** have been published. Jean and Devaquet[34] explored a geometrically restricted disrotatory opening of **6** at HF/STO-3G+P. Schleyer and co-workers[35] optimized both **5** and **6** at HF/3-21G and found the N atoms to be highly pyramidal. Isodesmic reactions comparing the ring strain energy of the diazetes relative to cyclobutene indicated that the former are about 10 kcal mol^{-1} more strained. Mo and Yanez[36] optimized the structures of **5** and **6** at HF/6-31G*. The structures shown in Figure 1 are virtually identical to their results. They estimated the aromaticity of the diazetes using a homodesmic reaction and found a negative result. All of these theoretical efforts confirm the NMR result that these compounds are not aromatic.

The transition structures for the conrotatory ring opening of **1–6** are drawn in Figure 2. The opening of **1** can proceed through two diastereomeric pathways: TS **7** leads to (*Z*)-1,3-diphosphabutadiene **17** while TS **8** leads to (*E*)-1,3-diphosphabutadiene **18**. The opening of **2** can occur through either TS **9** or **10**, producing diastereomeric products. The electrocyclic opening of **3** progresses through TS **11**. In an analogous manner, there are two paths for opening of **4** and **5** and one path for the opening of **6**. The TSs were confirmed by analytical frequency analysis; all possess one and only one imaginary frequency.

Relative to their respective reactants, all of the TSs show similar geometric trends. The 1–2 and 3–4 bonds contract while the 2–3 and 3–4 bonds lengthen. Bond angles about atoms 2 and 3 widen. The conrotatory motion is clearly apparent in the side views shown in Figure 2.

The relative position of the TS along the reaction path can be estimated using eq 12, where x is either a bond length or the value of the electron density at the bond critical point, $\rho(\mathbf{r}_c)$. The ratio obtained indicates how

$$\text{progress ratio} = \frac{x_{\text{reactant}} - x_{\text{TS}}}{x_{\text{reactant}} - x_{\text{product}}} 100 \qquad (12)$$

much progress has occurred in converting the variable of interest from reactant to product. Values of the "progress ratio" obtained using eq 12 are given in Table V. Since bond length and $\rho(\mathbf{r}_c)$ are linearly correlated, the values obtained using the two methods are similar. For bonds with orders less than 1 an exponential relation of bond order and $\rho(\mathbf{r}_c)$ exists, and therefore the extent of reaction based on $\rho(\mathbf{r}_c)$ will be much larger than that based on the bond distance, such as for $r(1\text{-}4)$. It is readily apparent that these reactions, while concerted, are not synchronous. Bonds are not broken and created to the same extent in the TS.

The diastereomeric TSs **7** and **8** differ in the direction of the rotation of the lone pair at P1; in **7** the lone pair rotates outward, while the lone pair rotates inward in **8**. Even though the P1–C4 distance in **7** is longer than in **8**, the overall extent of the reaction is further along in the latter. The progress ratio for the P1–C2 and C2–P3 bonds are much greater in **8** (bond orders, estimated using eq 11, of 1.61 and 1.43, respectively) than in **7** (bond orders of

---

[34] Jean, Y.; Devaquet, A. *J. Am. Chem. Soc.* **1977**, *99*, 1949–1952.

[35] Budzelaar, P. H. M.; Cremer, D.; Wallasch, M.; Wurthwein, E.-U.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 6290–6299.

[36] Mo, O.; Yanez, M. *THEOCHEM* **1989**, *201*, 17–37.

1.52 and 1.55), while the P3–C4 and P1–C4 bonds have progressed to similar extents. The analogous nitrogen systems, TS **12** and **13**, have a similar relationship. The path following outward rotation of the N lone pair arrives at an earlier TS (**12**) than the inward path (**13**).

