donors do not obey the constant-acid relationships described herein for oxygen and nitrogen donors. Work is underway to elucidate the electronic effects giving rise to this discrepancy.

Bonding, Proton Transfer, and Diradical Stabilization in Phosphonium Ylides

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Abstract: The phosphorus–carbon bond of phosphonium ylides is studied with semiempirical molecular orbital calculations. The primary effect of the inclusion of 3d orbitals on phosphorus is the anticipated electron transfer from the ylide carbon to the 3d orbitals, with an accompanying increase in P–C bond order. A novel effect of some significance is the hyperconjugative π-type interaction of CH_2 orbitals in a model H_3PCH_2 with a P 3d orbital of the appropriate symmetry. Intermolecular and intramolecular mechanisms for proton transfer in $(CH_3)_3PCH_2$ are studied. A concerted hydrogen switch involving two molecules is calculated to possess a high activation energy. The potential surface for a concerted intramolecular hydrogen migration leads to a transition state best described as a pentavalent phosphorus derivative. Carbon diradicals should be stabilized by intervening phosphorus or other second-row atoms. This type of stabilization is studied for a hypothetical $CH_2PR_3CH_2$. Such species are potential singlet states and should possess barriers to rotation of CH_2 groups but not of the PR_3 moiety.

Phosphonium ylides or alkylidene phosphoranes, whose electronic structure is commonly described as a resonance hybrid **1**, derive much of their current
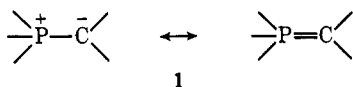
importance from the synthetic utility of the Wittig reaction.[1,2]
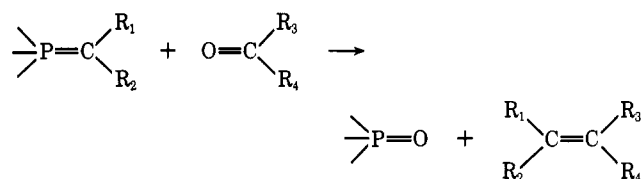
The ylides are fascinating compounds in their own right, exhibiting a remarkable variety of structural types exemplified by the species **2–5**.[3–6]

The resonance hybrid formulation **1** implies the verifiable existence of double bond character and the less verifiable concomitant participation of phosphorus 3d orbitals in bonding. The presence of partial double bond character is indicated by P–C interatomic distances[7–14] of 1.66–1.74 Å, intermediate between an

estimated double bond length of approximately 1.66 Å and single bond lengths of about 1.87 Å.[15,16]

Although p–d π bonding has been examined previously[17–19] and discussed qualitatively in relation to ylides,[2] no attempt has been made before to treat these compounds in detail theoretically. In this paper we report an analysis of the simplest ylides of the type **1**. Related to the question of π bonding in ylides is

(1) G. Wittig and G. Geissler, *Justus Liebigs Ann. Chem.*, **580**, 44 (1953), and subsequent papers.
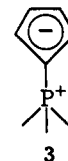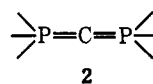
(2) An excellent source of information on phosphonium ylides is A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

(3) F. Ramirez, N. B. Desai, B. Hansen, and N. McKelvie, *J. Amer. Chem. Soc.*, **83**, 3539 (1961).
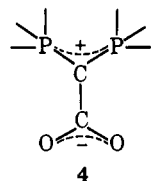
(4) F. Ramirez and S. Levy, *ibid.*, **79**, 67 (1957).

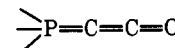(5) C. N. Matthews, J. S. Driscoll, and G. H. Birum, *Chem. Commun.*, 736 (1966).

(6) C. N. Matthews and G. H. Birum, *Tetrahedron Lett.*, 5707 (1966); *Accounts Chem. Res.*, **2**, 373 (1969).

(7) F. S. Stephens, *J. Chem. Soc.*, 5640, 5658 (1965).

(8) A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **87**, 5603 (1965).

(9) P. J. Wheatley, *J. Chem. Soc.*, 5785 (1965).

(10) T. C. W. Mak and J. Trotter, *Acta Crystallogr.*, **18**, 81 (1965).

(11) J. J. Daly and P. J. Wheatley, *J. Chem. Soc. A*, 1703 (1966).

(12) J. J. Daly, *ibid.*, *A*, 1913 (1967).

(13) G. Chioccola and J. J. Daly, *ibid.*, *A*, 568 (1968).

(14) J. C. J. Bart, *ibid.*, *B*, 350 (1969).

(15) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(16) T. Kojima, E. L. Breig, and C. C. Lim, *J. Chem. Phys.*, **35**, 2139 (1961).

(17) H. H. Jaffé, *J. Phys. Chem.*, **58**, 185 (1954).

(18) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954); D. P. Craig and E. A. Magnusson, *ibid.*, 4895 (1956); K. A. R. Mitchell, *Chem. Rev.*, **69**, 157 (1969).

(19) D. B. Boyd and W. N. Lipscomb, *J. Chem. Phys.*, **46**, 910 (1967); D. B. Boyd, *ibid.*, in press.

whether the hybridization at phosphorus is tetrahedral with σ bond donation and "back-bonding" from the p_π orbital of the carbanionic carbon to the $3d_\pi$ orbital
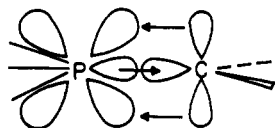
or whether the hybridization is trigonal bipyramidal with π bonding involving either an apical or basal position.[2]
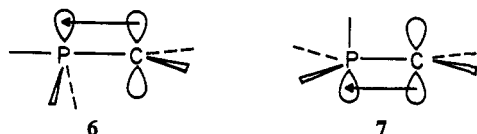
In addition to examining these possibilities we report in this paper the first of a series of studies concerned with the electronic structure of transition states and intermediates in the reactions of phosphorus and sulfur compounds. Prompted by the report[20] of the nmr equivalence at elevated temperatures of the 11 protons of $CH_2=P(CH_3)_3$ we were led to examine several intra- and intermolecular mechanisms for proton exchange in such species. We come to some interesting conclusions regarding pentacoordinated phosphorus intermediates and the stabilization of carbon diradicals by second-row atoms.

