(1965); (b) F. H. Cottee, B. P. Straughan, C. J. Timmons, W. H. Forbes, and R. Shilton, *J. Chem. Soc. B*, 1146 (1967); (c) R. Barlet, J. L. Pierre, and P. Arnaud, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **262**, 855 (1966); (d) J. J. Keirns and R. F. Curl, Jr., *J. Chem. Phys.*, **48**, 3773 (1968); (e) G. L. Carlson, W. G. Fately, and R. E. Witkowski, *J. Am. Chem. Soc.*, **89**, 6437 (1967); (f) D. F. Koster, *ibid.*, **88**, 5067 (1966); (g) J. E. Katon and W. R. Feairheller, Jr., *J. Chem. Phys.*, **47**, 1248 (1967); (h) W. O. George, D. V. Hassid, and W. F. Maddams, *J. Chem. Soc., Perkin Trans. 2*, 400 (1972).

(8) (a) K. Hagen and K. Hedberg, *J. Am. Chem. Soc.*, **95**, 1003 (1973); (b) J. R. Durig and S. E. Hannum, *J. Chem. Phys.*, **52**, 6089 (1970); (c) B. D. Saskena and R. E. Kagarise, *ibid.*, **19**, 987 (1951); (d) K. Hagen and K. Hedberg, *J. Am. Chem. Soc.*, **95**, 4796 (1973).

(9) (a) N. D. Epiotis and W. Cherry, *Chem. Commun.*, 278 (1973); (b) N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 3087 (1973); (c) N. D. Epiotis and R. L. Yates, submitted for publication; (d) O. Eisenstein, N. T. Anh, Y. Jean, A. Devaquet, J. Catacuzene, and L. Salem, *Tetrahedron*, **30**, 1717 (1974).

(10) See for instance (a) A. Dalgarno in "Quantum Theory", Vol. 1, D. R. Bates, Ed., Academic Press, New York, N.Y., 1961, Chapter 5; (b) J. O. Hirschfelder, W. Byers-Brown, and S. T. Epstein in "Advances in Quantum Chemistry", Vol. 1, P. O. Löwdin, Ed., Academic Press, New York, N.Y., 1964, p 255.

(11) (a) A. Imamura, *Mol. Phys.*, **15**, 225 (1968); (b) L. Salem, *J. Am. Chem. Soc.*, **90**, 543 (1968); (c) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **41**, 1989 (1968); (d) L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 1370 (1974); (e) R. Hoffmann, *Acc. Chem. Res.*, **7**, 384 (1974).

(12) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236 Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(13) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); W. J. Hehre, R. Ditchfield, R. F. Stewart, and J. A. Pople, *ibid.*, **52**, 2769 (1970).

(14) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

(15) (a) L. Radom, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 2371 (1972); (b) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *Aust. J. Chem.*, **25**, 1601 (1972); (c) W. J. Hehre, A. J. P. Devaquet, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 664 (1976).

(16) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*; **89**, 4253 (1967).

(17) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).

(18) Similar arguments have been used by Epiotis and Cherry in their treatment of the enhanced stability of the cis dihaloethylenes over their trans analogues.[9a,b] The following papers may also be consulted: (a) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **94**, 6221 (1972); (b) R. Hoffmann, C. C. Levin, and R. A. Moss, *ibid.*, **95**, 629 (1973); (c) N. D. Epiotis, D. Bjorkquist, L. Bjorkquist, and S. Sarkanen, *ibid.*, **95**, 7558 (1973); (d) see ref 15c.

(19) (a) B. Dumbacher, *Theor. Chim. Acta*, **23**, 346 (1972); (b) V. Pincelli, B. Cadioli, and B. Levy, *Chem. Phys. Lett.*, **13**, 249 (1972); (c) R. J. Buenker and J. L. Whitten, *J. Chem. Phys.*, **49**, 5381 (1968); (d) L. Radom and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4786 (1970).

(20) T.-K. Ha, *J. Mol. Struct.*, **12**, 171 (1972).

(21) U. Pincelli, B. Cadioli, and D. J. David, *J. Mol. Struct.*, **9**, 173 (1971).

(22) A. Devaquet, *J. Am. Chem. Soc.*, **94**, 5160 (1972).

(23) M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.*, **94**, 5296 (1972).

(24) (a) See ref 15a; (b) L. Radom, J. Paviot, J. A. Pople, and P. v. R. Schleyer, *Chem. Commun.*, 58 (1974).

(25) (a) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 2191 (1970); (b) W. J. Hehre, L. Radom, and J. A. Pople, *ibid.*, **94**, 1496 (1972).