Two conrotatory paths for ring opening of **2** are possible. When both P lone pairs rotate outward, the TS is **9** leading to product **19**. Inward rotation of the lone pairs proceeds through TS **10** on the way to **20**. On the basis of the progress ratios, TS **10** is later than **9**. Significantly greater bond making and breaking has occurred in **10** than in **9**. The bond orders for the P–C and C–C bonds in **10** are 1.57 and 1.61, respectively, and in **9** the corresponding bond orders are 1.46 and 1.70. The opening of **3** leads to **21**, which has one cis and trans C=P bond. Since the ring opening of **2** leads to the bis-cis or bis-trans product, it might be expected that the general structure of TS **11** be intermediate those of **9** and **10**. The P–C and P–P bond lengths increase in the order **10** < **11** < **9**, while the C–C distance increases in the order **9** > **11** > **10**. Thus, the extent of reaction at **11** is intermediate to **9** and **10**. The P1–C2, C–C, and C3–P4 bond orders in **11** are 1.52, 1.63, and 1.56, respectively.

The conrotatory ring openings of **4** and **5** were examined by Schleyer and co-workers.[35] They optimized the geometries of the reactants and TSs at HF/3-21G and calculated relative energies at MP2/6-31G* using the 3-21G geometries. In comparison to the HF/3-21G geometries, optimization at HF/6-31G* shortens the C–C, N–N, and N–N distances in the TSs **14**–**16** by about 0.03 Å. Exactly as in the P case, the TS for the conrotatory path with the lone pairs rotating inward (**15**) is later than the TS for the outward path (**14**), based on the progress ratios. The bond order for the C–C bond in the TSs is 1.93 (**14**), 1.78 (**15**), and 1.85 (**16**). The structural relationships among the N TSs are very similar to the P case.

Energies. The total energies of **1**–**26** are listed in Table II. The activation and reaction energies of eqs 1–10 are listed in Table III. Inclusion of electron correlation through MP2 reduces the E_a for all reactions by 5–15 kcal mol^{-1}, consistent with our previous study. Correlation also effects the reaction energy: the ring openings of **1**–**3** are less endothermic and **4**–**6** are less exothermic with inclusion of electron correlation. Hereafter, we will refer to the MP2 energies exclusively.

The ring opening of the dihydrodiphosphetes are endothermic. In contrast, the opening of the dihydrodiazetes are exothermic, strongly exothermic for the ring opening of **5** and **6**. We also observed that the ring opening of the monophosphetes were nearly thermoneutral, while the opening of the monoazetes were exothermic. For comparison, the energy for ring opening of cyclobutene is −7.8 kcal mol^{-1} at MP2/6-31G*//HF/6-31G*. Thus, P substitution stabilizes the four-membered ring. On the other hand, the diazetes are quite unstable toward ring opening.

The ring opening of **1**, **2**, **4**, and **5** can occur via two diastereomeric pathways—the lone pair(s) rotating inward or outward. The difference in the reaction energy of the two diastereomeric openings is small, ranging from 0.12 kcal mol^{-1} (reactions 3 and 4) to 2.68 kcal mol^{-1} (reactions 8 and 9). However, for all four of these molecules, the inward path has a lower activation barrier. The energetic preference for inward rotation for the ring opening is 5.72 kcal mol^{-1} for **1**, 9.21 kcal mol^{-1} for **2**, 11.76 kcal mol^{-1} for **4**, and 9.09 kcal mol^{-1} for **5**.

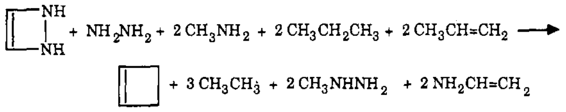
The ring opening of cyclobutene is 37.6 kcal mol^{-1} at MP2/6-31G*.[25] The ring openings of **1**–**6** are all less than this, except for the outward pathway of **4** (reaction 6) which has a barrier of 39.58 kcal mol^{-1}. The barriers for the ring openings of the P compounds are about 5 kcal mol^{-1} lower in energy than their N analogues, except that eq 7 has a slightly lower barrier than eq 2.

Discussion

The ring openings of cyclobutene and the monoazetes (see Table I) are exothermic, driven by the release of ring strain energy. In contrast, the ring openings of the monophosphetes are endothermic. This result, along with our studies of phosphiranes and phosphirenes,[22,24] supports the notion that replacement of C with P in a small ring is stabilizing. The long C–P bonds move these bonding electrons away from the other bonding electrons, and the ability of P to accommodate small bond angles dramatically reduces the ring strain. One might therefore imagine that the diphosphete would be particularly stable. On the other hand, the diazetes should be quite unstable, since substitution of C with N does not reduce the strain and multiple N atoms introduces lone-pair–lone-pair repulsions which would add to the strain.

