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Molecular and Electronic Structure of Phosphonium Cyclopropylide ($H_3P{=}C(CH_2)_2$): A Theoretical Study

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Abstract: Theoretical studies have been carried out for a phosphonium cyclopropylide model, $H_3P{=}C(CH_2)_2$. The molecule was shown to have a ground-state equilibrium geometry (structure I) with a pyramidal carbanion center, the details being in satisfactory agreement with experimental findings for the triphenylphosphine cyclopropylide homologue. One of the PH_3 hydrogen atoms is affected by the carbanion (partial) negative charge, and its position shows substantial distortion away from the idealized tetrahedral phosphorus geometry. In the energy profile for the carbanion inversion the stationary point of maximum energy (two imaginary vibrational frequencies) occurs not for the planar carbanion configuration but well beyond in a situation with a dihedral angle H0PC1C2 of 123° instead of 90°. The rotated configuration (a genuine transition state) is virtually the eclipsed analogue of structure I. The barriers to inversion and rotation are predicted to be 6.3 and 5.8 kcal, respectively. Calculated bond distances, bond angles, dihedral angles, total energy values, and total electron populations on atoms are given for all three conformations. Atomic orbital components and energies of frontier orbitals of the ground state are also discussed.

Introduction

Chemical bonding and the molecular structure of phosphorus ylides are classical problems of longstanding interest, which is reflected in an ever increasing number of publications on pertinent experimental or theoretical investigations. In the last 2 decades about 35 molecular structures of ylides have been determined by X-ray[1] or electron diffraction.[2] The ylidic electronic structure has been probed by dipole moment studies,[3] PES measurements,[4] ESR experiments,[5] multinuclei NMR,[6] vibrational[7] and UV[8] spectroscopy, and mass spectrometery.[9] Following the rapid advancement of theoretical chemistry, computational methods at various levels of sophistication were applied to simple model systems,[10] particularly of the type $R_3P{=}CH_2$[4a,4b,6h,8a,11] and led to a number of mostly complimentary descriptions of the bonding situation in ylides of phosphorus, be they real or hypothetical (like $H_3P{=}CH_2$).

It appears to be generally accepted that phosphorus ylides ("phosphonium ylides", "alkylene phosphoranes") should be referred to as molecules (or ions) in which a phosphonium center of nearly tetrahedral geometry is directly attached to a carbanionic center, as implied by one of Wittig's original canonical formulas:

$$R_3P^+{-}CR'^-_2 \leftrightarrow R_3P{=}CR'_2$$

The nature of the electronic interaction between phosphorus and the ylidic carbon, however, is already a point of controversy, not the least because of uncertainties about the actual geometry of the carbanion, and hence its hybridization. The significance of d orbital participation is closely associated with this problem, since a planar sp^2 geometry for the carbanion is believed to optimize (p → d) π interactions. This argument is questionable, since the short "P=C" distances found in ylides can be accounted for simply by a polarization effect of the d orbitals and even by considering solely the heteropolar (electrostatic) forces without any d orbital contributions.[12]

For $H_3P{=}CH_2$ a trigonally planar *carbanion* geometry has been predicted by both semiempirical and ab initio calculations,[10] but deviations from planarity are not associated with a great increase in energy. Rotation about the ylidic bond is virtually unrestricted, with activation barriers smaller than 1 kcal/mol. Structural studies seemed to bear out these results, as all molecular structures determined until recently showed indeed *planar* carbanion geometry.[1,2]

In this situation it was of great interest that the X-ray diffraction analysis of the triphenylphosphonium cyclopropylide provided unambiguous proof for a *pyramidal* carbanion geometry[13] (Figure 1). In fact, the angle between the ylidic bond and the three-membered ring is close to 60° and thus in keeping with the standard ligand arrangements of σ-bonded substituents of cyclopropane (60°).