(26) Other values have been reported for oxalyl chloride: 2.2 kcal/mol (Raman studies in the liquid)[8b] and 2.8 kcal/mol (ir studies).[8c] Our choice was guided by the fact that both values (1.38 kcal/mol for oxalyl chloride, 0.6 kcal/mol for oxalyl bromide) were obtained by the same experimental procedure (electron diffraction).

# Nucleophilic Additions to Phosphine Oxides. A Model Study of Anionic Trigonal Bipyramidal Intermediates

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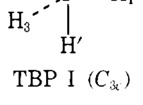
**Abstract:** $POH_3 + H^-$ has been used as a model to ascertain whether the phosphoryl oxygen will be more stable axial or equatorial compared with the alkyl groups in anionic trigonal bipyramidal transition states or intermediates formed via nucleophilic additions to phosphine oxides. Ab initio electronic structure calculations were carried out for a variety of geometries and we find that the trigonal bipyramid with the phosphoryl oxygen *equatorial* is more stable. This conclusion is in disagreement with the previously suggested order of preference for an axial site in a trigonal bipyramid, $OR(H) > O^- > CH_3$. We also find that the transition states or intermediates will be distorted trigonal bipyramids. The principal origin of equatorial preference derives from a symmetry controlled charge delocalization in the antibonding $\pi$ orbitals. The $\pi$-donor repulsion effect and phosphorus d-orbital participation also favor an equatorial site, but they are of lesser importance.

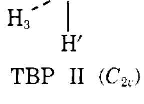
## I. Introduction

Nucleophilic additions to phosphorus-oxygen bonds are an important aspect of organic chemistry and biochemistry. Most nucleophilic additions to tetrahedral phosphorus compounds are believed to proceed via a trigonal bipyramidal (TBP) transition state or intermediate.[1] The most stable pseudorotamer of the TBP anions formed in the alkaline exchange or racemization reactions of phosphine oxides ($POR_1R_2R_3$) has remained unresolved and a principal purpose of this paper is to answer this question.

The preference rules which have been proposed for deciding the placement of ligands in a TBP are: (1) the entering nucleophile and the most electronegative ligand should occupy the axial positions;[1-6] (2) $\pi$ donors prefer to occupy equatorial sites.[7] Both a phosphoryl oxygen and an alkyl group are recognized as being very electropositive species and would thus tend to occupy an equatorial site.[1-6] However, in a TBP formed via nucleophilic addition to a phosphine oxide, either the phosphoryl oxygen or an alkyl group must occupy the second axial site. The order of preference for the axial sites in a TBP given by Richards and Wyckoff,[8] $OR(H) > O^- > CH_3$, suggests that the TBP with the incoming nucleophile and the $O^-$ axial will be the more stable transition state or intermediate in these reactions. In contrast, the large negative charge on the phosphoryl oxygen makes it an efficient $\pi$ donor which suggests that the more stable TBP will have the nucleophile and an alkyl group axial. In order to ascertain which of these trigonal bipyramids is more stable we have carried out ab initio electronic structure calculations for species I, symmetry $C_{3v}$, and II,



TBP I ($C_{3v}$)



TBP II ($C_{2v}$)

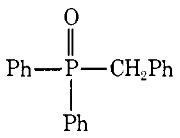
symmetry $C_{2v}$. Here the nucleophile is H′ and is constrained to occupy one of the axial sites. The relative stabilities of these

**Table I.** Optimized Bond Lengths and Selected Bond Angles

| TBP | $R_{PO}$, Å | $R_{PH_1}$, Å | $R_{PH'}$, Å | $R_{PH_{2,3}}$, Å | ∠OPH′, deg | ∠$H_1$PH′, deg | ∠$H_2PH_3$, deg |
|---|---|---|---|---|---|---|---|
| I | 1.67 | 1.48 | 1.62 | 1.48 | 180 | 90 | 120 |
| II | 1.65 | 1.60 | 1.60 | 1.45 | 90 | 180 | 120 |
| II′ | 1.65 | 1.60 | 1.60 | 1.45 | 92.5 | 175 | 115 |

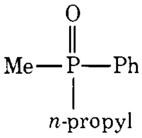
anions should be predominantly determined by electronic interactions since steric interactions will be minimized in these species.

