PREFERRED CONFORMATIONS OF STABILIZED PHOSPHORUS YLIDES

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The stabilized phosphorus ylides, $Ph_3P{=}C(CO.R')CO.OR$; 1, R=Et, R'=$CH_2P^+Ph_3$; 2, R=R'=Me; 3, R=Et, R'=Me; 4, R=Pr^i; R'=Me; 5, R=Bu^t; R'=Me, adopt a near planar conformation in the crystal which allows extensive electronic delocalization. The keto and alkoxylic oxygens are oriented and align favorably with the cationoid phosphorus. These conformations bring methyl hydrogens in the ester residue into proximity with the face of a phenyl group and lead to π-shielding and upfield shifts of the ^1H NMR signals of 3 over a wide temperature range (−50–95°C) in $(CD_3)_2CO$, $CDCl_3$ and $DMSO_{d\text{-}6}$. Geometries of 2 and 3, optimized by using the HF 3-21 (G) or 6-31 (G*) basis sets, are very similar to those in the crystal, but semiempirical treatments generate structures in which either the ester or keto moiety is twisted out of plane.*

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

Conformations of stabilized phosphorus ylides (shown in Scheme 1) depend on the balance between ylidic delocalization involving the P=C and C=O bonds and nonbonding dipole-dipole and steric interactions.[1,2] Electronic delocalization favors coplanarity, but steric repulsions have the opposite effect. Crystalline ylides **1–5** are approximately coplanar in the ylidic moiety (refer to Scheme 1),[3–5] reflecting the role of delocalization. The keto oxygen is oriented toward the cationoid phosphorus, and the ester moiety adopts the Z-(*trans*) conformation, as in simple carboxylic esters.[6] The presence of the phosphonium ionic center

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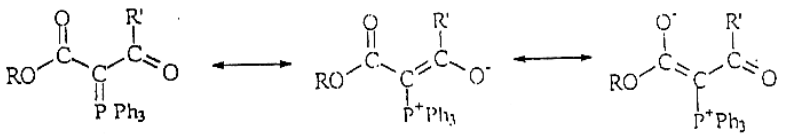


1 R = Et, R' = $CH_2P^+Ph_3$
2 R = R' = Me
3 R = Et, R' = Me
4 R = iso-Pr, R' = Me
5 R = tert-Bu, R' = Me

SCHEME 1 Conformations of stabilized keto-ester phosphorus ylides 1–5.

and $CHCl_3$ in crystalline **1**,[4] or the original cocrystallization of **3** with acetic acid,[3b] do not affect structures, which are apparently controlled by bonding and nonbonding interactions in the ylidic residue. Conformations with both carbonyl oxygens *syn* to phosphorus are excluded by x-ray crystallography and would not explain the observed NMR spectral evidence.[3–5]

In crystalline **1** and **3** the methyl of the ethoxy group is close to the face of a phenyl group and in solution shielding significantly decreases the ^1H NMR chemical shift of the methyl hydrogens.[4] Shielding had been observed earlier for some keto-ester ylides[3a,e,f] in solution and for a 2-triphenylphosphoranylidene succinic acid derivative[7] where the methyl of an ethoxy group could be close to the face of a phenyl group. These observations indicate that simple ^1H NMR spectroscopy can provide evidence on ylidic conformation in solution. Nishio et al.[8] give many examples of compounds in which a methyl group is in close proximity to the face of an aromatic group. They conclude that these interactions may be energetically favorable and involve weak, nonclassical, hydrogen bonding.[8,9] However, in some examples cited, interactions in other parts of the molecule may control the overall geometry and this could be the situation in our ylides.

Interactions between cationoid phosphorus and carbonyl oxygen are important in monoacyl ylides with significant barriers to rotation about the formal single bond between ylidic and carbonyl carbons.[2,10] Ylide monoesters can adopt conformations with the carbonyl oxygen *syn* or *anti* to phosphorus (refer to Scheme 2).[11] As with the monoacyl derivatives there are significant rotational barriers, but in the absence of large steric interactions, conformers do not have very different free energies.

SCHEME 2 Conformations of ylide monoesters.

Conformations in the crystal are well defined, but may differ from those in solution, which can be monitored by examining the NMR spectra.[1,2,10] We follow this general approach with ylides **1–5**, typically with $CDCl_3$ as solvent, although acetone-d_6 and DMSO-d_6 were used in studying temperature effects. Conformations often depend on temperature and solvent composition, and we used ^1H NMR spectroscopy to examine the conformation of **3** over a range of conditions. We also compared conformations of **2** and **3** from x-ray crystallography with those from geometrical optimization[12,13] because our preliminary work on an otherwise similar diacyl ylides **6**, $PH_3P{=}C(CO{\cdot}CH_3)_2$, indicates that it has different conformations in the crystal and in solution.

