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The Theoretical Structures of Neutral, Anionic, and Lithiated *P*-Allylphosphonic Diamide

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Theoretical structures have been calculated for *P*-allylphosphonic diamide at the HF/3-21G$^{(*)}$//HF/3-21G$^{(*)}$ level for the gas phase neutral, **1**, free anionic, **2**, and lithiated species, **3** (Figures 1–3). The bonding in the phosphondiamide unit of the neutral species strongly suggests hyperconjugative interactions between the amide nitrogens and the C–P–O moiety. The free anion was found to exist in both *E* and *Z* forms in which the planar allylic π-system is aligned with the P–O bond, with the *E* isomer, **2a**, preferred by 1.8 kcal/mol. Inclusion of lithium was found to distort the allyl system and change the relative energy ordering such that the *Z* isomer, **3b**, is preferred by 8.5 kcal/mol (3-21G$^{(*)}$) or 5.5 kcal/mol (6-31+G*//3-21G$^{(*)}$). In both isomers the lithium atom makes both oxygen and carbon contacts. The anions were characterized by charge localization and highly ionic bonding. Comparisons of the theoretical conclusions with NMR spectroscopic data for the anions showed good agreement in charge distribution and structure of the anion.

Introduction

The chemistry of heteroatom-stabilized anions has been a fertile area of investigation for synthetic, physical, and theoretical organic chemists alike. The study of heteroatom-stabilized *allyl* anions is an important subset of this field and one in which, for the moment, synthetic organic chemists are the most active. Stabilizing groups based on many different elements at various oxidation states have been explored,[1] and among these nitrogen,[2] oxygen,[1b,3] sulfur,[4] silicon,[5] and phosphorus[4i–j,6] have demonstrated significant potential for synthetic applications. In particular, recent advances have focused on the use of chrial, heteroatomic prosthetic groups to control diastereoselectivity. Our interest in this area, stimulated by recent observations in the carbanion-accelerated Claisen rearrangement,[7] is the development of stereoselective carbon–carbon bond-forming reactions using auxiliary-based, chiral, phosphorus-stabilized allyl anions.[8] To understand the issues of reactivity shown in Scheme I (α/γ-selectivity, and for chiral G*, diastereoselectivity) we chose to investigate the structure of these species spectroscopically[8a] and theoretically. From a theoretical standpoint both phosphorus-stabilized anions[9] and simple allyl anions[10] (and metalloderivatives[10e–f]) have been well studied. By comparison, the bonding and structures of heterosubstituted allyl anions have scarcely been examined.[11] In this paper we describe our studies on the equilibrium structures for *P*-allylphosphonic diamide (**1**), the derived anion (**2**), and the lithiated species (**3**), Chart I.

Scheme I

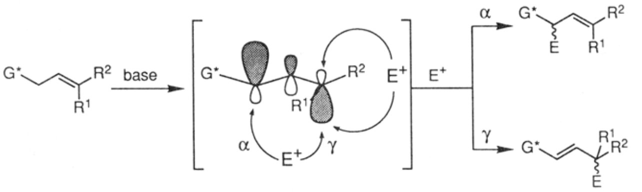
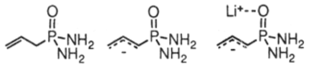


Chart I



1 **2** **3**

Table I. Selected Calculated Equilibrium Parameters for 1[a]

parameter	**1a**	**1b**	**1c**
energy, au	−640.111 33	−640.110 04	−640.110 05
relative, kcal/mol	0.0	0.8	0.8
bond lengths, Å			
P–O	1.470	1.468	1.473
P–N(1)	1.644	1.650	1.645
P–N(2)	1.650	1.647	1.652
P–C(1)	1.808	1.809	1.805
C(1)–C(2)	1.513	1.510	1.526
C(2)–C(3)	1.317	1.317	1.319
bond angles, deg			
O–P–N(1)	112.0	112.2	111.6
O–P–N(2)	119.3	118.0	119.1
O–P–C(1)	112.6	114.1	113.3
P–C(1)–C(2)	111.5	114.1	114.4
C(1)–C(2)–C(3)	124.6	124.7	124.7
dihedral angles, deg			
P–C(1)–C(2)–C(3)	117.5	119.6	39.8
O–P–C(1)–C(2)	61.1	177.3	63.0

[a] Calculated at the 3-21G$^{(*)}$ level.

Methods

Calculations were carried out at the RHF level using the GAUSSIAN 82[12a] and GAUSSIAN 86[12b] package of ab initio programs on a Cray X-MP1 at the University of Illinois National Center for Supercomputing Applications. All structures were fully optimized with the 3-21G$^{(*)}$ basis set[12c] provided in the program. Analytical normal mode frequency calculations were performed for all of the optimized structures. We have discussed the validity of using 3-21G$^{(*)}$ compared to other basis sets for simpler tri- and tetracoordinate phosphorus compounds.[13] While relative energies are at best fair, structural data are well reproduced. For anions **3a** and **3b** single-point calculations were also performed at the HF/6-31+G* level[12d] using the 3-21G$^{(*)}$ optimized geometries. Attempted calculation of electron correlation effects by second-order Møller–Plesset