Computational Methodology

The extended Hückel method[21] is used for computing the LCAO molecular orbitals. In addition, the NEMO II theory,[22] which is based on a parameterization from SCF matrices of related small molecules, is employed in checking some results. The latter attempts to approximate the last iteration of an *ab initio* SCF calculation and includes all electrons.

The extended Hückel parameters are taken from earlier work.[21,23,24] The off-diagonal Hamiltonian matrix elements are approximated as $H_{ij} = S_{ij}(H_{ii} + H_{jj})$ in this study of phosphorus compounds. The valence-state ionization potentials, H_{ii}, are the same as those previously used for carbon and hydrogen,[21] while for phosphorus we use -18.6 (P 3s), -14.0 (P 3p), and -6.0 eV (P 3d). The value for the 3d orbitals is slightly higher than that used in phosphorus–oxygen compounds[23,24] since carbon is less electronegative than oxygen. However, the energy of the 3d orbitals is low enough so that they can mix moderately well with the other valence orbitals, corresponding to the usual concepts of valence orbital or octet expansion. Orbital exponents are taken from Slater's rules, except for the H 1s and P 3d orbitals, for which we use 1.2 and 1.4, respectively.[23] The parameters, tabulated elsewhere,[22] for the NEMO II method are taken from SCF calculations on PH_3, C_2H_4, and PO.

A geometry for the hypothetical H_3PCH_2, which is used as a first model for studying bonding in the ylides,

is based on phosphine[19,25] for the PH_3 terminus and ethylene[26] for the CH_2 terminus. These calculations were completed before an important X-ray structure of a nonstabilized ylide appeared,[14] one which demonstrated a very short P–C bond. We used a longer P–C distance of 1.74 Å, based on previous structure determinations. One P–H bond is chosen to lie in the plane bisecting the HCH angle of H_3PCH_2. Likewise in $CH_2=P(CH_3)_3$ and $(CH_2)_2PH_3$ all P–C distances are taken as 1.74 Å; all C—H bond distances are taken as 1.07 Å, and the P—H bond distances are 1.4181 Å. The geometry at P is assumed to be tetrahedral in $CH_2=P(CH_3)_3$ and trigonal bipyramidal in $(CH_2)_2PH_3$.

Bonding in a Model Ylide

Extended Hückel charge distributions in the model compound H_3PCH_2 reflect the dramatic effect of including P 3d orbitals in the basis set. Of course, the
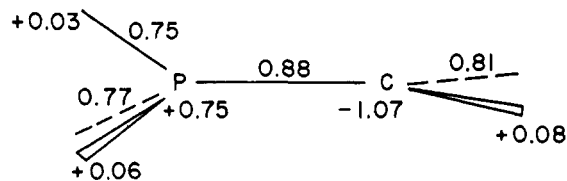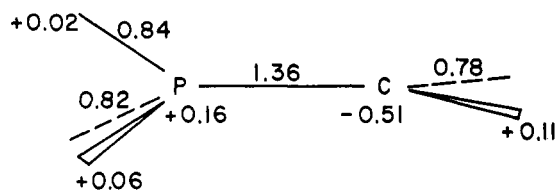
net atomic charges (signed numbers) are parameter dependent, but the effect of 3d orbital participation is clearly illustrated by these calculations. Without 3d orbitals in the basis set, the charge separation is unreasonably large. With their inclusion, the charge separation is greatly reduced and the P–C overlap population (unsigned numbers) increases, principally owing to overlap between the P $3d_{zz}$ and C $2p_x$ orbitals. Note that the ylide carbon remains quite negative despite considerable charge transfer.

The primary focus of interest in H_3PCH_2 is on the π bonding between the carbon $2p_x$ orbital and the phosphorus $3d_{zz}$. The measure of the 3d orbital participation may be found not only in the charge transfer illustrated above but even more directly in the energy and composition of the highest occupied molecular orbital (HOMO) of the ylide. In the absence of 3d orbitals the HOMO is essentially a lone pair on carbon, being the following combination of atomic orbitals

$0.965(C\ 2p_z) - 0.026(P\ 3p_z) -$

$$0.257(H_1) + 0.129(H_2 + H_3)$$

(20) H. Schmidbaur and W. Tronich, *Angew. Chem.*, **79**, 412 (1967); *Angew. Chem., Intern. Ed. Engl.*, **6**, 448 (1967).

(21) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(22) D. B. Boyd and W. N. Lipscomb, *ibid.*, **48**, 4955, 4968 (1968); D. B. Boyd, *Theor. Chim. Acta*, **14**, 402 (1969).

(23) D. B. Boyd and W. N. Lipscomb, *J. Theor. Biol.*, **25**, 403 (1969).

(24) D. B. Boyd, *J. Amer. Chem. Soc.*, **91**, 1200 (1969).

(25) M. H. Sirvetz and R. E. Weston, *J. Chem. Phys.*, **21**, 898 (1953).