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Table I. Predicted Bond Distances (nm), Bond Angles (deg) and Dihedral Angles (deg) in the Phosphonium Cyclopropylide Model[a]

triphenylphosphonium cyclopropylide			I (equilibrium)[b]	II (transition state)[c]	III (two imaginary vibr freq)[d]
PC1	181.5	PH0	141.3	138.6	139.8
PC2	180.0	PH10	138.1	139.4	139.2
PC3	181.6	PH11	138.1	139.4	139.2
PC4	169.6	PC1	168.2	168.0	163.4
C4C41	152.6	C1C2	150.4	150.6	148.6
C4C42	152.6	C1C3	150.4	150.6	148.6
C41C42	149.9	C2C3	152.8	152.5	153.7
C1PC4	109.7	H10PC1	110.9	118.6	116.4
C2PC4	110.2	H11PC1	110.9	118.6	116.4
C1PC2	107.1	H10PH11	104.6	101.9	103.8
C3PC4	117.0	H0PC1	129.0	115.4	120.3
C1PC3	105.3	H0PH10	99.3	99.5	98.3
C2PC3	107.0	H0PH11	99.3	99.5	98.3
C41C4P	117.1	C2C1P	127.6	127.1	141.8
C42C4P	117.8	C3C1P	127.6	127.1	141.8
C42C4C41	58.8	C2C1C3	61.1	60.9	62.3
C42C41C4	60.6	C1C2C3	59.5	59.6	58.9
C41C42C4	60.6	C1C3C2	59.5	59.6	58.9
inclination (P-C_{ylide} vs. triangle)	58.0		44.9	45.6	23.4
		H0PC1C2	39.9	140.6	123.3
		PC1C2H30	134.5	12.1	35.3
		PC1C2H20	12.7	134 7	112.9

[a] As determined for the equilibrium ground state (structure I), the stationary point for carbanion inversion (structure III), and the transition state (structure II) reached after carbanion inversion (for details see text). The experimental data for triphenylphosphonium cyclopropylide (by X-ray diffraction)[13] are given for comparison. See Figure 2 for numbering of atoms. [b] 458.226 13 hartree (0.0 kcal). [c] 458.216 86 hartrees (5.8 kcal). [d] 458.216 13 hartrees (6.3 kcal).

This result prompted a reinvestigation of the molecular orbital (MO) description of the prototype $H_3P{=}C(CH_2)_2$, which had been considered previously in two other studies, with a planar carbanion geometry at the extended Hückel MO level[11a] and with both planar and pyramidal geometries in CNDO/2- and MINDO/3-type calculations.[6h] A deviation from planarity was derived from these studies and from NMR correlations. The latter were subsequently found not to be meaningful, being based on erroneous data.[13]

Table II. Total Gross Population on Atoms as Determined from the Mulliken Population Analysis of the Three Phosphonium Cyclopropylide Model Configurations[a]

atom	I (equilibrium)	II (transition state)	III (two imaginary vibr freq)
1. C1	6.512	6.458	6.560
2. P	14.458	14.427	14.419
3. H0	1.050	0.988	1.023
4. H10	0.972	0.998	1.000
5. H11	0.972	0.998	1.000
6. C2	6.374	6.366	6.349
7. C3	6.374	6.366	6.349
8. H20	0.835	0.841	0.829
9. H21	0.835	0.841	0.829
10. H30	0.809	0.813	0.821
11. H31	0.809	0.813	0.821

[a] For atom numbering see Figure 2.

A temperature-dependent NMR investigation of $(C_6H_5)_3P{=}C(CH_2)_2$ has shown that inversion at the ylidic carbon is rapid on the NMR time scale even at −110 °C, indicating a very low activation energy for the inversion process in solution. Apart from a calculation of the optimized ground-state geometry of the $H_3P{=}C(CH_2)_2$ model, it was therefore one of the goals of the work presented in this report to determine the energy differences relative to the expected transition state and the inversomer obtained in the carbanion inversion.