RESULTS AND DISCUSSION

NMR-Spectroscopy

Initially ^1H NMR spectra were obtained in $CDCl_3$ at 25°C, but we varied both temperature and solvent and examined the spectrum of **3** in acetone-d_6 and DMSO-d_6 at low and high temperatures respectively. Signals were sharp in all conditions (down to −50°C), with no indication of isomeric mixtures. Complete NMR data are in the Experimental section.

Chemical shifts of the keto CH_3 in **2–5** are almost independent of other substituents, but those of β-CH_3 of the alkoxy group are lowered by π-shielding relative to δ O-CH_2-CH_3 of 1.26 ppm for ethyl acetate[14b] (see Table I). The upfield shift is most evident with the ethoxy derivatives, **1**[4] and **3**, and persists with the iso-propoxy derivative, **4**, but to a lesser extent, because the effect is averaged over six rather than three hydrogens. We saw only limited evidence of π-shielding with the

TABLE I Methyl ^1H NMR Chemical Shifts and Carbonyl Stretching Frequencies of Keto-Ester Phosphorus Ylides **1–5**. $Ph_3P{=}C(CO\,R')CO_2R$[a]

					ν, cm^{-1}	
	R	R′	δ(R), ppm	δ(R′), ppm	Ester	Ketone
1	$-CH_2CH_3$	$-CH_2P^+Ph_3$	0.57		1653	1562
2	$-CH_3$	$-CH_3$	3.10	2.49	1681	1560
3	$-CH_2CH_3$	$-CH_3$	0.63	2.46	1654	1555
4	$-CH(CH_3)_2$	$-CH_3$	0.75	2.50	1652	1552
5	$-C(CH_3)_3$	$-CH_3$	1.03	2.47	1662	1543

[a] NMR spectra in $CDCl_3$ at 25°C and IR spectra in a KBr disk.

t-butoxy derivative, **5**, where any effect would be averaged over nine hydrogens, although in the crystal the *t*-butoxy residue of **5** is close to the face of a phenyl group.[5] The ^{1}H chemical shifts of the *t*-butyl groups of *t*-BuOH and *t*-BuOMe are 1.28 and 1.19 ppm, respectively, in $CDCl_3$,[14] and are higher than that in **5**, although they should be lower in terms of electronic substituent effects (see Table I). The ^{1}H NMR signal of OCH_3 of the methyl ester, **2**, also is shifted upfield, by ca. 0.5 ppm (see Table I) relative to simple methyl esters (the corresponding chemical shift for methyl acetate is 3.67 ppm[14b]).

These spectra indicate that the alkoxylic moiety and the keto oxygen are *syn*- to phosphorus which reduces dipole repulsions between the carbonyl groups and allows favorable interactions between phosphorus and the keto and alkoxylic oxygens as in the crystal.[3,5] The chemical shifts of the keto CH_3 are approximately 2.5 ppm (see Table I) and there is no indication of shielding by a phenyl group, consistent with the keto oxygen being oriented toward phosphorus.

Temperature effects (from −50 to 95°C) on the ^{1}H NMR spectrum of **3** in the various solvents are much very smaller (see Table II) than those observed for monoacyl and monoester ylides, indicating a strong preference for a single average conformation. Signals are sharp, even at low temperatures, consistent with little hindrance to rotation about the

TABLE II Variable Temperature ^{1}H NMR Spectral Data of Ethyl 2-Triphenylphosphoranylidene-3-oxobutyrate (**3**).
$Ph_3P{=}C(CO{-}CH_3){-}CO_2CH_2CH_3$

	Chemical shifts; ppm			Line widths; Hz	
	$-CO{\cdot}OCH_2CH_3$		$-CO-CH_3$	$-CO{\cdot}OCH_2CH_3$	$-CO-CH_3$
Solvent temp. °C	CH_3-	$-CH_2-$	CH_3-	CH_3-	CH_3-
DMSO-d_6					
95	0.61	3.59	2.27	0.80	1.13
65	0.57	3.57	2.27	0.86	1.22
50	0.55	3.57	2.27	1.22	1.42
35	0.53	3.54	2.27	1.13	1.45
20	0.50	3.54	2.27	1.20	1.43
Acetone-d_6					
17.7	0.61	3.63	2.31	0.86	1.04
10	0.59	3.62	2.31	0.88	1.09
0	0.57	3.61	2.31	0.78	1.08
−10	0.55	3.61	2.31	0.79	1.12
−20	0.54	3.60	2.31	0.91	1.13
−30	0.52	3.59	2.31	1.14	1.32
−40	0.50	3.59	2.31	1.33	1.36
−50	0.48	3.59	2.31	1.69	1.51