(26) W. E. Palke and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2384 (1966).
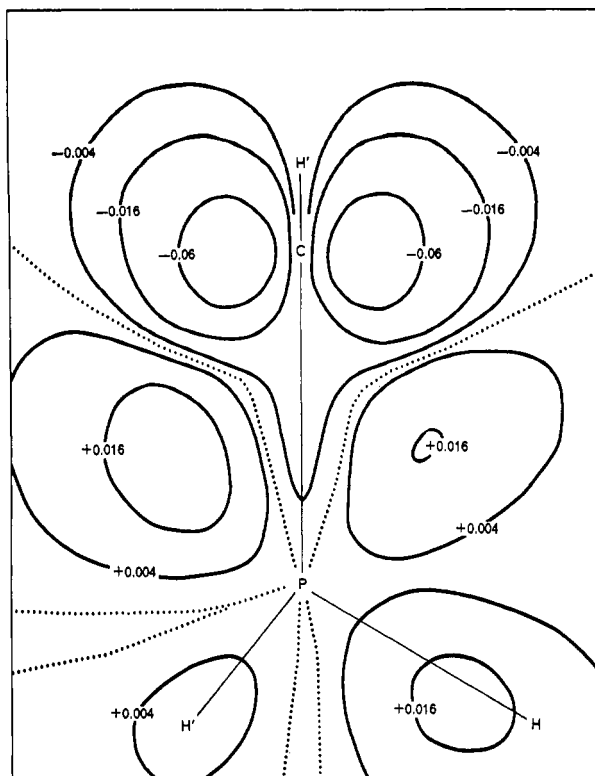
Figure 1. Electron density difference map for H_3PCH_2. The map shows contours of the difference in electron density between the total electronic density computed with 3d orbitals included, and the same density calculated without 3d orbitals. The contours are in atomic units (1 electron/au^3 = 6.749 electrons/Å^3), with positive numbers corresponding to regions gaining electron density when 3d orbitals are included in the basis set. Nodes are denoted by dotted lines. The map is in the xz plane and covers an area of 3 × 4 Å. Primed atoms are projections onto the xz plane.

Its one-electron energy is -11.20 eV. Upon inclusion of 3d orbitals in the basis set its composition changes to

$$0.748(C\ 2p_z) + 0.099(P\ 3p_z) + 0.328(P\ 3d_{zz}) -$$

$$0.097(P\ 3d_{x^2-y^2}) - 0.219(H_1) + 0.109(H_2 + H_3)$$

It has been stabilized as a result of 3d mixing, now being located at -12.39 eV in energy.

We would like to point out the enhanced extent of mixing of the phosphorus 3p orbital. In previous analyses of phosphorus bonding it has been tacitly assumed that this orbital cannot participate in π bonding since it is "used up" in forming normal covalent bonds to the three PX_3 substituents. Yet in any MO calculation there is nothing to preclude its mixing with orbitals of the same symmetry. We have found this mixing significant in the electronic structure of phosphonitrilic compounds and phosphabenzenes.[27]

Electron density *difference* maps furnish an incisive method for analyzing electron shifts upon bond formation. We may use such maps to illustrate for a given molecular orbital or for the entire molecular density either (1) the difference between the computed molecular density and the density due to superimposed, unperturbed atomic orbitals or (2) the difference between the molecular density computed without 3d orbitals and one computed with these orbitals included. The former procedure illustrates net electron shifts

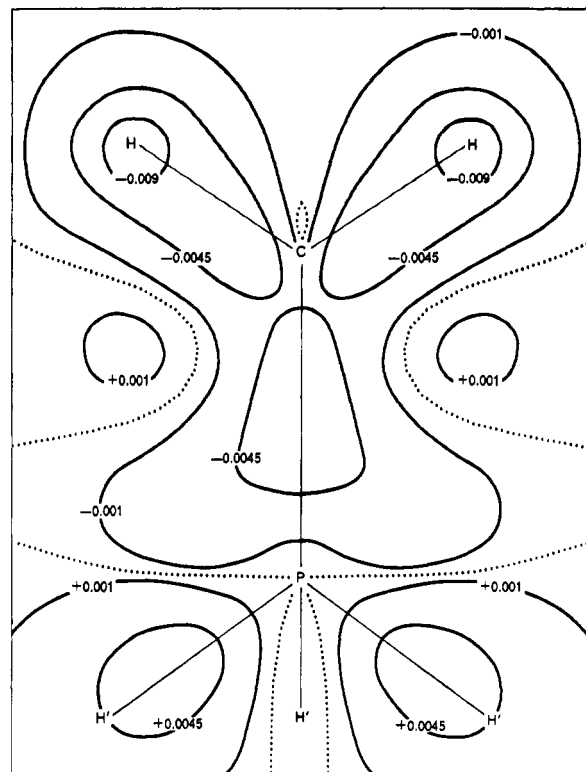(27) R. Hoffmann and M. Gheorghiu, manuscript in preparation.

Figure 2. Electron density difference map analogous to Figure 1, but now showing the yz plane, *i.e.*, the plane of the CH_2 group.

upon bond formation, while the latter focuses on the specific influence of 3d orbitals.

Figure 1 shows an electron density difference map of the second type. The changes in total electronic density upon inclusion of 3d orbitals are shown. The cross section chosen is the xz plane, and the figure clearly shows the pulling of electron density from the C $2p_x$ orbital into the P $3d_{xz}$. A similar difference map for the two electrons occupying the π HOMO alone is nearly identical, indicating that essentially all the charge transfer in the xz plane takes place in that MO.

Remarkably there is another type of interaction which we find contributes to P–C bonding when 3d orbitals are included. If one examines the gross atomic populations of the phosphorus 3d orbitals one finds the following

z^2	0.00	yz	0.10
xz	0.48	xy	0.01
$x^2 - y^2$	0.04		

We have already discussed the charge transfer to d_{xz}. The novel feature is the significant population of d_{yz}. Some thought reveals this to be the result of a hyperconjugative interaction in the yz plane between d_{yz} and a CH_2 bonding orbital of the same symmetry type, and
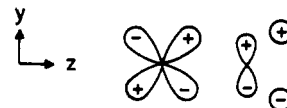
examination of the relevant orbitals confirms this. The result shows up as well in Figure 2, an electron density difference map analogous to Figure 1, but now showing a cross section in the yz plane, *i.e.*, the plane of the CH_2 group.

