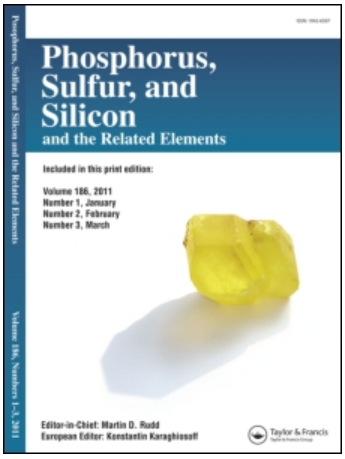

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CONFORMATIONAL ANALYSIS OF 3-TRIPHENYLPHOSPHORANYLIDENE-2,4-PENTANEDIONE BY NMR SPECTROSCOPY AND GEOMETRICAL OPTIMIZATION

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*The diacyl ylide, 3-triphenylphosphoranylidene-2,4-pentanedione (**2**) can adopt conformations stabilized by ylidic resonance with both acyl oxygens* syn- *or with one oxygen* syn- *and the other* anti- *to cationoid phosphorus, **2a**, Z, Z and **2b**, Z, E respectively. In solution the CH_3 groups give single ^1H and ^{13}C NMR signals indicating either that **2a** is dominant, or that conformational equilibration is fast on the NMR time scale. However, two sets of ^{13}C signals of* CH_3 *and* CO *are observed in the solid and comparison of the chemical shifts shows that **2a** is the dominant conformer in solution and **2b** in the solid. Calculations with* ab initio *HF basis sets indicate that the heat of formation of **2a** is slightly more favorable than of **2b**, and that the rotational barrier for interconversion is low. These energetic differences are much smaller than for the otherwise similar monoacyl ylides and are related to differences in ylidic resonance in conformational equilibration in mono- and diacyl ylides.*

Keywords: Conformation; NMR spectra; optimized structures; phosphorus ylides

Conformations of the stabilized acyl-ester ylides **1** (refer to Scheme 1) have been examined by x-ray crystallography and by NMR spectroscopy.[1–4] They are governed by ylidic resonance and interactions between cationoid phosphorus and alkoxy and carbonyl oxygens.

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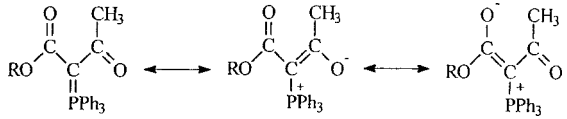


SCHEME 1 Conformations of stabilized acyl-ester ylides, **1** (**1a:** R=Me, **1b:** R=Et).

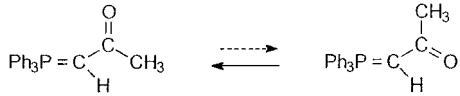
Classical structures are shown, although there is extensive electronic delocalization from phosphorus into the ylidic and acyl residues. In the crystal, the ylidic residue is near planar which allows electronic delocalization and brings hydrogens of the alkoxy groups close to the face of a phenyl group, consistent with the π-shielding seen in the ^{1}H-NMR spectrum.[1–4] The ^{1}H-NMR chemical shifts are insensitive to changes in temperature or solvent and signals are sharp with only slight line broadening due to increased solvent viscosity at low temperatures.[1,4] Geometries of acyl-ester ylides **1a,b** in the crystal[2] are similar to those optimized computationally with the HF 3-21(G*) or 6-31(G*) basis sets and are consistent with the ^{1}H-NMR spectra in solution.[1,4]

We have followed this general structural approach in examining conformation (s) of 3-triphenylphosphoranylidene-2,4-pentanedione, **2a** and **b**, Z, Z and Z, E respectively, which should be sensitive to interactions involving oxygen(s) and the cationoid phosphorus, and groups *anti-* to phosphorus. The conformation with both oxygens *anti-* to phosphorus should be destabilized relative to **2a,b** due to unfavorable dipolar interactions.