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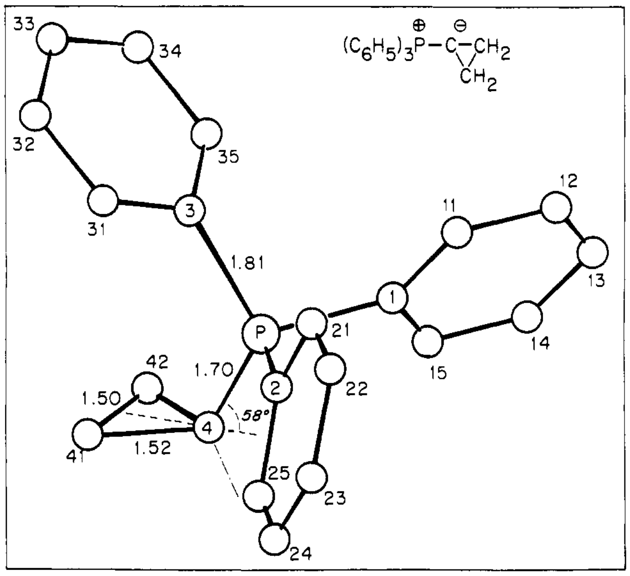

Figure 1. Molecular structure of triphenylphosphonium cyclopropylide as determined by X-ray diffraction.[13]

Theoretical Approach

Unfortunately, previous experience has shown that the reliable description of carbanions requires large basis sets, including diffuse s and p functions. This is especially true for the study of inversion barriers.[14] However, the presence of the positively charged phosphorus next to the carbon anion in ylides means that the charge buildup will be not one full electron but considerably less. Thus a set of orbitals similar to those used to describe inversion in a molecule like ammonia should be suitable. Carlsen et al.[15] have found that the smallest set of orbitals to give a reasonable barrier for ammonia is a double ζ plus polarization set. Hence a Dunning double ζ basis[16a] was used with a set of six d functions (exponent 0.75). Due to the size of the phosphonium cyclopropylide it was inadvisable to use such a large basis set on the nonylidic carbons. Thus only a double ζ basis was used for them.[16a] This inequality between the carbons is not expected to have any major effects. However, research by Dixon and co-workers[17] suggests that the omission of d functions on the other two carbon atoms may result in some overestimation of the inversion barrier.

Test calculations with and without one set of more diffuse p functions on the ylidic carbon were also carrier out. However the energy lowering relative to the straight double ζ basis was only 0.000 67 hartree, and such functions were thereafter omitted. In contrast the energy lowering due to the addition of ylidic carbon d functions is substantial, 0.024 87 hartree.

A double ζ^{16b} plus polarization (exponent 0.6) basis set was employed to describe phosphorus, as Lischka has shown that such a basis set is necessary to describe the quantitative features of phosphorus bonding in the related model ylide H_3PCH_2.[10d] For hydrogen it was decided, because of the size of the ylide, to use only a Dunning double ζ basis,[16] scaled by a factor of 1.2. The complete technical designation of this contracted Gaussian basis set is thus P(11s 7p 1d/6s 4p 1d), C(9s 5p 1d/4s 2p 1d), H(4s/2s). Determination of the geometrical structures was carried out via analytic gradient techniques, which guarantee stationarity with respect to variations of the coordinates of the system.[18] All geometries were determined by assuming a plane of symmetry for the molecule. This plane contained the unique hydrogen bonded to phosphorus, the phosphorus atom itself, and the ylidic carbon. Vibrational analyses later proved this assumption to be valid.