Our results show that a greater delocalization of charge in the lower symmetry species, TBP II ($C_{2v}$), leads to the lowest energy. This conclusion provides a partial explanation for the lack of $^{18}O$ exchange in benzyldiphenylphosphine oxide[9]



$$Ph-\overset{\overset{O}{\|}}{\underset{\underset{Ph}{|}}{P}}-CH_2Ph$$

as well as the optical stability of chiral methyl-*n*-propylphenylphosphine oxide[10]



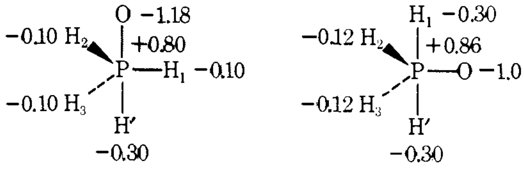
$$Me-\overset{\overset{O}{\|}}{\underset{\underset{n\text{-propyl}}{|}}{P}}-Ph$$

in the presence of $OH^-$, and other experimental results.[1,11,12]

## II. Computational Details

The calculations were carried out ab initio utilizing the GAUSSIAN 70 computer program and the split valence 4-31G s,p basis set[13] on an IBM 360-91 computer. An ab initio SCF calculation on phosphine oxide by Demuynck and Veillard[14] has indicated that the P-O bond in this compound can be described as a σ-dative bond with some π back-bonding. In addition, Keil and Kutzelnigg[15] have concluded from their ab initio SCF calculations on $PF_5$, $PF_3H_2$, $PF_2H_3$, and $PFH_4$ that the bonding in these molecules can be characterized without involving $sp^3d$ hybridized functions on the phosphorus. They find that the bonding is best represented by a three-center four-electron axial bond and ordinary two-center two-electron equatorial bonds. Thus, d orbitals are not required to describe the general features of bonding in the systems of interest here. P-O bonds have been shown to involve somewhat greater π back-bonding than P-F bonds,[16] but the observed back-bonding[15] in molecules such as $PH_3F_2$ is small enough to conclude that the P-O back-bonding in $POH_4^-$ will be small as well, thus again indicating that d orbitals are not necessary in a first-order treatment. This conclusion is also supported by work carried out by Bernardi et al.[17] on the $CH_2SH$ radical. Their nonempirical calculations indicate that $p_\pi$-$d_\pi$ conjugation is unimportant in this radical.

The geometries of the trigonal bipyramidal anions I and II utilized in our analysis were determined by optimizing all the bond lengths to ±0.01 Å for bond angles 90, 120, and 180°.



TBP I TBP II

**Figure 1.** Charge distributions (electrons).

We also carried out one calculation (II′) with the optimum bond lengths of II, but slightly distorted angles. The optimized bond lengths and selected bond angles are given in Table I.

## III. Results

The total energies, $E_T$, and energy components[18] for species I, II, and II′ at the optimized geometries are tabulated in Table II. $E_T$ values show that TBP II is more stable than TBP I by 15.5 kcal/mol. In addition, TBP II′ is more stable than TBP II by 3.6 kcal/mol.

Energy components, like population analysis, can in principle provide useful chemical insights into mechanisms, but sensitivity to basis set and geometry changes frequently yield misleading results. When geometry optimization has been carried out (as in this paper) a crude estimate of the component error[19] is $E_T[1 - (-V/2T)]$, but even when component changes considerably exceed this value they should only be employed in conjunction with other evidence. For our wave functions the largest deviation occurs for species I and the probable component error is 0.085 hartree.

Table III and Figure 1 give the Mulliken overlap populations and charge distributions.[20] Since the nucleophile H′ has the same charge in both trigonal bipyramidal anions (Figure 1), H′ attack on the $H_1$-$H_2$-$H_3$ face (TBP I) or on the O-$H_2$-$H_3$ face (TBP II) of the $POH_3$ tetrahedron yields the same charge transfer to the $POH_3$ group.

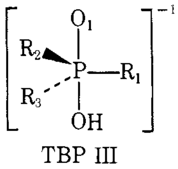
For both anions the oxygen atom has the largest negative charge. Table III shows that the P-O overlap in TBP II is almost twice that in TBP I, whereas the P-H overlaps are comparable in both molecules.

Figure 2 is an orbital energy level diagram for anions I and II. TBP I is a more symmetrical molecule ($C_{3v}$) than TBP II ($C_{2v}$) and the two degeneracies in TBP I are split in TBP II.

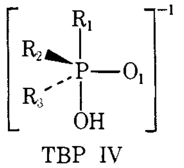
The π-donor orbitals are shown schematically in Figure 3. The other orbitals, MO's 1, 2, 5, and 8, are essentially unchanged in composition between I and II.