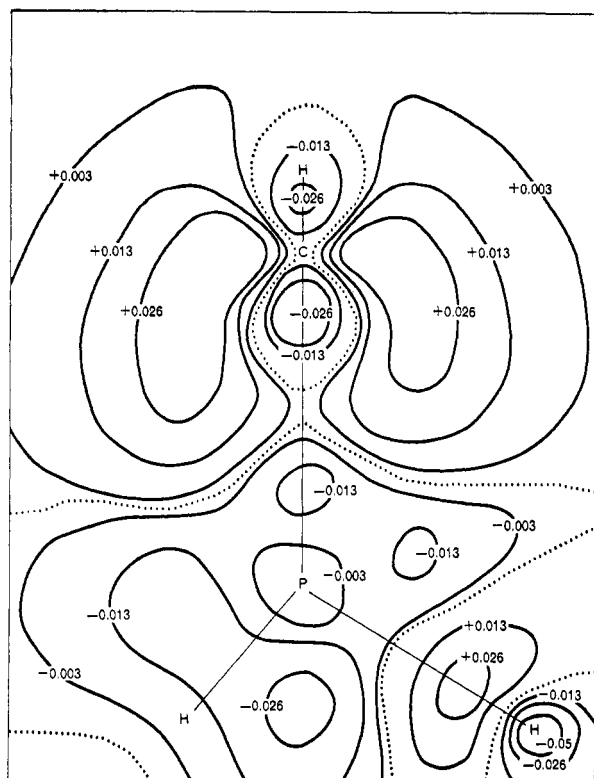*Hoffmann, Boyd, Goldberg / Phosphonium Ylides*

Figure 3. Electron density difference map for H_3PCH_2. This map shows contours of the difference in electron density between the computed molecular density with 3d orbitals included, and the density due to superimposed but noninteracting atoms. The map is in the xz plane.

Figure 4. Electron density difference map analogous to Figure 3, but now in the yz plane.

The ability of the phosphorus to enter into conjugation in two perpendicular planes is not surprising. It is this twofold ability to entertain charge transfer which is responsible for the great stability of phosphine oxides, R_3PO, and phosphine sulfides, R_3PS. It must also enter into the stabilization of cumulene-type species as **2** and **5**.

The ylidic carbon-phosphorus bond can be further examined by subtracting the sum of the atomic valence electron densities from the extended Hückel molecular electron density. Figures 3 and 4, which are computed by this procedure using molecular wave functions with 3d orbitals, clearly illustrate the buildup of electron density in the π-bonding region and in the C–H and P–H σ bonds as well. Surprisingly, the accumulation of electron density in the P–C σ bond is small. Note that the charge distribution in Figures 3 and 4 parallels that expected from the net atomic charges of the population analysis; i.e., P is positive, C is negative (due mainly to the C $2p_x$ orbital), and the H bonded to C is more positive than the H bonded to P.

The possibility mentioned in the introduction of utilizing a local trigonal bipyramidal geometry at phosphorus (**6, 7**) does not appear to be supported by the available ylid structures.[2,7–14] One way to examine the possibility of such a structure theoretically is to use a PH_3 group with threefold symmetry and equal bond lengths, as we did, and to scrutinize bond order differences for hints as to possible bond length changes. Our initial assumption was that weakening of the unique P–H bond would imply a possible distortion of it to an apical position in a trigonal bipyramid. The
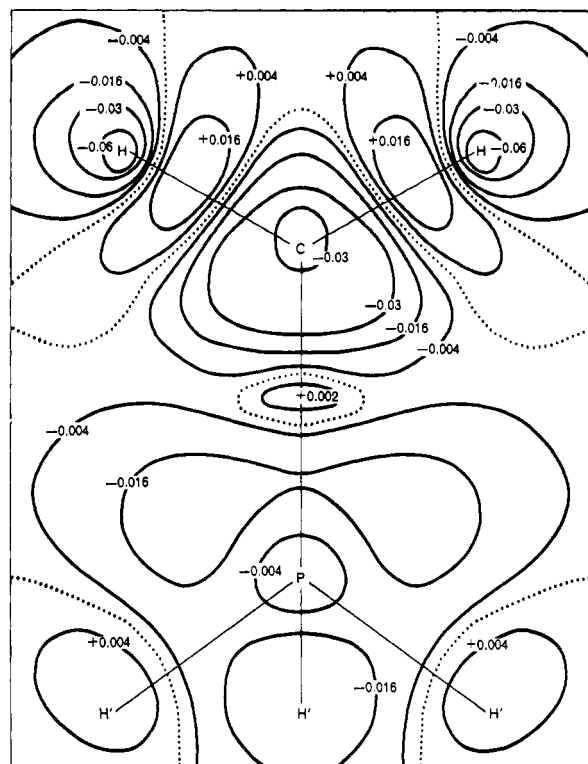
overlap populations for the P–H bonds (**8, 9**) indicate that the bond to the unique H is weaker than the bond to the other two H's in the calculation without 3d orbitals (**8**) but is stronger in the case with 3d orbitals (**9**). Hence it is not clear on the basis of the extended Hückel calculations whether the bond to the unique H, i.e., the one in the plane bisecting the HCH angle, tends to lengthen to an apical-like bond.