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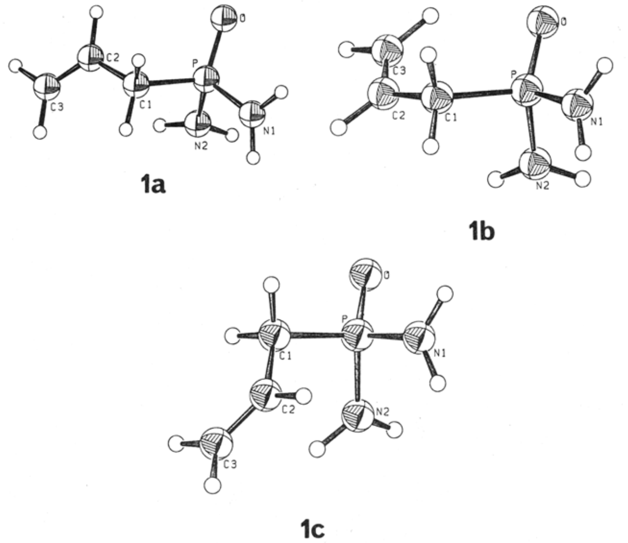
Table II. Mulliken Populations for 1[a]

structure	q(P)	q(O)	q(N1)	q(N2)	q(C1)	q(C2)	q(C3)
1a	1.62	−0.64	−0.31	−0.31	−0.36	0.01	−0.01
1b	1.64	−0.65	−0.31	−0.31	−0.36	−0.04	0.03
1c	1.63	−0.64	−0.31	−0.31	−0.35	−0.01	−0.01

[a] Calculated at the 3-21G$^{(*)}$ level.



1a

1b

1c

Figure 1. ORTEP diagrams of **1a–c** (atomic sizes not to scale).

perturbation theory (MP2)[12e] were found to be prohibitively time-consuming on molecules of this size.

Tables I, III, and V contain the absolute and relative energies of **1**, **2**, and **3** along with selected equilibrium parameters. Tables II, IV, and VI summarize the Mulliken population analyses for the atoms in these species. A complete list of the Cartesian coordinates and *Z*-matrices for all of the structures is provided as supplementary material.

Results

Neutral Species (1). Three equilibrium structures (C_1 symmetry) were located for neutral 1 (Figure 1). The lowest energy structure was **1a**, with **1b** and **1c** each lying 0.8 kcal/mole higher in energy. A collection of the most important geometrical parameters and the energies of the three structures may be found in Table I. These data are in good agreement with averages from X-ray crystal structures of a wide variety of phosphonic diamide derivatives in bond lengths (±0.008 Å) and angles (±5°).[14] In **1a** and **1c** the allyl units adopt a conformation in which the C(1)–P bond is anticlinical to the allylic plane (cf. dihedral angles Table I) and the C(2)–C(3) bond eclipses one of the allylic C(1)–H bonds. These two structures differ in the orientation of the phosphonamide unit with respect to the allyl moiety. In **1a** the P–O bond is synclinal (61.1°) to the C(1)–C(2) bond while in **1c** the P–O bond is antiperiplanar (171.3°) to the same bond. In **1b** the C(2)–C(3) bond is skewed between H–C(1)–P, a U-shaped structure. Here there is eclipsing between HC(1) and HC(2). The tendency of carbon–carbon double bonds to eclipse allylic C–H bonds has been verified experimentally.[15] It is also theoretically well documented and has been explained by perturbation molecular orbital arguments involving the two filled π-type orbitals of the allylic methylene and the π and π^* orbitals of the double bond.[16]

While the geometry of the allyl unit is unremarkable, the planarity of the nitrogens and their orientations relative to the P–O and P–C bonds are quite striking. In all three cases, N(1), which lies on the opposite side of the O–P–C(1) plane from the remainder of the allyl unit, is planar[17] and is rotated such that the nitrogen lone pair is parallel with the P–C bond. Analysis of Mulliken overlap

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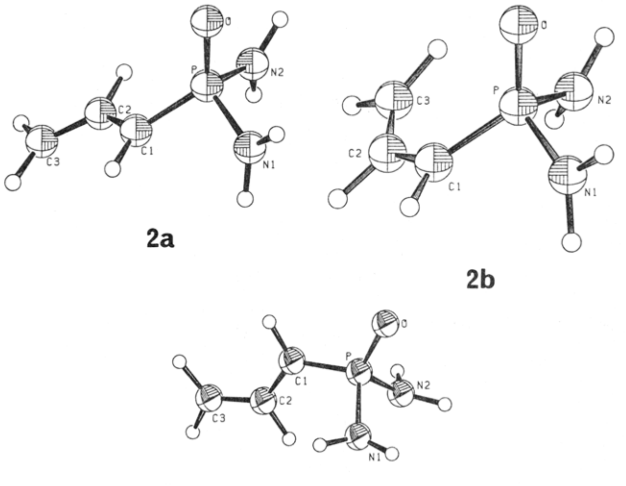
(17) The sum of the angles about nitrogen is >359.5°.