## IV. Discussion

For ease of analysis and computational reasons we have employed the simple species I and II. We therefore hypothesize that these provide adequate models for discriminating between the chemically more relevant species, III and IV, respectively,



TBP III



TBP IV

**Table II.** Energy Components and Total Energies (hartrees)

| TBP | $V_{nn}$[a] | $T$[b] | $V_{ne}$[c] | $V_{ee}$[d] | $E_{elec}$[e] | $E_T$[f] |
|---|---|---|---|---|---|---|
| I | 67.334 | 417.333 | −1134.626 | 232.795 | −484.498 | −417.1640 |
| II | 67.547 | 417.276 | −1134.478 | 232.466 | −484.735 | −417.1887 |
| II′ | 67.448 | 417.260 | −1134.163 | 232.261 | −484.642 | −417.1945 |

[a] Nuclear-nuclear repulsion. [b] Kinetic energy. [c] Nuclear-electronic attraction. [d] Electron-electron repulsion. [e] Electronic energy = $T + V_{ne} + V_{ee}$. [f] Total energy.

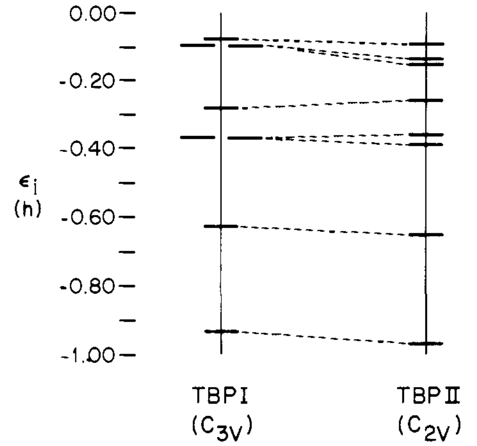


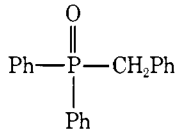
**Figure 2.** Orbital energy levels (hartrees) for trigonal bipyramidal anions I ($C_{3v}$) and II ($C_{2v}$).

**Table III.** Overlap Populations

| TBP | P-O | P-H′ | P-H$_1$ | P-H$_{2,3}$ | O-H′ | O-H$_{2,3}$ |
|---|---|---|---|---|---|---|
| I | 0.1603 | 0.5174 | 0.5560 | 0.5560 | 0.0335 | −0.2240 |
| II | 0.2990 | 0.4888 | 0.4888 | 0.4978 | −0.1698 | −0.00773 |

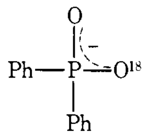
where OH is the nucleophile. Our calculations showed that the phosphoryl oxygen prefers an equatorial position (II) by 15.5 kcal/mol and we thus propose a parallel stability for IV such that any pseudorotations which place O$_1$ in an axial position are inhibited.[21] Unless pseudorotations occur which place both oxygens in equatorial positions no exchange or racemization is expected since the two oxygens cannot become equivalent.

These theoretical results are supported by experiment. Most phosphine oxides undergo alkaline exchange and racemization reactions sluggishly if at all.[1,9-12] For example, (1) the addition of $^{18}OH^-$ to



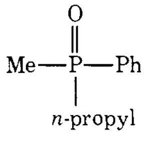
$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{\underset{\underset{Ph}{|}}{P}}{-}CH_2Ph}$$

results primarily in cleavage of the P-CH$_2$Ph bond[9] to form



$$\mathrm{Ph{-}\overset{\overset{O}{|}}{\underset{\underset{Ph}{|}}{P}}\overset{-}{\cdots}O^{18}}$$

Only a negligible amount of $^{18}O$ is incorporated into the phosphine oxide reactant. (2) Chiral



$$\mathrm{Me{-}\overset{\overset{O}{\|}}{\underset{\underset{\mathit{n}\text{-propyl}}{|}}{P}}{-}Ph}$$

is optically stable even in refluxing aqueous NaOH.[10] These experimental findings are unexpected if the reaction transition states or intermediates are III since protonation of the O$_1$ would make the two oxygens equivalent and exchange or racemization would be possible.