2a **2b**

Cooke and Goswami[5] had converted **2** into mono- and di-anions with *n*-butyl lithium or lithium di-isopropyl amide and generated a cyclic derivative by reaction of the dianion with 1,3-diiodopropane. They saw only one ^{1}H-NMR signal of **2** and all these results are consistent with conformer **2a** being dominant in solution because conformational equilibration of monoacyl ylides is slow on the NMR time scale,[6] and enthalpic barriers may be high due to ylidic resonance and the partial double bond character of the ylidic-acyl bond. The factors that control conformational equilibration and preferences have been enumerated[6] and structures of acyl stabilized ylides have been reviewed.[7]

However, a preliminary x-ray crystallographic examination of **2** showed that one CH_3 is *syn*- and the other *anti*- to phosphorus, as in **2b**, although the structure is not yet fully refined.[8] It appears that conformations of **2** differ in the solid and solution, or that **2b** is the preferred conformation but the CH_3 groups exchange positions rapidly in solution and equilibration of the anions permits formation of cyclic products.[5] We address this problem by examining the NMR spectra in the solid and in solution and using computational methods to explore conformational preferences in **2** and in the monomethyl derivatives, **3a** and **b**, where equilibration is slow and there is a strong preference for **3a**, with oxygen *syn*- to phosphorus.[9]



3a **3b**

RESULTS AND DISCUSSION

NMR Spectroscopy

The ^1H and ^{13}C-NMR spectra of **2** are very simple in solution and are insensitive to changes in solvent and temperature (refer to Table I). We saw only one ^1H or ^{13}C signal of the methyl group and the former is a sharp singlet in all conditions, in agreement with earlier results.[5]

TABLE I ^{13}C Chemical Shifts of Diacyl Ylide, **2**, $Ph_3P{=}C(CO{-}CH_3)_2$, in Solution and the Solid[a]

	Temp. (°C)				
Position	25[b]	27[c]	50[c]	80[c]	Solid
CH_3	30.6 (6.3)	30.7 (6.0)	30.7 (6.0)	30.4 (6.0)	28.8 and 50.4
C=O	193.1 (7.9)	191.9 (8.0)	191.8 (8.3)	191.2 (8.2)	193.0 and 168.3
P=*C*	88.8 (102)	87.5 (101)	87.1 (101)	87.5 (101)	71.6 (111)
ipso	126.6 (92.4)	126.9 (91.9)	127.1 (91.7)	127.3 (91.7)	119.9 (84.5)
o–	132.9 (9.7)	133.0 (9.7)	133.0 (9.7)	133.1 (9.7)	134.2
m–	128.5 (12.3)	129.1 (12.2)	129.0 (12.2)	129.0 (12.2)	129.7
p–	131.5 (2.9)	132.0 (2.8)	132.0 (2.9)	131.9 (2.9)	131.7

[a]Chemical shifts, ppm, referred to TMS in solution, coupling constants, $^1J_{P-C}$, Hz in parentheses.
[b]in $CDCl_3$.
[c]in $DMSO_{d\text{-}6}$.

There is no indication of significant π-shielding of CH_3. The aromatic ^{1}H signal is a multiplet, as is typical of these triphenyl derivatives. The ^{13}C chemical shifts and coupling constants are in Table I and are similar to those of the methyl keto groups in **1a, b**, where the carbonyl oxygen is *syn*- to phosphorus.[4] We found that some ^{13}C signals differ in solution and the solid, but in solutions solvent and temperature effects are small. The CH_3 signals in solution are also insensitive to solvent and temperature, viz., the ^{1}H chemical shifts are: in $CDCl_3$, 2.29 and 2.32 ppm at 25 and -40°C respectively; and in acetone$_{d\text{-}6}$, 2.15 ppm at -40°C; methanol$_{d\text{-}4}$, 2.15 ppm at 25°C; DMSO$_{d\text{-}6}$, 2.12 ppm at 80°C. The proton-decoupled ^{13}C spectrum in solution also is simple, as expected for a single conformer or a rapidly equilibrating mixture. The chemical shifts and coupling constants (shown in Table I) are in ranges typical of these stabilized ylides.[10]

Comparison of the preliminary crystallographic data[8] with the NMR results in solution, with equivalence of the acyl groups, shows that either conformations differ in the solid and solution, or that conformer **2b** is dominant, but that the acyl groups rapidly equilibrate by rotation about the bond between the ylidic and acyl carbons, which also fits the preparative results.[5] However, typically in these stabilized ylides partial double bond character in the acyl residues makes this rotation slow. We explored these possibilities by comparing the ^{13}C-NMR spectra in the solid and in solution. The spectrum in the solid shows that the CH_3CO groups are nonequivalent, which is in agreement with the preliminary crystallographical data.[8]