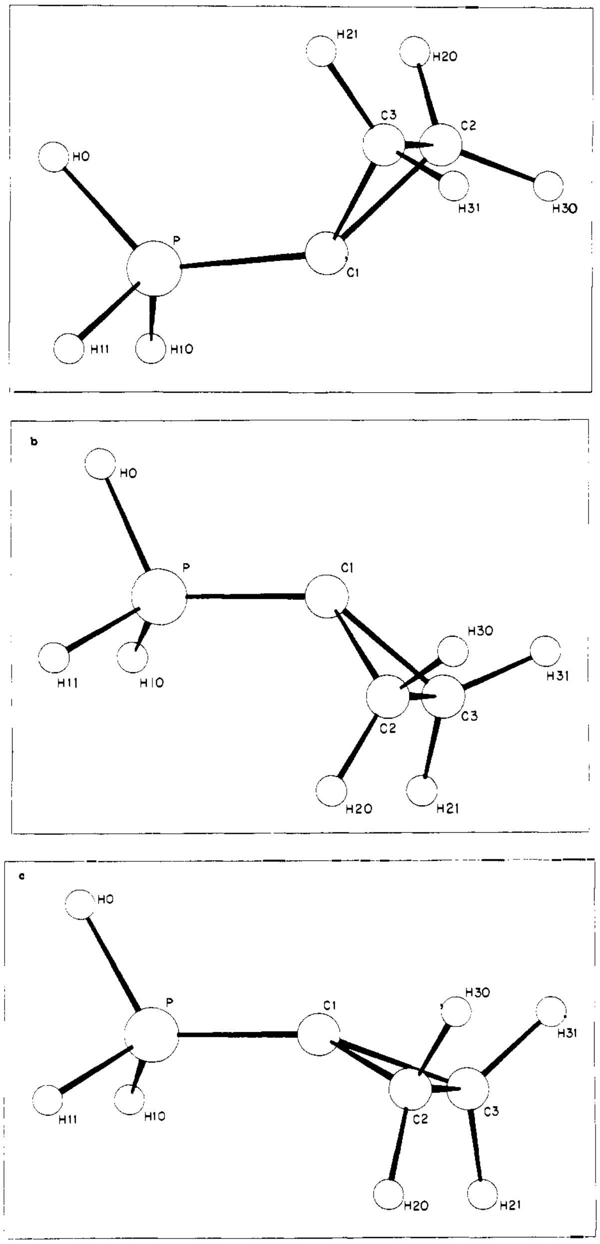

Figure 2. Perspective drawing of the phosphonium cyclopropylide model with molecular dimensions calculated for (a) the ground state (structure I), (b) the transition state for rotation (structure II), and (c) structure III, a stationary point having two imaginary vibrational frequencies (for details see text and Figure 3).

Pictorial Results. The final results for the ground-state equilibrium geometry of the molecule (structure I) and the charge distribution (as indicated by the Mulliken population analysis) are summarized in Tables I and II. . These tables also contain the corresponding data for the conformation that represents the energy maximum in the profile of the carbanion inversion process, referred to as structure III, and finally the configuration of the stationary point (structure II) reached as the cyclopropyl ring folds to the opposite side of the original ground-state equilibrium geometry. Note that the latter conformation is not geometrically identical with the ground state, because the cyclopropyl ring is in a different rotatory position relative to the PH_3 group: structure I is a staggered, structure II an eclipsed conformation. The molecular geometries are represented by the Cartesian coordinates of the 11 atoms and the meaningful atomic distances, bond angles, and dihedral angles. The perspective drawings of the three

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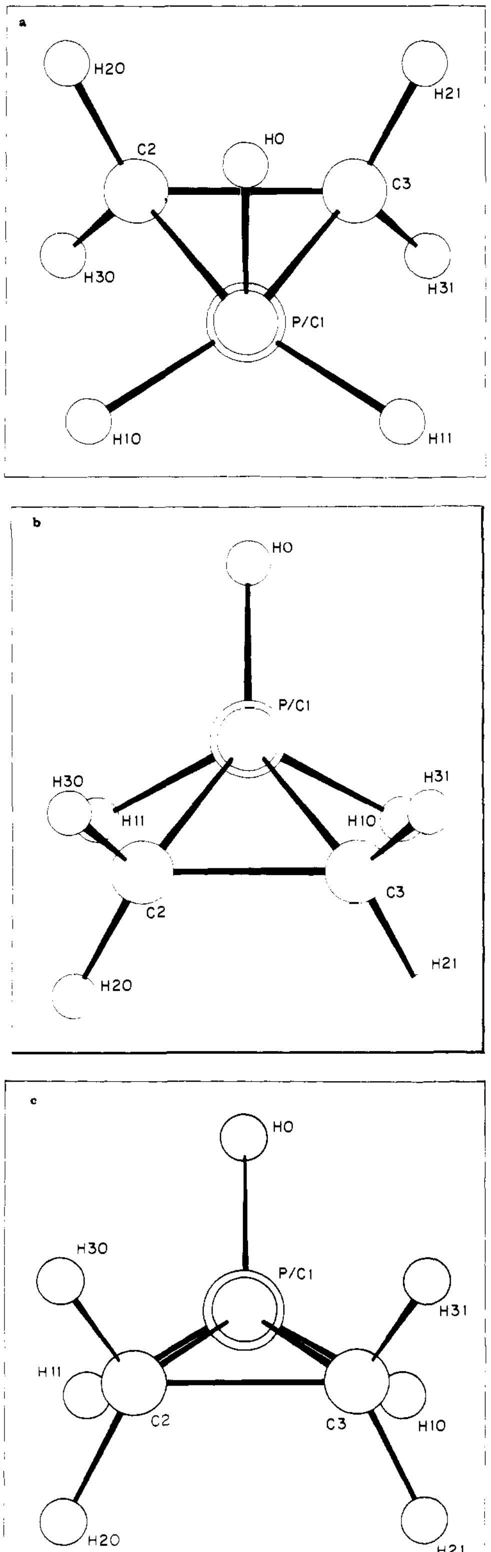