**Preference Rule Number 1.** Our theoretical result suggests that the relative tendency of ligands to occupy an axial site in a TBP is OR(H) > alkyl > O$^-$. The experimental[1-3] and theoretical[4] studies on pentaoxyphosphoranes clearly indicate that of these three types of ligands OR is most stable in an axial position. However, the experimental evidence regarding the alkyl groups and O$^-$ is less discriminating.[1,8-11] In their review article on ribonuclease A, Richards and Wyckoff[8] give the following order of preference for an axial site: OR(H) > O$^-$ > CH$_3$. Our order is supported by the CNDO/2 calculations carried out by Gillespie et al.[5,6] They have studied P(OH)$_3$(O$^-$)CH$_3$. Two of its five possible pseudorotomers are:

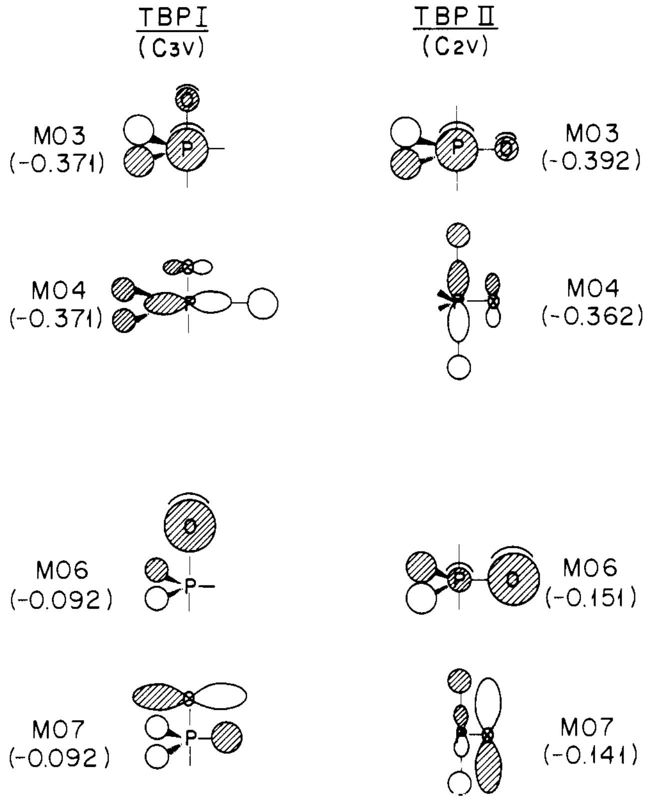
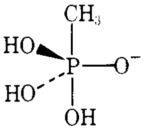
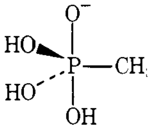


**Figure 3.** Schematic diagrams of molecular orbitals containing oxygen $\pi$ orbitals (orbital energies in hartree units).



V



VI

They find V more stable than VI, a greater double bond character, and a shorter bond for the equatorial position. Although in the correct direction, their rationalization in terms of d-orbital participation appears to over-emphasize this effect (see below).

**Preference Rule Number 2.** Hoffmann et al.[7] have given arguments why $\pi$-donor ligands (i.e., those with high-lying occupied MO's) should prefer equatorial sites in trigonal bipyramids. $\pi$ donors can interact with the occupied molecular skeleton orbitals and this interaction is destabilizing;[7,22-24] thus a $\pi$ donor will preferentially occupy the site which interacts least with the molecular skeleton.[25] Those orbitals for which this interaction is symmetry allowed are schematically shown in Figure 3. Hoffmann et al.[7] have treated the case for MO's 3 and 4 in TBP I and TBP II reasoning that oxygen-molecular skeleton interactions for MO 3 and 4 of TBP I will be very similar to that of MO 4 in TBP II while that of MO 3 in TBP II will be significantly lower, thereby stabilizing TBP II. The orbital energy level diagram, Figure 2, shows that qualitatively this hypothesis is correct and leads to the correct assignment of the phosphoryl oxygen position. Quantitatively, however, the $\pi$-donor repulsion effect is almost negligibly small; the splitting of degenerate MO 3 and 4 in TBP I by the lower symmetry of TBP II is almost symmetrical. The lower oxygen-molecular skeleton repulsion in MO 3 of TBP I is almost counterbalanced by the greater repulsion in MO 4. MO's 6 and 7 are the antibonding $\pi$ pair lying directly above the bonding $\pi$ pair (MO's 3 and 4) and $\pi$-donor repulsion would be expected to operate analogously.

**Delocalization in Equatorial Intermediates.** Lowering of the symmetry in the antibonding $\pi$ pair allows mixing of the ligand atomic orbitals with phosphorus and establishment of partial delocalization. This creates a bond between P and O in MO 6 and between the P and the axial ligands in MO 7. There is no differential delocalization due to symmetry lowering in MO's 3 and 4 because these $\pi$ orbitals all have maximum bonding between the atomic orbitals. The delocalization in MO's 6 and 7 for TBP II results in the energy of both orbitals being greatly lowered from the degenerate pair in TBP I and this is the principal source of stabilization in TBP II.