2a

2b

2c

Figure 2. ORTEP diagrams of **2a–c** (atomic sizes not to scale).

populations[18,19] shows a nontrivial overlap between N(1) and C(1), suggesting a stabilizing interaction of the nitrogen lone pair with the σ^*_{P-C} orbital. Similarly, N(2) is planar[17] and rotated such that the nitrogen lone pair is parallel to the P–O bond, suggesting a σ^*_{P-O} delocalization. Again, Mulliken overlap population analysis supports this suggestion.[18] It is noteworthy that there is also a 4-electron repulsive (electrostatic) interaction between this N(2) lone pair and the filled σ_{P-O} orbital as evidenced by the 6–8° larger N–P–O angle for N(2) than N(1). These first row anomeric effects through a second row atom are not insignificant[20] since the P–O and P–C bonds are noticeably lengthened relative to other phosphine oxides substituted with σ-electron-withdrawing groups.[21] Negative hyperconjugation, which has been suggested as an effect in fluorophosphines, does not seem likely here, since this effect leads to bond *shortening*.[20] The planarity of the nitrogen atoms doubtlessly also improves back donation into appropriately oriented phosphorus d orbitals,[22] but this effect is expected to be small.[23] It should be pointed out that the 3-21G basis set gives a barrier for pyramidal inversion of ammonia which is too small by 4.2 kcal/mol.[24]

Table III. Selected Calculated Parameters for 2[a]

parameter	2a	2b	2c
energy, au	−639.485 52	−639.482 72	−639.479 59
relative, kcal/mol	0.0	1.8	3.7
number of negative eigenvalues in Hessian	0	0	1
bond lengths, Å			
P–O	1.491	1.490	1.490
P–N(1)	1.678	1.677	1.692
P–N(2)	1.677	1.679	1.692
P–C(1)	1.703	1.708	1.700
C(1)–C(2)	1.420	1.419	1.420
C(2)–C(3)	1.349	1.354	1.349
bond angles, deg			
O–P–N(1)	106.0	105.9	111.7
O–P–N(2)	106.0	107.6	111.7
O–P–C(1)	127.4	127.0	117.6
P–C(1)–C(2)	124.6	128.3	124.3
C(1)–C(2)–C(3)	130.0	133.3	129.9

[a] Calculated at the 3-21G$^{(*)}$ level.

While this can be corrected by use of a larger basis set with polarization functions (6-31G*) our calculations do not include them (3-21G$^{(*)}$). Thus we cannot rule out the possibility that nitrogen planarity is an artifact of the basis set employed.

The polarization of charge in these structures is also worthy of comment. Mulliken populations[18] for **1a–c** may be found in Table II, where the populations on hydrogen atoms have been summed into the heavy atoms to which they are attached. The ionic character of the phosphonic diamide is evidenced by the large positive charge on phosphorus and the negative partial charges on the four atoms to which it is attached. Most surprising is the highly ionic nature of the P–C bond for these neutral species. The large negative charges on O and C(1) and the smaller ones on the nitrogens are again suggestive of the anomeric delocalization of nitrogen lone pairs. Finally, there is apparently a slight dipole induced in the C(2)–C(3) double bond in **1** opposing that of the P–O bond with which it is approximately aligned, an effect not observed in either **1a** or **1c**. This is an interesting example of how conformational effects may influence reactivity.[25]

Free Anions (2). Two equilibrium structures were located for the free anion **2** (Figure 2). In **2a** the allyl unit is planar, lying perpendicular to the P–O bond. The C(2)–C(3) bond is antiperiplanar to the P–C(1) bond, i.e. of the *E* configuration. In **2b**, which lies 1.8 kcal/mol in energy above **2a**, the geometry is essentially the same, except that the anion is *Z*. It is further evident that there is a nonbonded interaction between C(3) and N(2) in **2b**. A collection of important geometrical parameters and the energies of the two structures are presented in Table III.

The allyl anion subunits in **2a** and **2b**, while planar, are quite different from allyl anion itself which shows C–C bond lengths of 1.38 Å, and an internal angle of 133°.[10] These substituted structures appear approximately midway between a vinyl-substituted planar carbanion and a typical allyl anion.

The effects of anion formation on the P–C bond (0.1 Å shorter) and the O–P–C(1) angle (12–15° wider) are dramatic. This angle widening is due to repulsive electrostatic interactions of the negatively charged allyl unit and the phosphonic oxygen. The greater proximity of C(3) to O, and perhaps N(2) as well, in **2b** accounts for the larger increase in both the O–P–C(1) and C(1)–C(2)–C(3) angles. Interestingly, the nitrogen atoms remain planar, except for

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(18) Mulliken partitioning of total electron density has been criticized by many authors,[19] both in terms of its specification of atomic boundaries[19a] and in terms of its overemphasis on covalent bonding,[19a,b] which has been ascribed partly to basis set superposition error (BSSE)[19d] for bonds between atoms of widely different electronegativities (e.g. $C^- - {}^+Li$). On the other hand, a recent technique for assigning atomic charge based on the difference between molecular electron density and that of the "properly oriented" atoms was described as "correlating reasonably well" with Mulliken populations.[19e] We recognize that Mulliken population analysis is highly basis set dependent (see text, Table VI, ref 24, pp 336–341) and have attempted, for the most part, to present only relative results within these series of compounds, as opposed to describing absolute and quantitative charge descriptions for any single molecule.

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Table IV. Mulliken Populations for 2[a]

structure	imaginary frequencies	*q*(P)	*q*(O)	*q*(N1)	*q*(N2)	*q*(C1)	*q*(C2)	*q*(C3)
2a	none	1.57	−0.73	−0.40	−0.39	−0.70	−0.01	−0.33
2b	none	1.59	−0.73	−0.40	−0.38	−0.72	−0.01	−0.34
2c	216*i*	1.55	−0.72	−0.40	−0.40	−0.70	0.00	−0.33

[a] Calculated at the 3-21G$^{(*)}$ level.