The differences in the ^{13}C-NMR spectra in solid and in solution (see Table I) show that the relative amounts of **2a** and **2b** differ, but **2b** could be present in solution with rapid positional equilibration of its CH_3CO groups. However, comparison of the ^{13}C chemical shifts in the solid and in solution shows that **2a** is dominant in solution. In the solid the two sets of CH_3 and CO signals correspond to the two distinct acyl groups in **2b**, thus if it were dominant in solution, with rapid conformational equilibration, the NMR chemical shifts would be the approximate means of those of the methyl and carbonyl carbons corresponding to acyl groups with *syn*- and *anti*- oxygens with respect to phosphorus. However, the chemical shifts of one CH_3 group are similar in the solid and in solution, 28.8 and 30.6 ppm, respectively, and corresponding values for C=O are 193.0 and 193.1 respectively (refer to Table I). We note that the change from solution to solid introduces minor uncertainties in comparing values of the chemical shifts due to use of different references.

These observations require that conformer, **2a**, be dominant in solution, as suggested earlier,[5] although the ^{13}C NMR spectrum in the solid and crystallographic evidence[8] show that **2b** is the conformer in the

solid. We note that there is only one ^{13}C signal of an ylidic carbon in the solid, and that the melting point of **2** is sharp and does not change with time or on recrystallization. Therefore the separate conformers, **2a** and **b**, are not metastable isomers, but are stable, readily interconvertible, rotamers in solution. These results indicating ready interconversions were unexpected in view of earlier evidence on monoacyl ylides,[5–7] and we therefore applied *ab initio* optimization of molecular geometries to this problem.

Geometrical Optimization

Ylides, **2a,b**, were examined initially with the HF 3-21(G*) basis set and then with the 6-31(G*) basis set. Bachrach had optimized structures of a variety of stabilized and unstabilized ylides and found that use of more extensive basis sets had little effect on the geometries,[11] and structures of **2a,b** at the 3-21(G*) and 6-31(G*) levels were almost identical to the eye. Unless specified, our results are from use of the 6-31(G*) basis sets and **2a** is predicted to be preferred over **2b** by 2.6 kcal mole^{-1}. This difference is probably within the uncertainty of the calculations, although the NMR and preparative evidence show that **2a** is the preferred structure in solution. However, the ^{13}C-NMR spectrum of the solid (see Table I) and preliminary x-ray crystallography[8] show that **2b** is the structure in the crystal.

The hypothetical structure, **2c**, with one acyl oxygen *syn*- to phosphorus and the other acyl group constrained out of plane by 90°, should approximate the transition state for interconversion of **2a** and **2b**. These calculations, at the 3-21(G*) or 6-31(G*) levels indicated that **2c** would be disfavored energetically by 3.4 or 3.6 kcal mol^{-1}, respectively, relative to **2b**. These small differences in heats of formation show that conformational barriers should be small for these diacyl ylides and that small energetic changes in going from solid to solution could cause the observed changes in conformation.

Geometrically optimized structures of **2a** and **b** are in Figure 1 and some computed geometrical parameters are in Tables II and III. The ylidic carbon is designated C1, the acyl carbons C2 and the methyl carbons C3. For **2b** the prime superscript denotes atoms in the acyl groups with oxygen *anti*- to phosphorus. For **2a** the prime superscript denotes atoms to the left as viewed in Figure 1. We note that in **2a** the acyl groups in the geometrically optimized structure are not equivalent because a static structure is optimized, but these groups equilibrate rapidly on the NMR time scale. The computed bond lengths and angles of **2a** and **b** (see Tables II and III) are consistent with approximately planar ylidic residues, as expected for stabilized ylides. There is modest