Computations by the NEMO II method (where 3d orbitals are included) indicate that the unique P–H bond is slightly weaker than the other P–H bonds. That is, the overlap population for the unique bond is smaller than for the other P–H bonds, all with the same bond length.
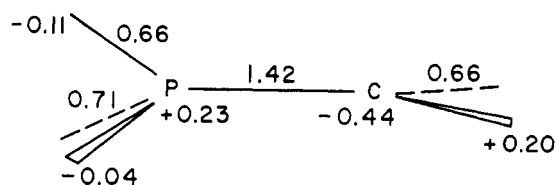
The apparent ambiguity in the extended Hückel results is further exemplified by trigonal bipyramidal PH_5. For this molecule we find when the 3d orbitals are included that the apical bonds are stronger than the basal bonds! This result is contrary to expectation, to what is obtained by extended Hückel without 3d orbitals,[28] and to what is found by NEMO II. The apparent anomalous result from extended Hückel theory arises because the calculated contribution of the 3d orbitals to the basal σ overlap population is less than to the apical σ overlap population. On the other hand,

(28) K. Issleib and W. Grundler, *Theor. Chim. Acta*, **8**, 70 (1967). For an earlier treatment of PH_5 see C. Carter, *Proc. Phys. Soc. B*, **69**, 1297 (1956).
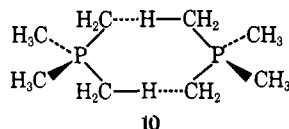
in trigonal bipyramidal PF_5, extended Hückel theory does predict[29] the apical bonds to be weaker (and hence longer) than the basal bonds. Here again, however, the overlap population of the 3d orbitals with the fluorine orbitals is greater in the apical σ bond than in the basal σ bond. But in PF_5, where the substituents have p orbitals available for π bonding with the 3d orbitals, the large π overlap populations in the basal bonds outweigh the anomalous effect of the 3d orbitals on the σ bonds. Experimental characterization of PH_5 might give an interesting test of the molecular orbital theories and of the importance of P 3d orbitals.

Extended Hückel calculations indicate a planar ylide carbon environment. However, the same calculations do not predict carbanion geometries correctly so that we cannot necessarily accept this conclusion as reliable. Similarly we cannot rely on our calculations for excited state energies. The lowest unoccupied orbitals are at -7.37 eV (mainly d_{zy}), -7.06 (d_{z^2}), and -6.76 ($d_{z^2-y^2}$), but their position is very sensitive to the initial 3d energy assumed. The calculated energy gaps between occupied and unoccupied levels are thus ≥ 5 eV. $(C_6H_5)_3PCH_2$ has a characteristic absorption band at 341 mμ (~ 3.6 eV).[30]

Proton Transfer in Methylenetrimethylphosphorane

A novel synthesis of methylenetrimethylphosphorane $(CH_3)_3PCH_2$ led to the observation of a single proton nmr signal at elevated temperatures.[20,31] This led us to examine several intra- and intermolecular mechanisms for proton interchange in phosphonium ylides. Actually the existence of a rapid, purely thermal proton rearrangement remains to be proved. The original interchange is catalyzed by trace amounts of acid,[31] and there is evidence for a catalyzed process proceeding through the intermediacy of phosphonium ions in related systems.[32,33]

In our theoretical study we began by considering an intermolecular concerted two-hydrogen transfer involving a monomer pair as shown in 10. To economize

$$
\begin{array}{c}
H_3C \diagdown \quad H_2C\cdots H - CH_2 \quad \diagup CH_3 \\
\quad \quad P \quad \quad \quad \quad \quad P \\
H_3C \diagup \quad H_2C - H\cdots CH_2 \quad \diagdown CH_3
\end{array}
$$

10

on computation times we replaced the inactive methyl groups by hydrogens, thus studying the proton exchange of $(CH_3)H_2PCH_2$.

The infinitely separated molecules were brought together in three different ways: (1) with no changes in bond distances or hybridization in the individual halves; (2) by maintaining the bridging hydrogens at the midpoint of the lines connecting the active carbon sites, but retaining the hybridization of the carbons (one sp^2, the other sp^3); and (3) by maintaining the bridging hydrogens at the midpoint of the lines connecting the active carbon sites while making the hybridization on all the active carbons sp^3. The potential energy curves for these motions are shown in

(29) P. C. Van Der Voorn and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 3255 (1966).
(30) S. O. Grim and J. H. Ambrus, *J. Org. Chem.*, **33**, 2993 (1968).
(31) H. Schmidbaur and W. Tronich, *Chem. Ber.*, **101**, 604 (1968).
(32) P. Crews, *J. Amer. Chem. Soc.*, **90**, 2961 (1968).
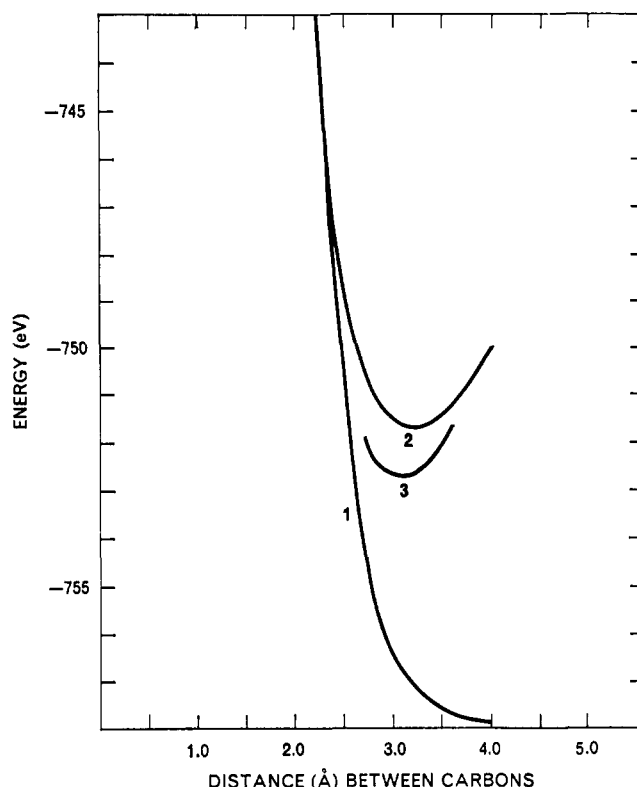(33) H. J. Bestmann, H. G. Liberda, and J. P. Snyder, *ibid.*, **90**, 2963 (1968).