The bonding to P and consequent favoring of equatorial oxygen in MO's 6 and 7 shows up directly in the overlap populations, Table III. The central discriminating feature in this table is the almost double P–O overlap for TBP II compared to TBP I and approximately one-third of this difference arises from $\pi$ overlaps. The other two-thirds arises from the shorter P–O bond distance in TBP II. Delocalization in these molecular orbitals also results in reduced electron–electron repulsion ($V_{ee}$). The central discriminating electronic feature in the energy components (Table II) is the 0.33 hartree $V_{ee}$ reduction in TBP II, a value several times the magnitude of the probable component error.

The bonding pattern characterized above manifests itself in bond length differences (Table I). As expected from the overlaps in MO's 6 and 7, the P–O and the P–H′ bonds are shortened in TBP II. In accordance with the greater stability of TBP II, the P–$H_{2,3}$ bonds are shortened.

**Influence of d Orbitals.** As discussed in section II, the weight of the present evidence strongly suggests that d orbitals are of minor importance in the systems of interest here and therefore they were not included in our basis set. If $P_{3d}$ orbitals had been included they would mix with the oxygen $\pi$ orbital. The $O_{p_\pi}$–$P_{d_\pi}$ interaction is stabilizing and favors substitution of the oxygen ligand at the site in the trigonal bipyramid for which the back-bonding is most efficient.[7] Calculations carried out by Hoffmann et al.[7] and Van der Voorn and Drago[27] indicate that this is the equatorial site. Keil and Kutzelnigg[15] report that the $P_{3d}$ AO's are about equally important in equatorial and axial P–F bond overlaps. It follows that $d_\pi$–$p_\pi$ back-bonding could make a marginal contribution to stabilization of the equatorial intermediate. In semiempirical methods, such as CNDO/2, the addition of unoccupied orbitals to the basis set almost always leads to a large overweight of their coefficients in the molecular orbitals because of the selective omission of repulsion terms in these schemes. In particular, 3d AO's are generally overestimated.[12]

**Distortion of the Equatorial Transition State.** Another possible explanation for the experimental results is that the transition states or intermediates in these reactions are not ideal trigonal bipyramids. A slight distortion from ideality could prevent exchange. To test this, a 5° distortion of both $\angle H_2PH_3$ and $\angle H_1PH'$ in TBP II was chosen in analogy to electron diffraction results on some pentacoordinate phosphorus compounds.[26] and this produced a further stabilization of 3.6 kcal/mol. Since closing these angles stabilizes the anion, it is possible that a species similar to TBP II′ is the actual transition state or intermediate in these reactions. It should be kept in mind, however, that the greater bulkiness of ligands other than H's (for example, Ph's) would prevent too large a distortion from occurring since the R–R repulsions would be closer to the $O_1$–R repulsions in magnitude.

**More Complex R Groups.** Gillespie et al.[5] have reported that the bulkier the substituents on the phosphorus, the less stable the trigonal bipyramid. Thus, replacing the hydrogens with other groups may destabilize the trigonal bipyramidal transition state or intermediate in these phosphine oxide reactions. According to the VSEPR theory,[28] TBP III will be destabilized more than TBP IV since the $O_1^-$ is diffuse and will have a larger repulsive interaction with the other ligands and the bonding electrons in an axial position, leading to higher stability for $O_1$ in the equatorial site.

Figure 1 shows that the axial hydrogens have a larger negative charge than the equatorial hydrogens in both TBP I and TBP II. TBP IV will be stabilized relative to TBP II whenever the axial ligand in TBP IV is better able to accept the larger negative charge than the hydrogen in TBP II. This will be true when R is a better leaving group than H.[29] For most of the phosphine oxides studied, the group lost in the reaction is a slightly better leaving group than hydrogen (i.e., $CH_2Ph$).[29,30] We conclude, therefore, that the trigonal bipyramid with the $O_1$ substituent equatorial and the best leaving group and the nucleophile axial will be more stable than with $O_1$ and the nucleophile axial.[31]

## Summary

Assuming a $POH_3 + H^-$ model for nucleophilic addition to phosphine oxides, $POR_1R_2R_3$, we have made the following conclusions about the transition state or intermediate:

(1) A phosphoryl oxygen will be more stable in an *equatorial* rather than axial position.

(2) The transition state or intermediate will be distorted trigonal bipyramid.

(3) Bulky substituents will not change the preference for an equatorial over an axial site.