Table V. Selected Calculated Equilibrium Parameters for 3

parameter	3a	3b	3c
energy, au (relative, kcal/mol)			
3-21G$^{(*)}$	−646.970 54 (8.5)	−646.984 12 (0.0)	−646.944 08 (25.1)
6-31+G*//3-21G$^{(*)}$	−650.258 54 (5.5)	−650.267 31 (0.0)	
number of negative eigenvalues	0	0	0
bond lengths, Å[a]			
P–O	1.527	1.520	1.518
P–N(1)	1.651	1.645	1.725
P–N(2)	1.652	1.649	1.721
P–C(1)	1.711	1.724	1.652
C(1)–C(2)	1.461	1.388	1.450
C(2)–C(3)	1.330	1.398	1.329
Li–O	1.782	1.754	1.901
Li–C(1)	2.266	2.908	
Li–C(2)	3.049	2.585	
Li–C(3)	4.026	2.146	
Li–N(1)			2.114
Li–N(2)			2.143
bond angles, deg[a]			
Li–O–P	92.9	114.6	82.2
O–P–N(1)	106.9	108.8	97.8
O–P–N(2)	106.4	112.8	98.2
O–P–C(1)	112.0	111.1	132.3
P–C(1)–C(2)	123.0	123.1	123.8
C(1)–C(2)–C(3)	127.5	130.3	127.4

[a] Calculated at the 3-21G$^{(*)}$ level.

Table VI. Mulliken Populations for 3

structure	*q*(P)	*q*(O)	*q*(N1)	*q*(N2)	*q*(C1)	*q*(C2)	*q*(C3)	*q*(Li)
3-21G$^{(*)}$								
3a	1.67	−0.75	−0.29	−0.28	−0.70	0.00	−0.13	0.48
3b	1.74	−0.75	−0.30	−0.29	−0.64	0.08	−0.34	0.50
3c	1.65	−0.73	−0.30	−0.29	−0.59	−0.03	−0.13	0.43
6-31+G*//3-21G$^{(*)}$								
3a	2.09	−0.90	−0.42	−0.42	−0.91	0.10	−0.20	0.45
3b	2.08	−0.89	−0.42	−0.41	−0.86	0.50	−0.47	0.47

a slight deviation in N(2) of **2b**. Now they are both oriented such that the nonbonding electron pair is perpendicular to the P–O bond, thus minimizing repulsive electrostatic interactions with the electron rich π-allyl–P–O system.

Polarization of charge is again worthy of comment. The Mulliken populations[18] for **2a** and **2b** are presented in Table IV with hydrogen contributions summed into the heavy atoms to which they are attached. The charge on the phosphorus atom in the anion has decreased by only about 3% relative to the neutral. One interpretation of this feature is the lack of valence type bonding to phosphorus d orbitals which would tend to decrease the positive charge on phosphorus.[23] The total negative charge on the allyl unit has increased by about 0.7, with almost equal distribution of that charge on C(1) and C(3). At first glance this result seems surprising given the asymmetry of the allyl unit, but closer inspection reveals that the remaining 0.3 units of charge have delocalized into antibonding orbitals of the P–O bond, and to a lesser extent the P–N bonds, as judged both by the lengthening of these bonds and the accumulation of charge on the heteroatoms. The net dipole of the charge then is still directed from C(3) to C(1), consistent with only partial allyl delocalization.

To evaluate the energetic preference for the parallel arrangement of allyl π-electrons and the P–O bond we optimized the anion **2c** constrained to C_s symmetry (Figure 2). This structure lies 3.7 kcal/mol in energy above **2a** and is a true transition structure with one imaginary frequency. Optimization of this structure in the absence of the C_s symmetry constraint led smoothly to **2a**. The relevant energetic, structural and Mulliken population data may be found in Tables III and IV. These data show that the allyl anion units in **2a–c** are quite similar, supporting the assertion that the charge stabilization in these species is primarily Coulombic. Indeed, the only significant changes in **2e** are: (1) the return of the O–P–C(1) angle to a value similar to that in the neutral structures, owing to the decreased interaction of the allyl system with the phosphonic oxygen, and (2) a lengthening of the P–N bonds due to the concomitant delocalization of the allyl anion into $\sigma^*_{\text{P–N}}$ orbitals. There is also a slight pyramidalization of the nitrogens, probably to avoid unfavorable lone pair–lone pair repulsions.

Lithated Anions (3). Although the free gas-phase anions **2** provide us with a great deal of information, extension to the lithiated anions may more accurately compare with the actual species in solution. We located three monomeric equilibrium structures for **3** (Figure 3). Selected energies and structural parameters may be found in Table V. Mulliken populations may be found in Table VI, again with the hydrogen atoms summed into the heavy