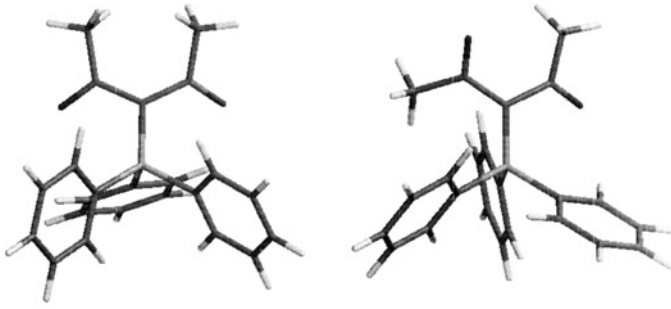
TABLE II Computed Geometrical Parameters (Å, °) for Diacyl Ylide, **2a**

Bond lengths (Å)			
P1—C1	1.77	C2′—O′	1.22
C1—C2	1.45	C2—C3	1.52
C2—C2′	1.44	C2′—C3′	1.52
C2—O	1.21		
Bond angles (°)			
P—C1—C2	116	O—C2—C3	117
P—C1—C2′	112	C1—C2′—O′	120
C2—C1—C2′	127	C1—C2′—C3′	123
C1—C2—O	121	O′—C2′—C3	117
C1—C2—C3	122		
Torsion angles (°)			
P—C1—C2—O	9.7	P—C1—C2′—O′	2.2
Contact distances (Å)			
CH_3—C3′	2.85	P—O	2.92
		P—O′	2.78

distortion from trigonal symmetry at the ylidic carbon which, for **2a**, can be ascribed to CH_3—CH_3 repulsion and favorable interactions of the acyl oxygens with the cationoid phosphorus. (The sums of the bond angles are close to 360° for **2b** and **2c** respectively). The CH_3—CH_3 center-center computed distance of 2.85 Å for **2a** is well within the sum of the van der Waals radius of 2.0 Å for CH_3[12] and the sum of the bond

TABLE III Computed Geometrical Parameters (Å, °) for Diacyl Ylide, **2b**

Bond lengths (Å)			
P—C1	1.75	C2′—O′	1.21
C1—C2	1.45	C2—C3	1.51
C1—C2′	1.46	C2′—C3′	1.53
C2—O	1.22		
Bond angles (°)			
P—C1—C2	112	O—C2—C3	119
P—C1—C2′	126	C1—C2′—O′	122
C2—C1—C2′	122	C1—C2′—C3′	122
C1—C2—O	119	O′—C2′—C3	116
C1—C2—C3	122		
Torsion angles (°)			
P—C1—C2—C3	169	P—C1—C2′—O′	159
Contact distances (Å)			
O′—C3	2.60	P—O	2.70



2a **2b**

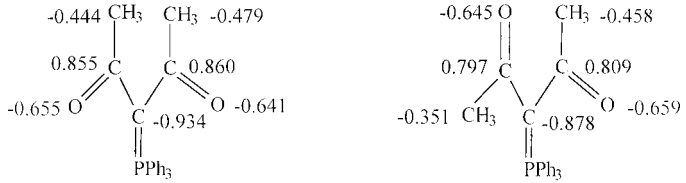
FIGURE 1 Geometrically optimized structures of **2a** and **b**, $Ph_3P{=}C(CO{-}CH_3)_2$.

angles at the ylidic carbon is 355° indicating the modest deviation from trigonal symmetry (refer to Table II).

The ylidic moiety of **2b** is near planar in the optimized structure (refer to Figure 1) although the $CH_3{-}O$ computed distance of 2.60 Å is within the sum of the van der Waals radii (1.40 Å for O), but the interaction should be less unfavorable than that of the methyl groups in **2a** (see Figure 1) and sums of the bond angles at the acyl carbons are close to the expected 360°. These computations neglect intermolecular interactions and those with solvents, but they are consistent with electronic delocalizations involving the acyl and ylidic moieties.

Conformations and NMR Spectroscopy

The different ^{13}C chemical shifts in the solid and in solution (shown in Table I) show that conformations differ in these conditions and that chemical shifts in solution exclude the possibility of rapidly exchanging *syn*- and *anti*-acyl moieties with respect, positionally, to cationoid phosphorus. Schlosser et al. have used ^{13}C chemical shifts in stabilized ylides as indicators of electronic environments,[13] and we therefore estimated electrostatic potentials of atoms in **2a** and **b** and examined the possibility of a relationship with the chemical shifts (refer to Table I). The assumption is that for otherwise similar groups increasing electron densities, or more negative electrostatic potentials, would lead to upfield chemical shifts. We note that computations are for isolated molecules, and althougt the ^{13}C NMR spectra in solution are independent of solvent and temperature (see Table I), proximity of molecules in the crystal may introduce significant intermolecular effects. The computed charges on the methyl, acyl, and ylidic carbons are in Figure 2.