Figure 5. Energy curves for three approaches in the intermolecular hydrogen exchange of $(CH_3)H_2PCH_2$. The numbers labeling the curves refer to the descriptions in the text.

Figure 5. The best symmetrical structure, presumably a good model for the transition state in this reaction, is of type **3**, with C–C separation of 3.1 Å. The reason for not considering symmetrical structures with sp^2 hybridization is that the tilt of the methylene group if maintained in that geometry leads to severe steric problems for an approaching hydrogen. This is best illustrated in Figure 6, which shows the energy as a function of proton position for both protons moving from one carbon to the other, while the C–C separation is fixed at 3.2 Å and the initial hybridization, one sp^2, the other sp^3, is maintained.

Figures 5 and 6 provide us with an estimate, really an upper limit, of the activation energy to an intermolecular concerted hydrogen exchange. It exceeds 100 kcal/mol and so we proceeded to examine intramolecular mechanisms.

Returning to $(CH_3)_3PCH_2$ we first searched for the optimum conformation of the methyl groups. This was found to have each methyl group staggered with respect to the other three carbons bonded to phosphorus. The sixfold barrier to methylene rotation was, as anticipated, negligible. The all-staggered conformation is not, however, prepared for a least-motion concerted hydrogen transfer. The requisite geometry, **11**, is achieved by rotating one methyl group,
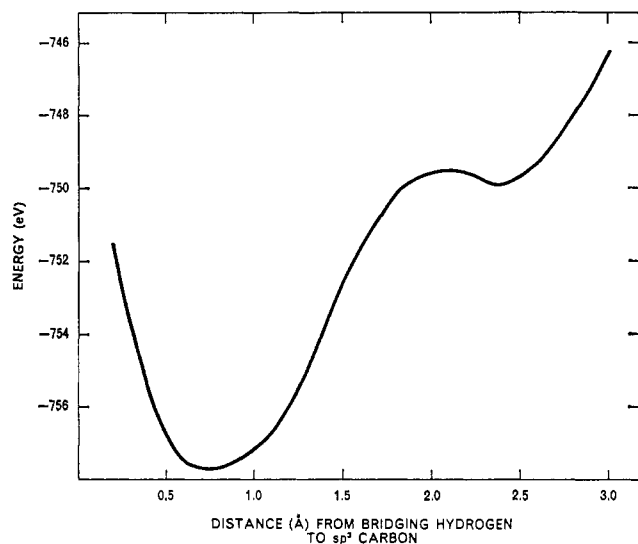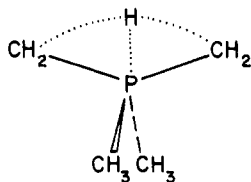

11
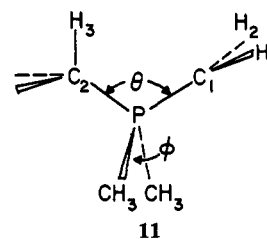
Figure 6. Potential energy as a function of distance of bridging hydrogen from sp³ carbon, when second carbon is sp². C-C distance is maintained at 3.2 Å.
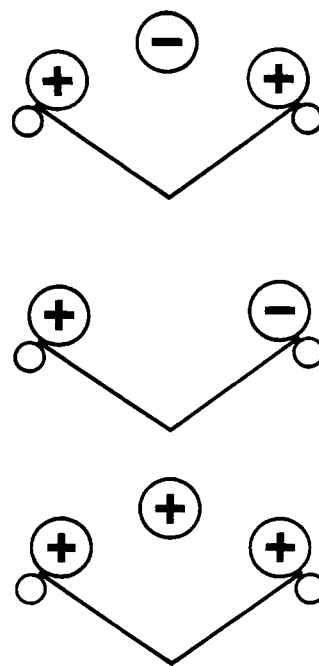

Figure 7. Molecular orbitals of an electron-rich three-center bond in the transition state for a 1,3 proton shift. The two lower orbitals are occupied.

the one from which a hydrogen will be transferred into an eclipsed position. The constraints operative in this system make such a process cost 0.25 eV, or approximately 6 kcal/mol.

Our initial exploration of the potential surface moved the hydrogen atom H_3 from C_2 to C_1, along an arc of constant $P-H_3$ distance. The computed activation energy for this motion is nearly as high as that for the intermolecular process. We did notice, however, that the energy of the transition state could be lowered by (1) having sp² hybridization at both C_1 and C_2, (2) shortening the $P-H_3$ distance, and (3) opening up the C_1PC_2 angle θ. We proceeded to study the symmetrical transition state, H_3 placed along the bisector of θ, allowing the transition state three degrees of freedom: the P-H distance, the angle θ, and the C_3PC_4 angle ϕ. The lowest energy was obtained for a P-H distance of 1.10 Å, $\theta = 135°$, $\phi = 112°$. At this point the P-H overlap population was a sizable 0.60. This fact coupled with the opening of the C_1PC_2 angle θ leads us to describe the transition state as a pentavalent phosphorus derivative where four centers (P, H, C_1, and C_2)

are bonded by four electrons.