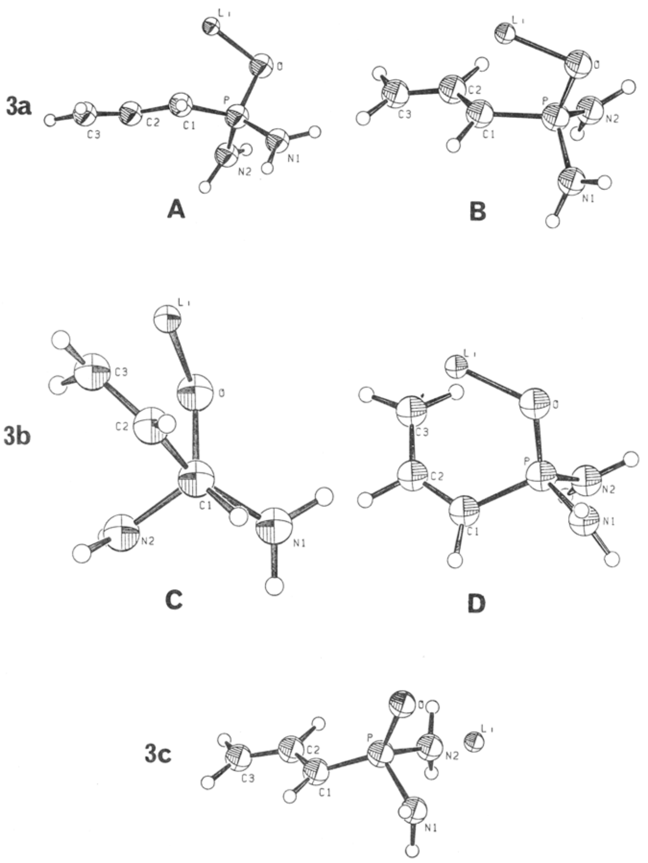

Figure 3. ORTEP diagrams of **3a–c** (atomic sizes not to scale).

atoms. In **3a**, the (*E*)-allyl anion, the allyl system remains parallel to the P–O bond and the lithium cation is bonded to both oxygen and C(1). In **3b**, the (*Z*)-allyl anion, the situation is strikingly different. Now the allyl π-system is rotated about 60° to the P–O bond, and the lithium cation is bonded to both oxygen and C(3). This anion lies 8.5 kcal/mol lower than **3a** in relative energy. Finally, in **3c** the lithium makes only heteroatom contacts. Since this species lies significantly higher in energy than either of the other two, we did not attempt to locate an analog in which the allyl unit adopted a *Z* geometry. We also did not attempt to find structures in which lithium and oxygen were on opposite sides of the phosphorus atom.

The lithiated (*E*)-allyl anion, **3a**, closely resembles **2a** from which it derives. While C(2) and C(3) remain planar, the sum of the angles about C(1) decreases to 356.0°. This pyramidalization occurs in such a fashion as to localize the carbanionic lone pair on the face to which lithium is coordinated (projection A, Figure 3). The net effect is to increase the degree to which this anion resembles a vinyl-substituted carbanion. In support of this is the lengthening of the C(1)–C(2) bond at the expense of the C(2)–C(3), the dramatic decrease in partial charge at C(3), and the close contact (2.27 Å) lithium makes with C(1), but not with C(2) or C(3) (projection B, Figure 3). The lithium cation also serves to bind together those negatively charged portions of the molecule which formerly repelled each other in **2a**. Thus, there is a decrease in the C(1)–C(2)–C(3) angle, the P–C(1)–C(2) angle, and especially in the O–P–C(1) angle, which decreases by a full 16°.

The (*Z*)-allyl anion **3b**, on the other hand, is dramatically different from its analogue **2b**. In the allyl unit itself, which has twisted away from being perpendicular to the P–O bond, the C–C bonds have almost equalized, and the pyramidalization towards lithium is *this* species occurs at C(3) (projection C, Figure 3). The sum of the angles about this atom is only 352.2°. This allyl geometry allows close contact of the lithium cation with C(3) (2.15 Å) and the phosphonic oxygen (projection D, Figure 3). In addition, although more distant from C(1) (2.91 Å), the Mulliken overlap population still shows a –0.062 electron overlap.[18] Here too, as in **3a**, the lithium cation serves to decrease the C(1)–C(2)–C(3) angle, the P–C(1)–C(2) angle, and the O–P–C(1) angle relative to **2b**.

No less dramatic is the sudden return of the amino groups to positions reminiscent of the neutral species; both are planar with one nitrogen lone pair parallel to the P–O bond, and one to the P–C bond. This seems to suggest that the bonding in **3b** may more closely resemble that in **1** than **2**.

In addition to the many structural changes brought about by inclusion of the cation,[26] there is the surprising change in relative energies of the *E* and *Z* anions. The *Z* anion is now the lower in energy, doubtless because the lithium cation is more able to effectively coordinate to all those portions of the allyl–PO system concentrating negative charge. In the *E* anion there is no molecular contortion which brings C(3) and O sufficiently close together that they may be bridged. It is consistent with this observation that single point calculations with the 6-31+G* basis set,[12e] which incorporates diffuse sp-type functions on non-hydrogen atoms, decrease the energy difference between the two structures. As the added diffuse functions allow the molecule to delocalize charge over a larger volume of space, there is less energy to be gained from bonding with a cation. Nevertheless a significant 5.5 kcal/mol difference between **3a** and **3b** remains.

Structure **3c** is less important to the understanding of these anions as it lies so high above the other two isomers in energy. This is quite in contrast to the computationally described lithio anions from dimethyl sulfone.[27] In this molecule, the energy difference between the C_1 anion in which the lithium atom makes one oxygen and one carbon contact and the C_s anion in which lithium makes two oxygen contacts and no carbon contacts is only 1 kcal/mol. The rationalization for that result lies in the roughly equal electrostatic potentials at each of the two positions lithium may occupy. It is evident that in our case the localization of electronic charge remains heavily in the region of the allyl unit.