(4) The origin of the stability of the equatorial intermediate is delocalization of charge in the antibonding $\pi$ molecular orbitals induced by symmetry lowering in going from the axial ($C_{3v}$) to the equatorial ($C_{2v}$) intermediate.

(5) Both the $\pi$-donor repulsion effect and phosphorus d orbitals are present and differentially stabilize the equatorial intermediate, but they are of minor quantitative significance compared to the antibonding $\pi$ orbital delocalization.

(6) The relative tendency of ligands to occupy an axial site in a TBP is OR(H) > alkyl > $O^-$.

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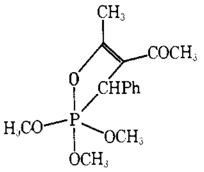
## References and Notes

(1) E. A. Dennis and F. H. Westheimer, *J. Am. Chem. Soc.*, **88**, 3431, 3432 (1966); F. H. Westheimer, *Acc. Chem. Res.*, **1**, 70 (1968), and references therein.
(2) D. A. Usher, *Proc. Natl. Acad. Sci. U.S.A.*, **62**, 611 (1969); D. S. Frank and D. A. Usher, *J. Am. Chem. Soc.*, **89**, 6360 (1967).
(3) E. L. Muertterties and R. A. Schunn, *Q. Rev., Chem. Soc.*, 245 (1966), and references therein.
(4) D. B. Boyd, *J. Am. Chem. Soc.*, **91**, 1200 (1969).
(5) P. Gillespie, F. Ramirez, I. Ugi, and D. Marquarding, *Angew. Chem., Int. Ed. Engl.*, **12**, 91 (1973), and references therein.
(6) P. Gillespie, R. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramierz, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971).
(7) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 3047 (1972).
(8) F. M. Richards and H. W. Wyckoff, "The Enzymes", Vol. IV, 3rd ed, P. D. Boyer, Ed., Academic Press, New York, N.Y., 1971, p 792.
(9) P. Haake and G. W. Allen, *Tetrahedron Lett.*, 3113 (1970).
(10) L. Horner and H. Winkler, *Tetrahedron Lett.*, 3271 (1964). On the basis of these experimental results, Gallagher and Jenkins have suggested that the anionic trigonal bipyramids involved in these reactions are transition states rather than intermediates. M. J. Gallagher and I. D. Jenkins, "Topics in Stereochemistry", E. L. Eliel and N. L. Allinger, Ed., Interscience, New York, N.Y., 1968, Chapter 1, p 75.
(11) B. R. Ezzell and L. D. Freedman, *J. Org. Chem.*, **35**, 241 (1970).
(12) J. Burdon, I. N. Rozhkov, and G. M. Perry, *J. Chem. Soc. C*, 2615 (1969)

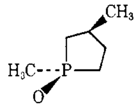
(13) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
(14) J. Demuynck and A. Veillard, *Chem. Commun.*, 873 (1970).
(15) F. Keil and W. Kutzelnigg, *J. Am. Chem. Soc.*, **97**, 3623 (1975).
(16) M. E. Dyatkina and N. M. Klimenko, *Zh. Strukt. Khim.*, **14**, 173 (1973).
(17) F. Bernardi, I. G. Csizmadia, H. B. Schlegel, M. Tiecco, M.-H. Whangbo, and S. Wolfe, *Gazz. Chim. Ital.*, **104**, 1101 (1974).
(18) L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968).
(19) P. W. Payne and L. C. Allen, "Modern Theoretical Chemistry", H. F. Schaefer, Ed., Plenum Press, New York, N.Y., in press.
(20) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).
(21) D. Gorenstein and F. H. Westheimer, *J. Am. Chem. Soc.*, **89**, 2762 (1967). The activation energy for the pseudorotation in TBP II which leads to TBP I must be greater than or equal to their energy difference of 15.5 kcal/mol. One species for which pseudorotation is inhibited is the tetraoxyphosphorane:



From the proton resonance spectrum data obtained by Gorenstein and Westheimer, Usher[2] determined a value of 12 kcal/mol for the free energy of activation of the exchange process. This number provides a rough estimate for pseudorotation inhibition; thus if the energy barrier for placing an O$^-$ ligand in an axial site in TBP IV is similar to that for TBP II, it will make pseudorotation unlikely.
(22) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971).
(23) L. Salem, *J. Am. Chem. Soc.*, **90**, 543 (1968).
(24) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, and references therein.
(25) J. M. Howell, *J. Am. Chem. Soc.*, **97**, 3930 (1975). In this paper the $\pi$-donor repulsion effect is used to explain the observed bond length variations[26] in substituted phosphoranes. Successive hydrogenation or methylation[26] in the equatorial positions of pentafluorophosphorane results in a decrease in the axial P–F bond overlaps and a consequent increase in the axial P–F bond lengths. On the basis of semiempirical calculations for several fluorophosphoranes Howell concludes that the repulsion between the lone pairs of the axial fluorine atoms and the equatorial $\sigma$ bonds is responsible for tha axial P–F bond lengthening.
(26) L. S. Bartell and K. W. Hansen, *Inorg. Chem.*, **4**, 1777 (1965).
(27) P. C. Van der Voorn and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 3255 (1966).
(28) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963); *Inorg. Chem.*, **5**, 1634 (1966).
(29) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hill, New York, N.Y., 1968, pp 290–294.
(30) R. Breslow, "Organic Reaction Mechanisms", 2nd ed, W. A. Benjamin, New York, N.Y., 1969, pp 14–16.
(31) Note Added in Proof. (1) D. Perahia, A. Pullman, and H. Berthod, *Theor. Chim. Acta*, **40**, 47 (1975), have recently carried out an ab initio study on the effect of the phosphorus 3d orbitals on some of the properties of the dimethylphosphate anion. They also concluded that omitting the phosphorus 3d orbitals does not qualitatively affect the general results obtained for most of the properties studied.

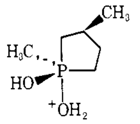
(2) We have recently carried out calculations for $R_1 = R_2 = R_3 = H$ in TBP III and TBP IV to determine which is more stable. Our results indicate that TBP IV is more stable than TBP III in agreement with the conclusions reported in the main body of this paper.

(3) In his mechanism for the acid-catalyzed interconversion of the cis and trans isomers of the phospholane oxide VII,



*trans*-VII

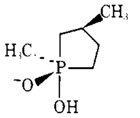
K. L. Marsi, *J. Am. Chem. Soc.*, **91**, 4724 (1969), postulates that the first step involves protonation of the phosphoryl oxygen and addition of $H_2O$ to the oxide to form TBP VIII.



TPB VIII

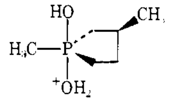
This TBP then pseudorotates twice, first with the OH group as the pivot and then with the $OH_2^+$ group as the pivot. After the first pseudorotation, the two most electronegative groups, OH and $H_2O^+$, both occupy equatorial sites making this pseudorotamer a relatively unstable species. After the second pseudorotation, the OH group leaves (perhaps, after proton shift) yielding the isomer crossover.

The cis and trans isomers of VII do not interconvert under basic conditions. Yet it seems likely that the mechanism postulated by Marsi would work equally well, if not better, under basic conditions. The initial TBP formed would be TBP VIII′. Under basic conditions, the phosphoryl oxygen would not be protonated and an electropositive O$^-$ rather than an electronegative OH would occupy an equatorial site. Furthermore, the subsequent step would involve the more probable pseudorotation with an electropositive O$^-$ ligand rather than an electronegative OH ligand as the pivot. This would result in only one electronegative group (OH) being equatorial. Consequently, both pseudorotamers formed via Marsi's scheme would seem to be more stable under basic conditions.



TBP VIII′

Since the interconversion is not observed under basic conditions, it seems more probable that the initial step in the acidic reaction yields TBP IX. We have shown that its analogous anionic structure is not stable; thus, interconversion via IX would be expected to go in acid but not in base.



TBP IX

# Carbon-13 Nuclear Magnetic Resonance and Ring Currents in Vinyl Cross-Linked Annulenes

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**Abstract:** Carbon-13 NMR spectra were determined for pyracylene and several of its dihydro- and phenyl-substituted derivatives. Comparison of the data confirmed earlier indications from proton NMR spectra that pyracylene exhibits paratropism. A simple additive procedure for comparison of model compounds in determining ring current effects was developed in the course of this analysis and was applied to acepleidylene to estimate the magnitude of its diatropism. Carbon-13 NMR spectroscopy was shown to be useful for the evaluation of ring current effects when good model compounds are available.

The concept of a ring current in conjugated cyclic hydrocarbons was first proposed from a purely classical viewpoint by Pauling to rationalize the large diamagnetic susceptibilities and diamagnetic anisotropies of certain molecules, such as benzene.[1,2] In 1937, London[3] offered the first quantum mechanical rationalization for ring currents by modifying the one-electron Hamiltonian of HMO theory to include the potential of the applied magnetic field, and showing that the