We would like to elaborate on this bonding description. The normal molecular orbital scheme for the transition state for an abstraction of a proton by a carbanion would involve an electron-rich three-center bond.[34] The orbitals for such a system are shown in Figure 7. Of the five 3d orbitals on the phosphorus two interact most effectively and in a stabilizing manner with the two occupied orbitals of the three-center bond. They are d_{z^2} and d_{xz}, and their mixing is shown below. Indeed, analysis of the orbital overlap populations in

(34) R. Gleiter and R. Hoffmann, *Tetrahedron*, 24, 5899 (1968).

our transition state confirms the heavy contribution of d orbital σ bonding to the P-H bond. The exclusion of d orbitals from the computations destabilized various configurations by some 2.5-3.0 eV, and the d orbitals had their greatest stabilizing effect for the transition state.
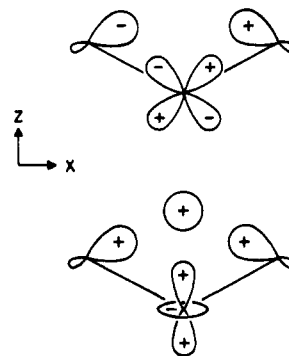

The importance of d orbitals in methylenetrimethylphosphorane can also be assessed by examining the hypothetical 1,3 shift in the propyl anion, $CH_3CH_2CH_2^-$. This system is analogous to $(CH_3)_3P=CH_2$ but the presence of carbon as the central atom would render a transition state involving the bonding of the moving hydrogen to the central atom most unlikely. Indeed it is found that the activation energies for the possible modes of rearrangement of the carbanion are very large. Furthermore, there is no tendency whatsoever for the moving hydrogen to approach the central carbon and no bond is formed between these two atoms.

However, the energy of the unusual pentavalent phosphorus transition state discussed above is still 2.94 eV above the starting geometry. We are thus hesitant to suggest this pathway for the observed hydrogen exchange, and tend to favor a catalyzed protonation–deprotonation sequence suggested in recent work.[32,33]

Stabilization of Carbon Diradicals by Intervening Phosphorus

The considerations of the previous section led us to examine a model dimethylene phosphorane CH_2PH_3-CH_2, **12**, in which two methylene groups occupy the apical positions on a pentavalent phosphorus atom.


12
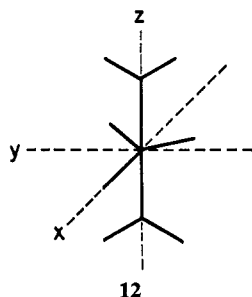
Such a species would appear to be a typical diradical. In the specified geometry of **12**, where both methylene groups lie in the yz plane, the two carbon atoms are 3.48 Å apart. The direct π overlap of their $2p_z$ orbitals is 0.0032, and accordingly one would expect the splitting between the symmetric (**13a**) and antisymmetric (**13b**) combinations of carbon $2p_z$ orbitals to be minute. A typical diradical situation would be

S   A
13a   **13b**
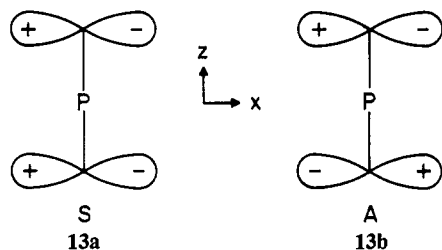
expected[35] and a triplet ground state would seem probable. However, the introduction of d orbitals on phosphorus modifies this picture dramatically. A splitting of 1.63 eV is produced with the A combination at lower energy. The gap could be sufficient to make the ground state of this species a singlet.[35]

The interaction is easy to analyze. Of the five 3d orbitals not one can by symmetry overlap with the S combination of carbon $2p_z$. Thus to a first approximation the S combination is unaffected by the PH_3 group. Only one d orbital, d_{zz}, can overlap with the A combination. It does so most effectively, stabilizing the A combination. After interaction the latter has the shape **14**.
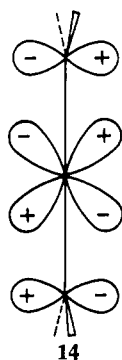
14

There are some further remarkable consequences of this interaction. *There is essentially no barrier to rotation of the PH_3 group* while keeping the CH_2 groups fixed. This is the result of the rotational properties of the 3d orbitals—no matter what the orientation of the PH_3 group there will always be available some linear combination of d_{xz} and d_{yz} to interact with the carbon orbitals. *There is a 1.45 eV barrier to rotating a single methylene group by 90°.* In the 90° form the symmetry[36] of the P 3d orbital set and the methylenes is D_{2d}, and the two methylene p orbitals, $2p_x$ and $2p_y$, transform as an e representation, as do d_{xz} and d_{yz}. Thus both methylene p orbitals are stabilized, and no gap is produced.

In summary the species **12** may be described as possessing a partial double bond, with the attendant torsional barrier. But it is a most peculiar double bond: first, it is an antiethylene,[35a] with the A orbital occupied, and second, **12** has in the midst of it a freely rotating phosphine group. A structural formulation such as **15** would be justified.

$$CH_2 \cdots PH_3 \cdots CH_2$$
15
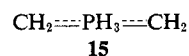
Unfortunately we calculated that species **16** and **17**,

16   **17**
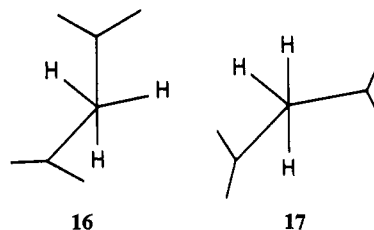
in which, respectively, one or both methylene groups are optimally placed in basal positions, are both by approximately 1 eV more stable than **12**. A pseudorotation itinerary[24,37,38] would convert **12** → **17** → **16**. We have also calculated that both **17** and **16** would collapse to **18**, an as yet unsynthesized but not improbable compound. It would thus appear that the