Its high relative energy notwithstanding, **3c** has several interesting aspects which are worthy of comment. Not surprisingly, the nitrogen atoms have pyramidalized to more effectively coordinate lithium. Furthermore, a significant amount of charge is withdrawn from the allyl unit into the heteroatoms, and this effect manifests itself in several ways. First, the allyl unit is even less internally delocalized than in **3a**, with the C(2)–C(3) bond length reduced to 1.33 Å, and C(1)–C(2) increased to 1.45 Å. Nevertheless, all the carbon atoms remain planar. Second, the lithium atom draws the negatively charged heteroatoms close to it, and in the process exposes the highly positive phosphorus as the O–P–C(1) angle increase to a very wide 132.3°. This effect causes the P–C(1) bond to shorten to 1.65 Å, becoming almost ylidic in character. Finally, the charge buildup in the heteroatoms appears to be primarily in P–N antibonding orbitals as these bonds have increased in length dramatically.

It is also worthy of note that the Mulliken populations on most of the atoms are dramatically increased in magnitude by use of the 6-31+G* basis set.[18] This is another

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(26) These changes are expected to be highly medium dependent.

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Table VII. Selected Spectral Data for Major Anionic Species in THF[a]

substrate	%[b]	$\Delta\delta$ ^{31}P,[c] ppm	δ ^{7}Li, ppm	$\Delta\delta$ ^{13}C (Δ^1J_{CH}, Δ^nJ_{PC}), ppm (Hz)[c,d] C(1)	C(2)	C(3)	sign of $^2J_{PCH}$[e]
4a	60	16.74	0.12	6.90 (–, 85.4)	10.17 (–20.7, –)	–39.29 (3.3, –)	
5a	85	20.42	–0.10	2.96 (30.2, 94.9)	8.94 (–19.5, 0.5)	–36.10 (–2.7, –)	(+)
6a	70	21.29	0.04	7.00 (–, 98.5)	9.05 (–16.3, –)	–34.68 (–, –)	(+)
4b	80	15.73	–0.09	15.40 (35.8, 76.8)	10.39 (–24.2, –)	–36.53 (–, –)	(+)
5b	>95	28.47	–0.12	2.88 (–, 85.5)	9.24 (–18.0, 0.07)	–36.85 (7.5, 6.5)	(+)
6b	50	23.23	–0.13		9.53 (–25.5, –)	–34.86 (–, –)	

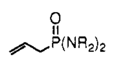
[c] Concentration 0.6 M, observed spectra were mixtures of two species, see Table VIII. [b] Approximate percentage of major species as compared to minor species based on signal intensities. [c] Changes in chemical shift and coupling constants after metallation ($\Delta\delta(\Delta J)$ refer to $\delta(J)$ anion – ($\Delta(J)$ neutral). [d] Unreported data are due to obscurement by other peaks or significant signal broadening. [e] As determined by spin tickling.

indication of how ionic the bonding in these species is. Indeed, overlap populations indicate that the nitrogen atoms share more electrons with C(1) and O than they do with the phosphorus atom to which they are formally attached. It appears from inspection that back bonding to phosphorus d orbitals, which decreases overall phosphorus charge, may well be an artifact in calculations not done with basis sets incorporating diffuse functions. It has been shown, however, that structural parameters are little changed upon reoptimization with basis sets to which diffuse functions have been added.[28] We may thus rely on the accuracy of our calculated structures relative to the 3-21+G$^{(*)}$ basis set.

Discussion

We have carried out an extensive NMR spectroscopic investigation of the solution structure of allylphosphonic diamide anions.[8a] This study examined nine different substrates in four solvents (ranging in polarity from DMSO to toluene) with two (Li$^+$ and K$^+$) cations and various additives. While a full account will be reported elsewhere it is instructive to compare the conclusions from the theoretical study with some of the spectroscopic results. For the most part, changing solvents affected only the *E*/*Z* ratio of anions; hence we restrict our discussion to a single representative solvent, THF.

The allyl anions of phosphonic diamides **4–6** were generated with *s*-BuLi in THF-d_8/THF 1:2 (0.6 M) at -78 °C. The spectra were recorded at ambient temperature. These spectra were compared with reference spectra of the neutral compounds taken under identical conditions. In addition to ^{1}H, ^{13}C, ^{31}P, and ^{7}Li NMR chemical shift information, we also collected $^1J_{CH}$, $^1J_{PC}$, $^2J_{PCH}$ and determined the sign of the latter by a spin tickling experiment.[29]



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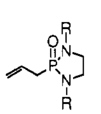

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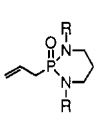

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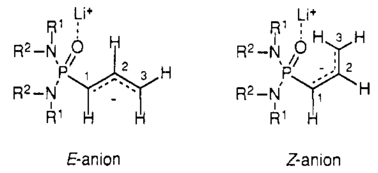
a: R = Me, b: R = *i*-Pr

In all cases except **5b**, two species were observed in solution. Selected spectroscopic data for the major and minor components are collected in Tables VII and VIII, respectively. General trends for both species include: (1) downfield shifts for δ^{31}P, δ^{13}C(1), and δ^{13}C(2), (2) an upfield shift for δ^{13}C(3), (3) increases in $^1J_{CH}$ and $^1J_{PC}$ for C(1), and (4) a decrease in $^1J_{CH}$ for C(2). For the anions from **4a**, **6a**, and **5b**, overlap of the C(1) signal with that of the *N*-alkyl carbon prevented ascertainment of $^1J_{CH}$. The resonance due to C(1) in Li$^+$ **6b**$^-$ was not assignable.