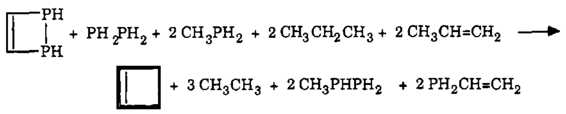
Examination of Table III confirms these ideas. The ring-opening reactions of **1**–**3** are endothermic, ranging from 6.06 kcal mol^{-1} for eq 5 to 13.17 kcal mol^{-1} for eq 2. Both P atoms stabilize the four-membered ring. The ring opening reactions of **4**–**6** are exothermic, much more exothermic than the monoazetes. Schleyer et al.[35] pointed out two reasons for the large exothermicity for the opening of **5** and **6**. First, the ring opening results in the breaking of the weak N—N bond coupled with forming two strong C=N bonds. Second, they demonstrated that these ring systems were nearly as strained as cyclobutene.

Compounds **5** and **6** are formally 6 π-electron systems, if the N lone pair electrons delocalize into the π-system. The highly pyramidal N atoms and the lack of diamagnetic resonance discount this delocalization. Using eq 13, a homodesmic reaction slightly modified from the one employed by Schleyer, we can demonstrate that **5** is as strained as cyclobutene, and no aromatic stabilization is present. The energy for eq 13 is −0.27 kcal mol^{-1} at MP2/6-31G*//HF/6-31G*.



eqn 13

Similarly, compounds **2** and **3** might be aromatic. The energy of eq 14, which compares **2** with cyclobutene, is 17.08 kcal mol^{-1}. This can be interpreted as (1) **2** is less strained than cyclobutene and/or (2) **2** is aromatically stabilized relative to cyclobutene. The latter is unlikely since each P atom is highly pyramidal and the P–C bond order, using eq 11, is only 1.06. Therefore, the simplest explanation is that the P substitution stabilizes the strained ring.



eqn 14

As expected, **2** is more stable than **3** (by 2.57 kcal mol^{-1}) and **5** is more stable than **6** (by 5.58 kcal mol^{-1}). These differences in energy between the cis and trans forms reflect the lone pair repulsions on the adjacent heteroatoms. The greater difference in the N system can be attributed to two factors: (1) the N–N bond distance is considerably shorter than the P–P distance, so the lone pairs are closer in the N case, and (2) the N lone pair has greater p-character than the P lone pair and is, therefore, more diffuse.

The energy difference between **4** and **5** is 30.15 kcal mol^{-1}, and this is reflected in the larger exothermicity of the ring opening of **5**. If one uses standard bond energies, the difference in energy of these two isomers is 35 kcal mol^{-1}. This reflects the weak N—N bond strength and the stronger C=N than the C=C bond. The difference in energy between **1** and **2** is much smaller, only 4.42 kcal mol^{-1}. Since accurate evaluation of the P=C bond strength is not available, we cannot estimate the energy differences, but since the C—P bond is weaker than the C—N bond and the P—P bond is stronger than the N—N bond, the relative energy differences of the N and P systems are sensible.

The activation barriers for ring opening of **1**–**6** are all smaller than for the ring opening of cyclobutene. The low activation energies and the exothermic reaction energies for the ring opening of the dihydrodiazetes clearly indicate that isolation of this ring systems will be very difficult. Isolation of a 1,2-dihydro-1,3-diazete may be possible since the barrier is about 28 kcal mol^{-1} and the opening is much less exothermic than for the 1,4-diazete. On the other hand, the dihydrodiphosphetes are calculated to be stable with respect to their open-chain isomers, and their isolation has been accomplished.

Mathey's group has speculated that the 1,2-dihydro-1,2-diphosphete may exist in equilibrium with its open chain isomer, 1,3-diphospha-1,3-butadiene.[33] While they could not accomplish a Diels-Alder reaction with the tetraphenyl derivative, denying the existence of the open-chain species, the bistungsten-1,2-dihydro-1,2-diphosphete complex did undergo Diels–Alder chemistry, with stereochemistry completely in agreement with the Woodward–Hoffman rules. The X-ray structure of this complex did possess a significantly stretched P—P bond.