Figure 3. Projection of the phosphonium cyclopropylide model along the P–C1 axis ("ylide bond") with the molecular dimensions calculated for (a) the ground state (structure I), (b) the transition state for rotation (structure II), and (c) structure III, a stationary point having two imaginary vibrational frequencies (for details see text and Figure 2).

configurations in Figure 2 are complementary to the three projections parallel to the P–C_{ylide} bond shown in Figure 3.

From the latter figures the different rotamers are again immediately obvious. Structure II would require a 60° rotation of the PH_3 group around the P–C_{ylide} axis to relax to the configuration of structure I. A compilation of the energies of the individual molecular orbitals and their individual atomic orbital components are available from the authors on request. Some of these data are used in the discussion below where appropriate. Energy gradients for specific stretching and bonding movements were also calculated. They are useful to characterize the various energy profiles associated with distortions of the individual geometries.

Table III. Breakdown of the Three Highest Occupied Molecular Orbitals for the Equilibrium Geometry of $H_3P{=}C(CH_2)_2$ According to Contributions from Different Atomic Orbitals

orbital	14a' (0.2755)[a]	6a" (0.4035)[a]	13a' (0.4070)[a]
C1			
s	0.07	0.00	0.02
p	0.63	0.43	0.10
d	0.00	0.01	0.01
P			
s	0.01	0.00	0.01
p	0.05	0.00	0.07
d	0.04	0.01	0.00
H0			
s	0.08	0.00	0.00
H10 = H11			
s	0.01	0.02	0.01
C2 = C3			
s	0.00	0.00	0.00
p	0.03	0.21	0.37
H20 = H21			
s	0.01	0.02	0.02
H30 = H31			
s	0.02	0.02	0.00

[a] Orbital energy (hartrees).

Ground-State Equilibrium Configuration (Structure I). The calculations have clearly shown that phosphonium cyclopropylide indeed has an equilibrium geometry with a carbanion center C1 of a pronounced *pyramidal* array of the neighboring atoms (P, C2, C3). With valence angles PC1C2 = PC1C3 = 127.5° and C2C1C3 = 61.1° the orientation of the ylidic bond relative to the cyclopropyl plane is 44.9°. These values are in reasonable agreement with the experimental data for the triphenyl (!) homologue (117.1, 117.8, and 58.8°, respectively).[13] The agreement is even better for the *PC1 bond length* of 168.3 pm in the model as compared to 169.6 pm in the triphenyl homologue and for the ring distances C1C2 = C1C3 = 150.4 pm and C2C3 = 152.8 pm [152.5 and 149.9 pm in $(C_6H_5)_3P{=}C(CH_2)_2$].