Table VIII. Selected Spectral Data for Minor Anionic Species in THF[a]

substrate	%[b]	$\Delta\delta$ ^{31}P,[c,d] ppm	$\Delta\delta$ ^{13}C (Δ^1J_{CH}), ppm (Hz)[c,d] C(2)	C(3)
4a	40	19.50	27.33 (0.3)	–43.99 (3.3)
5a	15		27.30 (1.1)	
6a	30	26.00	26.95 (3.6)	–37.35 (–)
4b	20	21.74	26.84 (–)	–44.01 (–)
6b	50	26.62	26.46 (1.3)	–39.88 (–)

[a] Concentration 0.6 M, observed spectra were mixtures of two species, see Table VII. [b] Approximate percentage of minor species as compared to major species based on signal intensities. [c] Changes in chemical shift and coupling constants after metallation. [d] Unreported data are due to obscurement by other peaks or significant signal broadening.



E-anion *Z*-anion

Figure 4. Major *E* and minor *Z* anions of allylphosphondiamides.

The two species observed in solution are assigned the *E* (major) and *Z* (minor) configurations of the allyl anion, Figure 4. The basis of this assignment rests primarily on (1) the higher field shift of C(3)[30] in the minor species in all cases, (2) the large $^3J_{HH}$ to HC(2) for HC(1) (11.0–12.5 Hz) in the major isomers which is in agreement with other (*E*)-allyl anions,[31] (3) the insensitivity of the spectra to the addition of 12-crown-4 (thus ruling out different order aggregates), and (4) the isolation of *E* olefins as major products in γ-substitution reactions under kinetic control.[32] With respect to the latter, it is intriguing that in toluene, compared to THF, a greater proportion of *Z* anion was

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(32) Of course, the *Z* anion may still predominate but react more slowly.

both observed spectroscopically, and inferred from the *E*/*Z* ratio of electrophilically trapped products.[8a] In a very qualitative sense, the free anions **2** may be said to represent the actual anionic species in solvents which are better at coordinating lithium than the substrate (e.g., THF) and the lithio anions **3** are representative in solvents which are poorer at such coordination (e.g., toluene). There is thus qualitative agreement between theory, spectroscopy, and experiment in the greater preponderance of *Z* products in and from toluene compared to THF.

Given the small differences in energy between the various anion conformations in **2** and **3** and the expected large solvent effect on such highly charged structures, it is not surprising that there is *quantitative* disagreement between theory and experiment (vide infra).[33] Nevertheless, many of the trends observed spectroscopically are in agreement with the general conclusions from the calculations.

First, the consistent downfield shift of the C(1) signals from neutral to anion is well precedented[34] and arises from a hybridization change from sp^3 to sp^2. This effect slightly overwhelms the upfield shift induced by accumulation of negative charge. In contrast C(3), where hybridization did not change, was shifted dramatically upfield from build up of charge. In addition, C(2) shifted downfield upon anion formation. These data are in good agreement with the computational results which suggested a planarized α-carbon in the anion and, based on Mulliken population analyses,[18] accumulation of positive and negative charge respectively on C(2) and C(3) in the anion.

Second, the changes in $^1J_{CH}$ for C(1) and C(2) agree with the computational results. For C(1) this value increased by 29–36 Hz, consistent with the predicted change in hybridization from sp^3 to sp^2. On the other hand, the value for C(2) dropped by 10–25 Hz. This is not a manifestation of sp^2 to sp^3 rehybridization but rather has been interpreted to arise from widening of the C(1)–C(2)–C(3) angle in the anion.[35] This again is predicted computationally (Tables I, III, and V).

Third, both the increase in $^1J_{PC}$ (70–100 Hz)[34g–i,36] and the change in sign of the $^2J_{PCH}$ for C(1)[29] in the anions are supportive of a change in hybridization from sp^3 to sp^2 at C(1), as found computationally.

Finally, the consistent downfield shift (15–28 ppm) of the ^{31}P resonance upon anion formation is informative. This surprising result suggests that $p\pi$–$d\pi$ charge delocalization is not important,[23,24d] but that stabilization occurs by electrostatic interactions consistent with a charge alternating structure O^-–P^+–$C(1)^-$–$C(2)^+$–$C(3)^-$.[37] This pattern is consistent with our Mulliken population analysis,[18] which shows a significant increase in the positive charge on phosphorus at the 6-31+G* level.

Conclusions

In summary, three equilibrium structures for neutral *P*-allylphosphonic diamide were found with two lying 0.8 kcal/mol higher in energy than the other. Anomeric effects through phosphorus were noted. Mulliken population analyses of these molecules showed them to have ionic character in their bonding to phosphorus. The gas-phase free anions of *P*-allylphosphonic diamide exist in both *E* and *Z* forms in which the π system of the allyl anion is parallel to the P–O bond, with the *E* form being preferred by 1.8 kcal/mol over the *Z*. The two isomers are approximately midway between allylically delocalized species and vinyl-substituted carbanions. Again, bonding was determined to be highly ionic, with phosphorus stabilization occuring primarily via Coulombic interactions. Furthermore, the transition state for P–C bond rotation was located for the *E* isomer and shown to lie 3.7 kcal/mol above it in energy. Upon inclusion of lithium the energy ordering of the two anions reversed, with the *Z* anion now favored by 8.5 and 5.5 kcal/mol at the 3-21G$^{(*)}$ and 6-31+G* levels, respectively. The reason for this reversal is the more facile stabilization of charge in the *Z* isomer in which lithium may coordinate all of the carbons and the phosphonic oxygen. A third structure was located in which the lithium cation makes only heteroatom contacts but it was more than 20 kcal/mol above the other two isomers. Once again d orbitals on phosphorus were implicated to be less important in stabilization of the anion than were Coulombic effects.