2a **2b**

FIGURE 2 Electrostatic charges on carbons and oxygens of diacyl ylide, **2a** and **b**.

In the optimized static structure of **2a** the two methyl and the two acyl carbons are not identical and computed charges on them differ slightly; both are given. The situation is simple for the methyl carbons in that the groups *anti-* to phosphorus have similar partial atomic charges at carbon, and ^{13}C chemical shifts are also similar in the solid and in solution. For **2b** the charge on the carbon of the methyl group *syn-* to phosphorus is less negative than on that which is *anti-* to phosphorus and its ^{13}C signal in the solid is correspondingly shifted downfield (see Table I). The situation is less obvious for the acyl carbons, ^{13}C chemical shifts for **2b** differ and that for the upfield signal it is similar to that for **2a**, where both acyl carbons are identical on the NMR time scale. However, partial atomic charges on the acyl carbons of **2b** are not very different, although they are slightly less positive than on the acyl carbons of **2a** (see Figure 2). The correlation between partial atomic charges and ^{13}C chemical shifts breaks down for the ylidic carbons, because that in **2a** is predicted to be slightly more negative than in **2b**, but the ^{13}C chemical shift is higher (refer to Table I).

Correlations of ^{13}C chemical shifts and computed atomic charges are reasonably robust for the methyl carbons, but less so for those in the electron-delocalized ylidic moieties. An additional complication is the predicted distortion from strict planarity in the ylidic moiety for the computed static structure of **2a**, where the calculated sum of the bond angles at the ylidic carbon (355°) reflects this distortion for a static, but not a time-averaged structure. In addition the quantitative significance of these charges is uncertain for atoms that are not close to the molecular surface and other limitations in the estimation of atomic charges are noted in the Experimental section.[14]

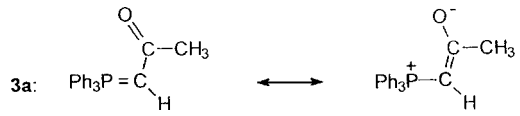
Conformational Equilibration

The change in conformation of the diacyl ylide, **2a**, and **b**, in going from solid to solution is indicative of a low barrier to rotation about the bond between the ylidic and acyl carbons, and NMR spectra in solution are

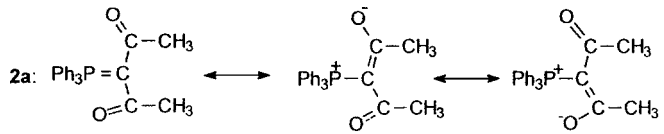
insensitive to changes in temperature or solvent (refer to Table I). This behavior contrasts with that for monoacyl ylides where conformational barriers are typically high.[5,6]

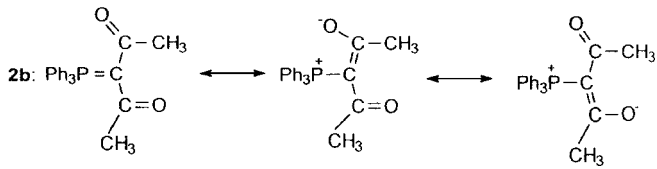
We estimated heats of formation of the monoacyl ylides, **3a** and **b**, with the HF 3-21(G*) and 6-31(G*) basis sets. Values at the 3-21(G*) level are in parentheses. The computed heat of formation of **3b** is less favorable than that of **3a** by 9.5 (13.8) kcal mol^{-1}, and that of the hypothetical structure, **3c**, with the acyl group twisted out of plane by 90°, is disfavored by 21.3 (25.3) kcal mol^{-1} relative to **3a**. The structure of **3c** should approximate that of the transition state for rotation about the partial double bond, although in view of the difference in heats of formation of **3a** and **b** we underestimate the enthalpic barrier to rotation. These values are consistent with experimental evidence on conformational barriers in monoacyl ylides.[5,6]

The preference for **3a** over **3b** is consistent with ylidic resonance and interaction between oxygen and cationoid phosphorus in **3a**.