Our calculations indicate that the ring is unlikely to exist in equilibrium with its open-chain isomer. Shifting this equilibrium will require significant electronic changes forced by the proper substituents. The bistungsten complex favors the open chain isomer by stabilizing the P—C bonds in the open chain and sterically crowding the ring, which forces a weakening of the P—P bond. The fact that the Diels–Alder reaction proceeds is accordance with the Woodward–Hoffman rules supports our allowed conrotatory ring-opening pathways.

Just as for the ring opening of the monoazacyclobutenes and -phosphacyclobutenes, the TSs examined here are all asynchronous, but the reaction is concerted. The formation of the new double bonds proceeds before the breakage of the 2–3 and 1–4 bonds. The extent of reaction is further along in the P systems than in the N systems, in accordance with the Hammond postulate—the more exothermic reactions will have earlier TSs. For all reactions, the TSs can be roughly characterized as "early". There is excellent correlation between the "progress ratio" based on distance and density, except for the 1–4 bond. For bond orders less than 1, an exponential relationship between distance and density exits, rather than the assumed linear relationship, which is quite acceptable for bond orders larger than unity.

For the ring openings of **1**, **2**, **4**, and **5**, two allowed diastereomeric conrotatory paths are possible. The two possible products for the opening of **1**, **2**, and **4** are nearly isoenergetic, while for the opening of **5**, product **24** is 2.68 kcal mol^{-1} more stable than **25**. Even though the diastereomeric reactions are nearly degenerate, their activation energies are quite different.

The structural difference between the reaction paths described by eq 1 and 2 is that the P lone pair rotates outward in eq 1 and inward in eq 2. The ring-opening reactions of the monoaza- and monophosphacyclobutenes clearly showed a preference for the lone pair rotating inward.[3] Following Houk's[37,38] explanation of the substitution effect on the ring opening of cyclobutene, we explained this preference in terms of the lone pair donation into the σ^* orbital of the breaking 1–4 bond. This donation stabilizes the σ^* orbital and reduces the energy of the TS, relative to outward rotation of the lone pair, which limits its interaction with the σ^* orbital. In accordance with this explanation, the TS for eq 2, **7** (having the P lone pair rotated inward), is 5.72 kcal mol^{-1} lower in energy than TS **8**.

The more favorable path for ring opening of **2** proceeds with both P lone pairs rotating inward, eq 4. The TS for this path **10** is 9.21 kcal mol^{-1} more stable than TS **9**, which has the lone pairs rotating outward. Both lone pairs donate into the σ^* orbital of the breaking P–P bond, substantially reducing the activation energy (only 18.0 kcal mol^{-1}) for the ring opening. The activation energy for eq 5, which has one P lone pair rotating inward, is slightly larger than for eqn 4. This is due to less stabilization of the P–P σ^* orbital along with a less stable reactant, due to the syn-lone pairs.

Exactly analogous results are found for the dihydrodiazetes. The pathway having the N lone pair(s) rotating inward has a lower activation energy than the outward pathway. Thus, the activation energy for eq 7 is 11.76 kcal mol^{-1} lower than for eq 6, and the barrier for eq 9 is 9.09 kcal mol^{-1} lower than for eq 8. The latter results are very close to the energies obtained by Schleyer.[35]

We found that the ring openings of the monodihydrophosphetes generally had lower activation energies than their corresponding monodihydroazetes. The same trend is true for the diheterosubstituted cyclobutenes. This was rationalized by considering the hybridization of the N and P lone pairs. The P lone pair has more s character than the N lone pair. The N lone pair will be more strongly directed away form the ring and will not be able to interact with the σ^* as effectively as the P lone pair which is located closer to the atom.