In the triphenylphosphonium group of the cyclopropylide, one *phenyl* group is unique in that it forms valence angles at phosphorus that differ markedly from the remaining bond angles at phosphorus (see C3PC4 in Table I). This situation is met again for the *unique hydrogen H0* in the model with its longer P–H0 distance (141.3 pm as compared to 138.1 pm for P–H10 and P–H11) and its angle H0PC1 = 129.0°. Obviously this hydrogen is interacting most strongly with the carbanion lone pair, and the resulting repulsive forces lead to a substantial distortion away from the idealized tetrahedral phosphorus geometry.

The Mulliken population analysis (Table II) ascribes a significant negative charge to H0 and, of course, to C1 (–0.05 and –0.51 electrons, respectively), suggesting again repulsive Coulombic forces. The remaining Mulliken population analysis data characterize phosphorus as an onium center (+0.54), as expected. Cyclopropyl hydrogens are also positive, cyclopropyl carbons negative. The *dipole moment* of the ground-state molecule is μ = 3.34 D. No experimental value is available for comparison, but estimations based on data for noncyclic ylides[3] could lead to a value of around 4 D.

The molecule has 20 occupied MO's with a frontier HOMO of ionization potential IP(20) = 0.2755 au, according to Koopman's theorem. Surprisingly, this orbital is largely a 2p orbital (of C1) with an out-of-phase contribution from H0. The second highest occupied MO is a ring-bonding orbital comprised mainly of p functions on C1, C2, and C3 [IP(19) = 0.4035]. The population analysis for the highest three occupied orbitals is shown in Table III. The molecular orbital picture does not impose a hybridization upon the ylide carbon, C1. Nevertheless, one can deduce from the orbitals an approximate hybridization midway between sp^2 and sp^3.

Pathway for Inversion (Structure III). The energy difference between structures I and III leads to a calculated barrier to carbanion inversion of 6.3 kcal/mol. Note that structure III has two imaginary vibrational frequencies, i.e., it is a maximum with respect to both inversion and rotation. It is very important to note that this energy maximum does *not* correspond to the situation where the ylidic carbon atom C1 is in a planar configuration (P*C1*C2C3). The conformational constraints caused by the relative orientation of the PH_3 group apparently shift the maximum toward larger dihedral angles H0–P–C1–C2. For the almost planar situation (H0–P–C1–C2 = 92.5°) the energy is calculated to be −458.217 98 au, or 1.2 kcal lower than for structure III (−458.216 13 au). In the projectional drawing in Figure 2c this means that the C2–C3 horizontal is well above the P–C1 axis, whereas P–C1 would point toward the center of C2–C3 for the fully planar configuration at C1.

In structure III, characterized by a dehedral angle H0–P–C1–C2 = 123.2° with its inverted P*C1*C2C3 pyramid, the P–C1 ylide bond distance has been shortened to 163.4 pm. This value is extremely low and in fact lower than any of the experimental values available to date. It may indicate, however, that "P═C bonding" is indeed an optimum at a virtually planar ylidic carbon, were it not that other factors destabilize such a configuration, as it is evidently the case for $H_3PC(CH_2)_2$. The angle between the PC1 bond and the cyclopropane ring is −23.4° for structure III. Note, however, that this initially surprising result is consistent that Hammond's postulate. That is, for the exothermic (by 5.8 kcal) inversion of II to I, the stationary point structurally resembles structure II. Most other of its structural and charge distribution data follow more or less expected trends.

Transition State (Structure II). As pointed out above, the transition state for rotation is fixed in an eclipsed conformation regarding the position of the PH_3 group relative to the cyclopropane moiety (Figure 2b). It is therefore as expected that the energy of this conformation is higher (by 5.8 kcal) than that of the equilibrium geometry (structure I) with its relaxed staggered conformation. The barrier is of course much greater than that predicted (~1 kcal) previously[10] for the model ylide H_3PCH_2. Calculated bond lengths are similar to those already found for structure I. The dihedral angle H0–P–C1–C2 = 141.2° is about complementary to the 39.8° value for structure I, showing that the dihedral angle is indeed a reasonable indicator for the state of the inversion process. Accordingly, the angle of the ylidic P–C1 bond relative to the cyclopropane ring is −45.6°, very similar to the arrangement in structure I (+44.9°).