ylidic or other bonds.[2] Line widths of CH_2-CH_3 and $COCH_3$ are higher in $DMSO_{d\text{-}6}$ than in $acetone_{d\text{-}6}$, due to differences in solvent viscosities and decrease modestly with increasing temperature (see Table II). Chemical shifts of CH_2—CH_3 and $COCH_3$ depend only slightly on temperature and solvent, but those of CH_2—CH_3 increase with increasing temperature, probably because the increase in mobilities within the ylide decreases π-shielding by the phenyl groups.

Structural Optimization

We used an ab initio quantum mechanical treatment of structures of **2** and **3**,[12,13] and compared them with those in the crystal.[5] Initially we carried out a conformational search with MMFF parameters and followed it with semiempirical AM1 or MNDO/d treatments which gave structures with one carbonyl group approximately coplanar with the P=C bond and the other approximately orthogonal to it, which were very different from those in the crystal.[5] However, approximately planar ylidic structures with both carbonyl groups *anti*- to phosphorus were disfavored, probably by dipolar repulsions. Those with both keto and ester carbonyl groups oriented towards phosphorus were also disfavored. Some of these structures are inconsistent with the observed π-shielding of the alkoxylic CH_3 and the lack of shielding of the keto CH_3 signals (see Tables I and II). All differ markedly from those in the crystal. It appears that these semiempirical treatments do not account for the balance between ylidic delocalization and nonbonding interactions.

Structures of **2** and **3** optimized by using the HF 3-21 (G*), followed by the 6-31 (G*) basis set, are very similar to those in the crystal and structures from the two basis sets are identical to the eye.[5] We started the calculations from different initial structures, e.g., an MMFF best conformation followed by AM1 or MNDO/d predicted structures, or an initial input geometry with keto and ester carbonyl groups respectively *syn*- and *anti* to phosphorus. These independent calculations gave almost identical heats of formation enthalpies, but with small differences in C=P phenyl torsional angles. As a test we took an ab initio derived structure of **3**, and applied the AM1 treatment, which gave a nonplanar structure, but the subsequent ab initio treatment restored the near planar ylidic structure almost identical to that from the original computation.

Structures optimized in ab initio calculations allow extended electronic delocalization and orientation of oxygen lone pairs toward cationoid phosphorus and no inter-carbonyl dipolar repulsions, as in the crystal.[5] Structures in solution apparently are mobile, with relatively rapid rotation about the P=C bond[2] and sharp, temperature

independent, ^{1}H NMR signals (see Table II). Small changes in geometry probably do not significantly affect formation enthalpies. These calculations neglect interactions with the solvent which seem to be relatively unimportant.

Structures in the Crystal and in Solution

Conformations in solution depend on a balance between electronic delocalization, and nonbonding dipole-dipole and steric interactions, but packing forces can be important in the crystal. Interactions with solvents are relatively unimportant, based on the similar ^{1}H NMR spectra in different solvents and differences between $CHCl_3$, $(CH_3)_2SO$, and $(CH_3)_2C{=}O$ as hydrogen bond donors/acceptors[15] (see Tables I and II).

Structures in the crystal generally can be defined unambiguously, but conformers may interconvert rapidly in solution, and relatively slow methods, such as NMR spectroscopy, then provide only averaged geometries. Structures from theoretical calculations are limited by the rigor of the basis set, the time required for the calculation, and allowance for solute-solvent interactions.[13,16]

TABLE III Selected Computed and X-Ray Geometric Parameters (Å, °) for Methyl 2-Triphenylphosphoranylidene-3-oxobutyrate (2). $Ph_3P{=}C(CO{-}CH_3){-}CO_2CH_3$[a]