The activation energy for eqs 6 and 7 are similar to those for the opening of 1,2-dihydroazete, while the activation energy of eqs 1 and 2 are slightly larger than those for 1,2-dihydrophosphete. The second heteroatom substitution into the 3 position is not strongly affecting the systems. However, the second heteroatom substitution into the 2 position gives rise to rings having much lower activation barriers towards ring opening. This is attributable to the significant weaker N–N and P–P bonds than the C–C bond, making the substituted systems easier to open.

Conclusions

The ring-opening reactions of **1**–**6** proceed via a conrotatory concerted mechanism with relatively small activation energy, in complete agreement with orbital symmetry concepts. Aza and phospha substitution does not preclude the applicability of the orbital symmetry rules developed for hydrocarbons. The preference for one of the diastereomeric conrotatory pathways for the opening of **1**, **2**, **4**, and **5** is understood using MO concepts. The pathway

---

(37) Kirmse, W.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. soc.* **1984**, *106*, 7989–7991.

(38) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099–2111.

involving inward rotation of the heteroatom lone pair results in a stabilization of the σ^* orbital and a lower TS than for outward rotation.

The TSs for the electrocyclic reactions of **1**–**6** are asynchronous and early. The breaking of the double bond lags behind the formation of the new double bonds.

The N compounds **4**–**6** are all unstable with respect to their open-chain isomers. Since the barrier to ring opening is not large, isolation of these species will be difficult. On the other hand, the P analogues **1**–**3** are stable with respect to their open-chain isomers, and many examples of derivatives of **1** and **2** are known. The possibility of the dihydrodiphosphetes acting as masked diphosphabutadienes is discounted since the rings are much lower in energy than the open chains. However, bulky substituents that can sterically disfavor the ring and stabilize $P{=}C$ bonds may alter the equilibrium in favor of the open chains.

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and to the National Science Foundation for equipment grant DIR-8907135.

Supplementary Material Available: Optimized geometries in the form of Z matrices for all structures at the HF/6-31G* level (4 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.

Solid-State and Solution Conformational Analysis of Tartrate-Derived 1,3-Dioxolanes and 1,3,2-Dioxaborolanes

William R. Roush,* Andrew M. Ratz,[1] and Jill A. Jablonowski

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Received November 5, 1991

Solid-state (X-ray) and solution conformational analyses of tartrate ester derived 1,3-dioxolanes and 1,3,2-dioxaborolanes are described. The solid-state conformation of dimethyl benzylidenetartrate (**5**) was found to be one in which the two carbomethoxy groups are pseudoaxial and the ester carbonyls eclipse the adjacent dioxolane C–O bonds. This parallels exactly the conformation previously proposed for the 1,3,2-dioxaborolane unit in the transition state of the reactions of tartrate ester modified allylboronates **1**–**3** and aldehydes. A correlation was developed between the solution and solid-state conformations of 1,3-dioxolanes **5**–**7** based on the observed $J_{4,5}$ coupling constants and the H_4–C–C–H_5 dihedral angle obtained from the X-ray crystal structures. A high resolution variable-temperature ^{1}H NMR study of 1,3-dioxolane **5** in THF-d_8 revealed that $J_{4,5}$ decreased from 3.72 Hz at 23 °C to 2.91 Hz at −80 °C, providing evidence that the diaxial conformation is increasingly favored as the temperature is decreased. A high resolution variable-temperature ^{1}H NMR study of ortho ester **12**, prepared from dimethyl tartrate and trimethyl orthoacetate, in THF-d_8 similarly revealed $J_{4,5}$ = 5.25 Hz at 23 °C and $J_{4,5}$ = 4.60 Hz at −80 °C. An analogous solution conformation analysis was also performed with 1,3,2-dioxaborolane derivatives **16** and **17** prepared from methyl trifluoroethyl tartrate (**15**). Variable-temperature ^{1}H NMR analysis of **17** in toluene-d_8 revealed that $J_{4,5}$ decreased to a value of $J_{4,5}$ = 5.0 Hz at 23 °C to $J_{4,5}$ = 4.3 Hz at −60 °C. The significance of these data to the mechanism of asymmetric induction in the reactions of the tartrate ester modified allylboronates **1**–**3** and aldehydes is discussed.