The three hydrogen atoms attached to phosphorus show very similar P–H distances, HPH or C1PH angles, and net atomic charges (from Mulliken population analysis), and there is accordingly no evidence for a unique bonding situation for H0 as compared to structure I. No doubt this finding is again the consequence of the eclipsed conformation. The cyclopropane ring is a nearly equilateral triangle in all three stationary point structures (I–III). The Mulliken population analysis also points to a roughly similar charge distribution for the cyclopropane part of the models.

Vibrational Analyses. In order to precisely ascertain the nature of the stationary point geometries reported above, it was necessary to carry out vibrational analyses of structures I and III. Structure I was found to be a genuine equilibrium geometry, this is, all vibrational frequencies are real. Structure III, lying 6.3 kcal higher in energy, was found to have *two* imaginary vibrational frequencies. This means that structure III represents a maximum on the potential-energy hypersurface with respect to both inversion and rotation. It follows that structure II, lying 5.8 kcal above the equilibrium geometry, is the true transition state.

Table IV. Predicted Vibrational Frequencies (cm^{-1}) for $H_3P{=}C(CH_2)_2$

struct I (equilibrium)			struct III		
A'	3372	C–H	A'	3356	C–H
A''	3356		A''	3340	
A'	3280		A'	3267	
A''	3269		A''	3257	
A'	2726	P–H	A'	2635	P–H
A''	2720		A''	2628	
A'	2450		A'	2525	
A'	1652		A'	1658	
A''	1624		A''	1625	
A'	1428	P=C	A'	1550	P=C
A'	1339		A'	1340	
A''	1281		A''	1338	
A''	1274		A''	1264	
A''	1247		A''	1247	
A'	1196		A'	1184	
A'	1179		A'	1160	
A'	1142		A'	1116	
A''	1044		A''	1086	
A'	1014		A''	1021	
A''	997		A'	1012	
A'	887		A'	904	
A'	795		A''	828	
A''	761		A'	810	
A'	623		A'	626	
A''	271		A''	247	
A'	212		A'	158i	ring inversion
A''	180		A''	229i	PH_3 internal rotation

Predicted vibrational frequencies are given in Table IV. However, it should be noted that frequencies predicted at this level of theory are typically ~10–12% higher than the observed fundamentals.[22] The assignment of the phosphorous–carbon stretching frequency is not entirely unambiguous, but the normal modes at 1428 (equilibrium) and 1550 cm^{-1} (structure III, two imaginary vibrational frequencies) seem to best fit this description.

Discussion

This theoretical study is connsistent with the experimental finding[13] that ylidic carbon atoms can adopt a pyramidal ground-state configuration at least in the special situation of the cyclopropylides, where drastic ring strain and a unique state of bonding have to be assumed. The predicted barrier to rotation about the P–C bond is 5.8 kcal, in harmony with the experimental finding that this barrier is ≤8 kcal. The results parallel previous reports on the unusual configurational stability of *aziridines* as compared to amines,[19] both of which are isoelectronic with the ylidic carbanionic fragments. Spectroscopic and mechanistic data for phosphonium[13] and sulfonium[20] cyclopropylides had also indicated a preference of these systems for a pyramidal geometry.

There are other implications associated with the details of the theoretical predictions, however, which should be considered. As judged from the equilibrium bond distance P–C1, the ylide bond originating from a pyramidal carbon appears not to be very different from bonds observed with planar carbon atoms. A very flat energy profile for the carbanion inversion is thus suggested and in fact observed both in the calculations[10] and experiment.[13a] Also, conformational effects are perhaps often underestimated in the discussion of ylidic bonding. The relatively short P–C1 contact and the partial negative charge at C1 clearly can cause distortions at the phosphane moiety, as also detected experimentally in a study of hindered rotation in ylides and their com-

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plexes.[21] The above examples are illustrative of the importance of an inversion process associated with a rotational movement to reach again a true energy minimum state.

Unfortunately, the present unavailability of the model compound $H_3P{=}C(CH_2)_2$ precludes further cross-checking of the calculated data by experiments. Photoelectron spectroscopy and dipole moment studies would be the obvious means of control. Nevertheless, data from simple homologues may well be sufficient to probe some of the expected or unexpected details.