18
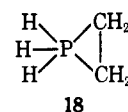
prospects for realizing **12** are not good. This is not necessarily so. First of all the substitution of sterically bulky groups for the phosphorus hydrogens would favor the extreme of **12**. Second the pseudorotation process which converts **12** into **17** is a forbidden reaction.[39] Species **12** has two electrons in the molecular orbital **14**. A pseudorotation takes this molecular
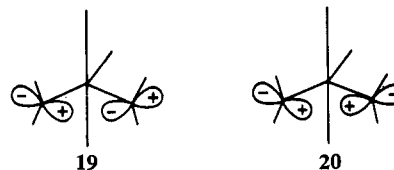

19   **20**

(35) (a) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); (b) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967); (c) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *ibid.*, **90**, 1485 (1968); (d) R. Gleiter and R. Hoffmann, *ibid.*, **90**, 5457 (1968); *Angew. Chem.*, **81**, 225 (1969).

(36) The actual symmetry is, of course, C_s. But the PH bonds, which reduce the symmetry from D_{2d} to C_s, are a small perturbation.

(37) F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968).

(38) F. Ramirez, *ibid.*, 1, 168 (1968).

(39) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965); *Accounts Chem. Res.*, 1, 17 (1968); R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

orbital into the higher energy unfilled MO of **17**, represented in **19**, and not into the lower energy occupied MO, **20**. We would encourage synthetic efforts directed toward derivatives of species **12**. We would also like to direct the reader to some similarly inspired work by Ashe[40] on the ability of phosphorus to transmit conjugation.

(40) A. J. Ashe, III, *Tetrahedron Lett.*, 359 (1968).

Reaction of Aqueous Vanadium(II) Ions with Maleic Acid, Fumaric Acid, and Derivatives. II. Kinetics of Reduction and Isomerization

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Abstract: Kinetic data on the reduction by V_{aq}^{2+} of maleic, fumaric, citraconic, and chloromaleic acids as well as methyl maleate were found to fit the general rate expression $R = (k_a[A] + k_b[A][H^+] + k_c[A]^2 + k_d[A]^2[H^+])[V_{aq}^{2+}]^2$, where R is the rate and $[A]$ the concentration of the organic acid. With the half-ester, the rate law contains a term inverse in hydrogen ion concentration. In the isomerization of maleic to fumaric acid, caused by vanadium(II) ion, there are two terms in the rate law, one independent of and the other inverse in $[H^+]$, both first order in maleic acid and vanadium(II) ion. The empirically determined rate constants, activation energies, etc., are interpreted on the basis of a mechanism which combines complex ion formation, reduction, and isomerization.

It has already been shown[1] that the reduction by V_{aq}^{2+} of maleic acid, fumaric acid, and some of their derivatives, require two vanadium(II) ions for each molecule of unsaturated acid, V(II) being oxidized to V(III). The only products detected were those corresponding to this stoichiometry; they were therefore formed by an overall two-electron transfer process.

In the present paper we determine the empirical rate laws for the reduction under a variety of conditions in order to obtain information about the main paths leading eventually to reduction and the composition of the activated complexes involved. We also tried to follow in more detail the various stages of the reaction as well as the sequence of these stages. The two-electron change seems to break down into distinct steps that can be subject to independent experimental investigation.

One of the steps of the overall reaction is the complex ion formation equilibrium. Evidence already presented[1] indicates that the equilibrium established between V_{aq}^{2+} and the organic acids studied may be related to electron transfer from V_{aq}^{2+} to the system of the conjugated double bonds. It seems likely that complex formation is the first step in the interaction and that it is essential for the subsequent reactions. Complex formation provides the necessary preliminary placement of the reactants in space, in relative positions favorable for further reaction. In this paper we attempt to clarify this point further and also broaden the experimental basis for the study of the other stages of the interaction between V_{aq}^{2+} and the conjugated dibasic acids.

One of the consequences of this interaction is isomerization of maleic acid to fumaric acid, catalyzed by vanadium(II) ion. Preliminary results[2] indicate that complex formation may be important in this respect too. We here compare the kinetics of reduction to the kinetics of isomerization.

Experimental Section

Most of the experimental techniques used here have already been described.[1]

The progress of the reaction was in most cases followed spectrophotometrically using a Cary 14. The mixing of the reactants was done direct in the spectrophotometer cells.

The extinction coefficients of V_{aq}^{2+} and V_{aq}^{3+} used[3] agree with those reported by Gordon and Tewari.[4] The extinction coefficients of the complexes forming in the system depend on hydrogen ion concentration. Measurements at two or more wavelengths are necessary in order to determine the concentrations of all the vanadium species present. Appropriate wavelengths for most cases were 400 and 510 mμ. The extinction coefficients of V_{aq}^{2+} and V_{aq}^{3+} at 510 mμ have essentially the same value and any change in absorbance at this wavelength is practically due to the change in the concentration of the complex.

Results

1. Reduction of Maleic Acid (HM). In the hydrogen ion concentration range from 0.43 to 2.0 M the two complexes between V_{aq}^{2+} and maleic acid have comparable concentrations.[1] Two series of kinetic runs were made in this acid range, one with a large excess of maleic acid and the other with a large excess of V_{aq}^{2+}.

(1) E. Vrachnou-Astra, P. Sakellaridis, and D. Katakis, *J. Amer. Chem. Soc.*, 92, 811 (1970).

(2) E. Vrachnou-Astra and D. Katakis, *ibid.*, 89, 6772 (1967).
(3) E. Vrachnou-Astra, Doctor of Engineering Thesis, National Technical University of Athens, 1968.
(4) G. Gordon and P. H. Tewari, *J. Phys. Chem.*, 70, 200 (1966).