In monoacyl ylides the $P^{+}\ ^{-}O$ interaction favors the Z-conformers, although in some ylides with bulky substituents it is offset by unfavorable steric interactions.[6] The situation is very different for a diacyl ylide, e.g., **2a** and **b** where ylidic resonance involves two acyl groups, viz.





Ylidic resonance is therefore maintained, to some extent, in interconversion of **2a** and **2b** by rotation about a bond between ylidic and acyl carbons, which should be assisted by a decrease in the steric repulsions between groups *anti*- to phosphorus.

TABLE IV Bond Length, Å, and Angles, °, at Ylidic Carbons for Diacyl Ylide, **2**, Ph_3 P=C $(CO–CH_3)_2$, and Monoacyl Ylide, **3**, Ph_3P=CH–CO–CH_3

	Length			Angles		
Ylide	C1–C2, 2′	P–C1–C2,2′	C2–C1–C2′	P–C1–H	H–C1–C2	Sum
2a[a]	1.45, 1.44	116, 112	127			355
2b[a]	1.45, 1.46	112, 126	122			360
2c	1.43, 1.51	117, 121	121			359
3a	1.41	121		117	122	360
3b	1.43	130		114	116	360
3c	1.49	123		109	108	340

[a]From Tables II and III.

This explanation of differences in conformational mobilities of mono- and di-acyl ylides is consistent with structural changes which affect extents of ylidic resonance and are shown in Table IV. The changes in computed bond lengths and angles illustrate how covalent and steric interactions change during interconversion of *syn*- and *anti*-conformers by rotation about a bond between the ylidic and acyl carbons. For interconversion of **2a** and **b** via **2c** the bond between the ylidic and one acyl carbon lengthens, due to decreased conjugation and the other shortens slightly. The change in bond angles at the ylidic carbon reflects the decreased interference between the methyl groups and the sum of the computed bond angles increases to 359°, as expected for a planar trigonal center.

The situation is different for **3a**, **b**, and **c** (see Table IV). The structural change in going from **3a** or **b** to **3c** apparently lengthens the bond between the ylidic and acyl carbons and it becomes similar to that in an aliphatic ketone. The bond angles at the ylidic carbon correspondingly change and their sum is 340°, indicating nonplanarity at the ylidic center in **3c**. These changes in optimized geometries show how ylidic resonance is lost in interconversion of monoacyl ylides, but largely maintained with diacyl ylides.

The different conformations of **2** in the solid and in solution depend on a balance between favorable interactions between oxygen and phosphorus, steric interference between groups *anti*- to phosphorus and crystal packing. Ylidic resonance and phosphorus-oxygen interactions are favored by a strictly planar ylidic system but it generates maximun steric interferences involving the acyl groups. Interactions between phosphorus and acyl oxygens are important in the diacyl ylide, **2a,b** although in the mixed ylides, **1**, keto and alkoxylic oxygens are oriented toward

phosphorus in the solid and in solution, illustrating the favorable interactions between the anionoid and cationoid centers.[4]

Infrared Spectroscopy

The infrared spectra were monitored in the solid (KBr disk) or in $CHCl_3$. We had hoped that differences in the carbonyl stretching frequencies of **2a** and **b** in the solid and solution would be informative in observing conformers that rapidly equilibrate on the NMR time scale. However, frequencies are similar in KBr (1600 and 1557 cm^{-1}) and in $CHCl_3$ (1601 and 1540 cm^{-1}), and are in the range observed for a variety of mono- and diacyl ylides with electronic delocalization involving the ylidic and acyl moieties.[15]. Motions associated with stretching vibrations in **2a** and **b** were identified by using the semi-empirical PM3 basis set[16] with the 6-31(G*) optimized structures. In **2a** interference between the CH_3 groups couples bending with C=O stretch to give symmetrical and antisymmetrical vibrations. In **2b** oxygen-phosphorus interaction lowers the force constant for one C=O stretch and the C=O stretching vibrations are not strongly coupled. The predicted are higher than the observed frequencies by approximately 15% and this procedure always overestimates stretching frequencies.[16] The similarities in these frequencies are consistent with our assumption that we are observing changes in conformation rather than in covalency.