The asymmetric allylboration reaction has been extensively studied over the past several years.[2,3] We have contributed the tartrate ester modified allylboronates **1**–**3** to this rapidly evolving field and have applied this technology in the synthesis of several stereochemically complex systems.[4,5] While these applications clearly define the synthetic utility of **1**–**3**, the mechanism of asymmetric induction remains a topic of considerable interest, especially with respect to the design of more highly enantioselective chiral auxiliaries.[6] We have suggested that reagents **1**–**3** preferentially react with aldehydes by way of transition state **A** in which (i) the aldehyde and the two tartrate ester units occupy axial positions with respect to the dioxaborolane unit, and (ii) the tartrate esters are syn coplanar to the adjacent dioxaborolane C–O bonds. We have suggested further that the stereochemically favored transition state **A** is stabilized by a favorable dipole–dipole

---

(1) Eli Lilly Undergraduate Summer Research Fellow, 1989.

(2) For reviews of the reactions of allylmetal compounds and aldehydes, see: (a) Hoffmann, R. W. *Angew, Chem., Int. Ed. Engl.* **1982**, *21*, 555. (b) Yamamoto, Y.; Maruyama, K. *Heterocycles* **1982**, *18*, 357. (c) Roush, W. R. In *Comprehensive Organic Synthesis*; Heathcock, C. H., Ed.; Pergamon Press: Oxford; Vol. 2, in press.

(3) For leading references to the most highly enantioselective classes of chiral allyl- and crotylboron reagents, see: (a) Jadhav, P. K.; Bhat, K. S.; Perumal, P. T.; Brown, H. C. *J. Org. Chem.* **1986**, *51*, 432. (b) Brown, H. C.; Bhat, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 5919. (c) Garcia, J.; Kim, B.-M.; Masamune, S. *J. Org. Chem.* **1987**, *52*, 4831. (d) Hoffmann, R. W.; Dresely, S.; Lanz, J. W. *Chem. Ber.* **1988**, *121*, 1501 and previous papers in this series. (e) Reetz, M. T.; Zierke, T. *Chem. Ind. (London)* **1988**, 663. (f) Hoffmann, R. W.; Dresely, S. *Chem. Ber.* **1989**, *122*, 903. (g) Hoffmann, R. W.; Ditrich, K.; Köster, G.; Stürmer, R. *Chem. Ber.* **1989**, *122*, 1783. (h) Short, R. P.; Masamune, S. *J. Am. Chem. Soc.* **1989**, *111*, 1892. (i) Corey, E. J.; Yu, C.-M.; Kim, S. S. *J. Am. Chem. Soc.* **1989**, *111*, 5495. (j) Brown, H. C.; Randad, R. S.; Bhat, K. S.; Zaidlewicz, M.; Racherla, U. S. *J. Am. Chem. Soc.* **1990**, *112*, 2389.

(4) (a) Roush, W. R.; Walts, A. E.; Hoong, L. K. *J. Am. Chem. Soc.* **1985**, *107*, 8186. (b) Roush, W. R.; Hoong, L. K.; Palmer, M. A. J.; Park, J. C. *J. Org. Chem.* **1990**, *55*, 4109. (c) Roush, W. R.; Hoong, L. K.; Palmer, M. A. J.; Straub, J. A.; Palkowitz, A. D. *J. Org. Chem.* **1990**, *55*, 4117. (d) Roush, W. R.; Ando, K.; Powers, D. B.; Palkowitz, A. D.; Halterman, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 6339. (e) Roush, W. R.; Palkowitz, A. D.; Ando, K. *Ibid.* **1990**, *112*, 6348.

(5) (a) Roush, W. R.; Palkowitz, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 953. (b) Roush, W. R.; Brown, B. B.; Drozda, S. E. *Tetrahedron Lett.* **1988**, *29*, 3541. (c) Coe, J. W.; Roush, W. R. *J. Org. Chem.* **1989**, *54*, 915. (d) Roush, W. R.; Palkowitz, A. D. *J. Org. Chem.* **1989**, *54*, 3009.

(6) Roush, W. R.; Banfi, L. *J. Am. Chem. Soc.* **1988**, *110*, 3979.

0022-3263/92/1957-2047$03.00/0 © 1992 American Chemical Society