Given the size of these systems, and the concomitant restrictions on the employed levels of theory, we do not believe a prediction can be made regarding the relative energies of the two isomeric anions *in solution*. It is likely, given that we have noted a number of local 4-electron electrostatic repulsions in these species, that the energy difference between **3a** and **3b** would continue to drop as the molecular electron density is allowed to become more diffuse by delocalization into a larger volume of space. Hence, use of the more flexible 6-31+G* basis set[12d] for geometry optimization and inclusion of correlation effects would both be expected to decrease the relative energy differences. Given that assessment, and noting, as discussed above, that the coordinating ability of the solvent will place the relative energies of the *E* and *Z* anions somewhere between those of **2** and **3**, the most which can be said is that the observed equilibrium mixtures are not surprising. On the other hand, we do not believe that the *structural* features of the allyl unit, in which we are primarily interested, would change significantly at higher levels of theory.[13,38] It is here that theory has proven most useful to us in its correlation with our spectroscopic results.[39]

Acknowledgment. We wish to thank Professor S. D. Kahn for enlightening discussions and technical assistance. This work was supported in part by the National Science Foundation (NSF CHE-84-51321) and the National Center

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(39) A different phosphondiamide anion calculated at this level has been found to correlate structurally with X-ray crystal structures of related compounds. Denmark, S. E.; Cramer, C. J.; Dorow, R. L.; Young, P. M., unpublished results from these laboratories.

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Registry No. **1**, 125251-46-9; **2**, 125251-47-0; **3**, 125251-51-6; **4a**, 17070-81-4; **4b**, 125251-48-1; **5a**, 20628-90-4; **5b**, 125251-49-2; **6a**, 125281-11-0; **6b**, 125251-50-5.

Supplementary Material Available: Cartesian coordinates and *Z*-matrices are provided for **1**, **2**, and **3** (10 pages). Ordering information is given on any current masthead page.

Energetic and Rate Effects of the Trifluoromethyl Group at C-2 and C-4 on the Aliphatic Claisen Rearrangement

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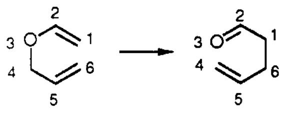
The rate of the Claisen rearrangement is accelerated by a factor of 73 over the parent system when a trifluoromethyl group is present at C-2 of allyl vinyl ether. Ground-state destabilization by the trifluoromethyl group may be responsible for this rate effect. There is little polar character in the transition state, and the transition-state structure has little carbonyl character and only moderate (ca. 1/3) bonding character between the two terminal carbons. The rate enhancement is not observed in the Cope rearrangement of the all-carbon analogue that has a trifluoromethyl group at C-2. At C-4, the trifluoromethyl group does not bring about a significant rate effect in the Claisen rearrangement relative to the parent system; this result is in contrast to an energetic benefit of 3.5 kcal/mol enjoyed by the system when a cyano group is at C-4, which suggests that radical-stabilizing ability and not electron-withdrawing ability is important in stabilizing the transition state.

Introduction

The synthetic usefulness of the Claisen rearrangement of aliphatic allyl vinyl ethers[1] to γ,δ-unsaturated carbonyl compounds has been well established.[2,3] That the Claisen rearrangement proceeds through a cyclic chair transition state[4] (when possible) as an intramolecular, concerted 3,3-sigmatropic rearrangement[5] has also been well established.[6] The high-energy species of the reaction is an aromatic[7] transition state that leads to the rearrangement product rather than an intermediate(s), although this picture is not without criticism.[8] The loss of entropy that would be expected for a cyclic transition state is confirmed by a −7.7 eu entropy of activation for allyl vinyl ether (AVE) in the gas phase at 180 °C.[9] The rearrangement is highly exothermic, downhill in enthalpy by 17 kcal as calculated by heats of formation of AVE and 5-hexenal.[10]



AVE

(1)

Substituent effects on the rate of the Claisen rearrangment have been investigated, and various models have been proposed. One complication which should be addressed by a model is that 3,3-shift transition structures seem to respond to substituents as judged by secondary deuterium kinetic isotope effects.[11] A model suggested in our work is a nonlinear free-energy relationship to correlate the rates of a variety of substituted allyl vinyl ethers.[12] This model assumes that the transition-state structure takes on characteristics of reactant or product based on the exothermicity and takes on associative or dissociative character depending on how and where substituents can best stabilize such character.

Dewar[8a] has presented a model, based on MNDO calculations, that shows a biradical intermediate for the Claisen rearrangement (2-oxacyclohexane-1,4-diyl), which then decomposes to products without activation. This diyl is a highly polarizable specie, and the oxygen atom is said to favor a zwitterionic pathway. Most Claisen rearrangements do not respond dramatically to polar solvents (a rate factor of ca. 200 between benzene and aqueous environ-

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