Conclusions

The diacyl ylide, **2**, adopts different conformations in the solid and in solution as shown by differences in the ^{13}C-NMR spectra in these conditions. Computations indicate that the conformers have similar heats of formation and that barriers to interconversion are low, in contrast to the situation for monoacyl ylides.[6,7]

Conformations in solution are insensitive to such solvent properties as dielectric constant and hydrogen bond donation, for both acyl-ester ylides, **1**,[4] and the diacyl ylide, **2a**. Therefore conformations in solution are governed by intramolecular interactions although intermolecular packing force and dipolar interactions in the crystal affect the conformation. Geometries and estimated charge distributions of these stabilized ylides indicate that the acyl groups have significant enolate character due to conjugation with the ylidic residue. Berry and Patenaude[17] have shown that two carbonyl phosphonium salts can exist as keto and enol tautomers with protonation of an ylide on carbon or oxygen. However, in the ylides there is resonance between carbanion and enolate classical

structures whose contributions depend on conformation and electronic effects of substituents.

EXPERIMENTAL

Materials

(**3**), 1-Triphenylphosphoranylidene-2-propanone was a commercial sample (Aldrich) recrystallized from benzene/cyclohexane (1:1), m.p. 207°C.

(**2**), 3-Triphenylphosphoranylidene-2,4-pentanedione was obtained by reaction of monoacyl ylide, **3**, with acetic anhydride,[18] yield 80%, m.p. 164–165°C from ethyl acetate/cyclohexane (1:1); ν_{max} (KBr)/cm^{-1}: 1600, 1557, 1363, 1323, 1101; ν_{max} ($CHCl_3$)/cm^{-1}: 1601, 1540, 1363, 1325, 1104; ^{1}H NMR δ_{ppm} (300 MHz; $CDCl_3$): 2.3 (6H, s, CO—CH_3), 7.4–7.7 (15H, m, aromatic); ^{13}C-NMR δ_{ppm} ($CDCl_3$): 30.6 (d, $^3J_{P-C}$ 6.3, CO—CH_3), 88.8 (d, $^1J_{P-C}$ 102, *P*═*C*), 126.6 (d, $^1J_{P-C}$) 92.4, C_6H_5), 128.5 (d, $^3J_{P-C}$ 12.3, C_6H_5), 131.5 (d, $^4J_{P-C}$ 2.9, C_6H_5), 132.9 (d, $^2J_{P-C}$ 9.7, C_6H_5), 193.1 (d, $^2J_{P-C}$ 7.9, *C*O—CH_3); ^{31}P NMR δ_{ppm} ($CDCl_3$): 16.4.

NMR Spectroscopy

The ^{1}H, ^{13}C, and ^{31}P spectra in $CDCl_3$, CD_3OD, $DMSO_{d-6}$, and $acetone_{d-6}$ were monitored on Bruker DRX 300 or Varian INOVA 500 spectrometers and referred to TMS, or external 85% H_3PO_4 for ^{31}P. The ^{13}C NMR spectrum in the solid was monitored on a Bruker DSX 300 spectrometer (75.5 MHz for ^{13}C) at 25°C with a 4 mm magic angle spinning probe, spin speed 8.8 kHz, CPMAS pulse sequence and 19000 scans. The recycling delay was 3 s, the mixing time for the RAMP cross polarization was 2 ms, and the TPPM proton decoupling uses 4.5 μs. Chemical shifts are referred to adamantane at 39.5 ppm with respect to TMS at 0 ppm.

Infrared Spectroscopy

Spectra were monitored on a Bruker IFS 56 FT spectrometer with a KBr disk or in acid-free $CHCl_3$.

Structural Optimization

Calculations were made with Spartan 02 for Windows XP (Wavefunction) software. As a test of the optimization structure **2c** was reoptimized without any constraint on rotation about the bond between the ylidic and acyl carbons. It relaxed to a structure in which the ylidic

residue was superimposable on that of **2a**, heats of formation were within 0.3 kcal mole^{-1} and there were slight differences in conformations of the phenyl groups. Calculations of heats of formation neglect contributions of zero-point energies but they should be similar for the various conformers which have similar infrared spectra. We note that estimation of partial atomic charges is an artificial procedure in that it involves fitting overall electrostatic potentials to local atomic charges whose values therefore are sensitive to assumptions in the fitting procedure.[14]

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