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Ab Initio Study of the Hydration of Ketenimine ($CH_2{=}C{=}NH$) by Water and Water Dimer

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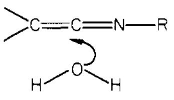
Abstract: The detailed reaction pathway for the hydration of the ketenimine $CH_2{=}C{=}NH$ by H_2O and by $(H_2O)_2$ has been investigated by ab initio methods using STO-3G, 4-31G, and 6-31G** basis sets. The optimized geometries of the points on the reaction surface were determined by the gradient method. The preferred reaction pathway is with the water dimer through a "preassociation" mechanism where a small amount of initial bonding occurs via attack (by oxygen) at the central carbon of the ketenimine. Proton transfer (to the β-carbon) then occurs at or just after the transition state without any appreciable changes in the C–O bond distance. The reaction (which is calculated to have an activation barrier of 22 kcal mol^{-1} in 4-31G) is therefore concerted but highly asynchronous.

Ketenimines (>C=C=N–), which are tautomeric with aliphatic nitriles ($>CC{\equiv}N$), belong to the general class of cumulenes (>C=C=X).[1] They are in general highly reactive and undergo electrophilic and nucleophilic substitution, together with cycloaddition reactions. They have also attracted attention (when generated in situ) as condensation agents in peptide[2] and related syntheses. In these reactions, the ketenimine, in effect, becomes hydrated to the corresponding amide (>CHCONH–).

We have previously reported on the kinetics of the addition of water to ketenimines.[3] With simple *N*-alkylketenimines reaction occurs via rate-determining proton transfer to the terminal carbon (C_β) from H_2O (pH >7) or from H_3O^+ (pH <7) or from other general acids (such as CH_3CO_2H, RNH_3^+) that are present. The evidence for rate-determining protonation on carbon (rather than on nitrogen) was indirect, coming largely from structural studies. The preferred carbon site is supported by ab initio calculations[4] on the protonation of the model ketenimine $CH_2{=}C{=}NH$ (**1**) that show that $CH_3C{\equiv}NH^+$ (**2**) is the most stable species compared to $CH_2{=}C{=}NH_2^+$ (**3**) or $CH_2{=}CH{=}NH^+$ (**4**).

From the basis set 4-31G, the β-protonated ketenimine **2** is calculated to be 10.5 kcal mol^{-1} more stable than the N-protonated form ($CH_2{=}C{=}NH_2^+$ (**3**)). Although this energy difference is less than that calculated for β-C protonation of ketene compared with O-protonated form (37 kcal mol^{-1}),[5] it is sufficient to indicate with confidence the thermodynamically favored site of protonation. The large pH-independent rate of reaction shown by *N*-alkylketenimines in the region pH 7–13 could be due to water acting as a nucleophile at the central carbon (see **5**) or acting as a general acid to protonate carbon (**6**) or nitrogen (**7**). Alternatively one or more water molecules may be acting in a concerted fashion in which two or more processes occur in the transition state. We have now examined the reaction pathway in detail using ab initio methods using the simple model ketenimine $CH_2{=}C{=}NH$ and one or two water molecules as the reactants.



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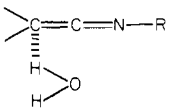

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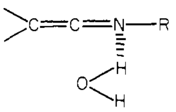

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Table I. Calculated (4-31G) Energies (in au) for the Ketenimine in Deformed Geometries[a]

structure[b]	α, deg 170	155
8	−131.67249	−131.66265
9	−131.66925	−131.65361
10	−131.67103	−131.65345
11	−131.66606	−131.64374

[a] Total energy of ketenimine is −131.67308 au. [b] See Figure 1.

Experimental Section

Calculation Methods. The three basis sets of Pople were used for the ab initio SCF calculations: the minimal STO-3G,[6] the split valence set 4-31G,[7] and the basis set with polarization functions, 6-31G**.[8] The STO-3G and 4-31G were used to optimize the geometry of stationary points on the energy surfaces. With these geometries we have then

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