Bond lengths (Å)					
P1–C1	1.74	[1.747(2)]	C2-O4	1.23	[1.243(2)]
P1–C(C)	1.81	[1.802(2)]	C2–C3	1.52	[1.510(3)]
P1–C(A)	1.82	[1.815(2)]	C5–O7	1.22	[1.212(2)]
P1–C(B)	1.81	[1.819(2)]	C5–O6	1.37	[1.349(3)]
C1–C2	1.44	[1.428(3)]	O6–C8	1.45	[1.435(3)]
C1–C5	1.43	[1.441(3)]			
Bond angles (°)					
C1–P1–C1C	115	[115.61(10)]	C1A–P1–C1B	103	[108.24(9)]
C1–P1–C1A	116	[108.97(10)]	C2–C1–C5	121	[123.05(19)]
C1C–P1–C1A	106	[106.92(9)]	C2–C1–P1	118	[113.18(15)]
C1–P1–C1B	110	[111.13(10)]	C5–C1–P1	120	[123.63(16)]
C1C–P1–C1B	107	[105.66(10)]			
Torsion angles (°)					
P1–C1–C2–O4	10.6	[12.0(3)]	P1–C1–C5–O7	166	[162.47(19)]
Contact distances (Å)					
P1···O4	2.94	[2.806(2)]	P1···O6	2.84	[2.971(2)]
C8(H)···Ph	3.16				

[a]X-ray crystallographic values[5] are in parentheses with the estimated SD, and positions are numbered as in Figure 1. (Reproduced by permission from the International Union of Crystallography.)

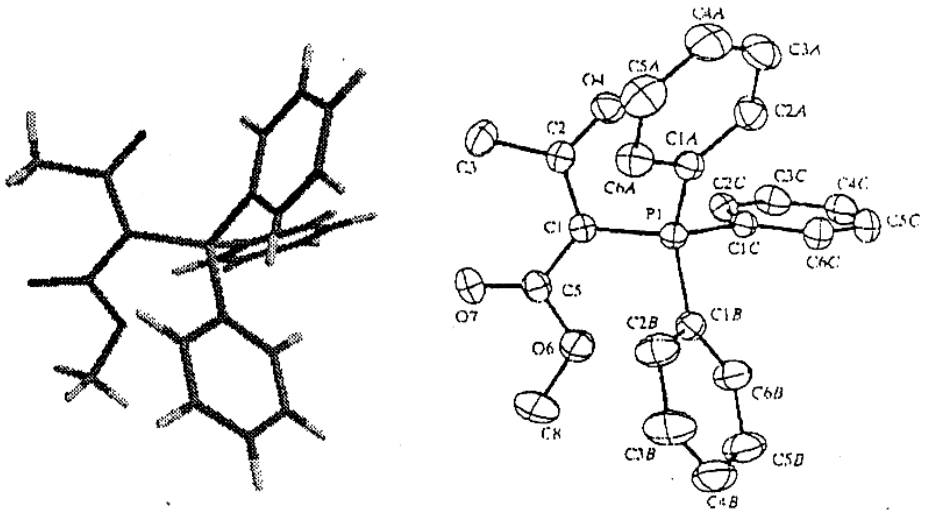
TABLE IV Selected Computed and X-Ray Geometric Parameters (Å, °) for Ethyl 2-Triphenylphosphoranylidene-3-Oxobutyrate (**3**). $Ph_3P{=}C(CO{-}CH_3){-}CO_2CH_2CH_3$[a]

Bond lengths (Å)					
P1–C1	1.73	[1.757(3)]	C2–C3	1.52	[1.507(4)]
P1–C(A)	1.81	[1.804(3)]	C5–O7	1.22	[1.197(4)]
P1–C(B)	1.80	[1.817(3)]	C5–O6	1.38	[1.352–1.360(8)]
P1–C(C)	1.81	[1.821(3)]	O6–C8	1.46	[1.457–1.466(8)]
C1–C2	1.45	[1.434(4)]	C8–C9	1.53	[1.494–1.497(10)]
C1–C5	1.43	[1.444(4)]			
C2–O4	1.23	[1.248(4)]			
Bond angles (°)					
C1–P1–C1A	115	[109.67(14)]	C1B–P1–C1C	107	[101.19(14)]
C1–P1–C1B	113	[113.78(14)]	C2–C1–C5	121	[123.5(3)]
C1A–P1–C1B	109	[107.20(15)]	C2–C1–P1	117	[109.9(2)]
C1–P1–C1C	111	[114.37(15)]	C5–C1–P1	118	[126.4(3)]
C1A–P1–C1C	100	[110.18(15)]			
Torsion angles (°)					
P1–C1–C2–O4	11	[1.7(4)]	P1–C1–C5–O7	178	[170.7(3)]
Contact distances (Å)					
P1···O4	2.95	[2.699(4)]	P1···O6	2.70	[3.014–3.026(7)]
C9(H)···Ph	3.7				

[a]X-ray crystallographic values[5] are in parentheses with the estimated SD, and positions are numbered as in Figure 2. (Reproduced by permission from the International Union of Crystallography.)

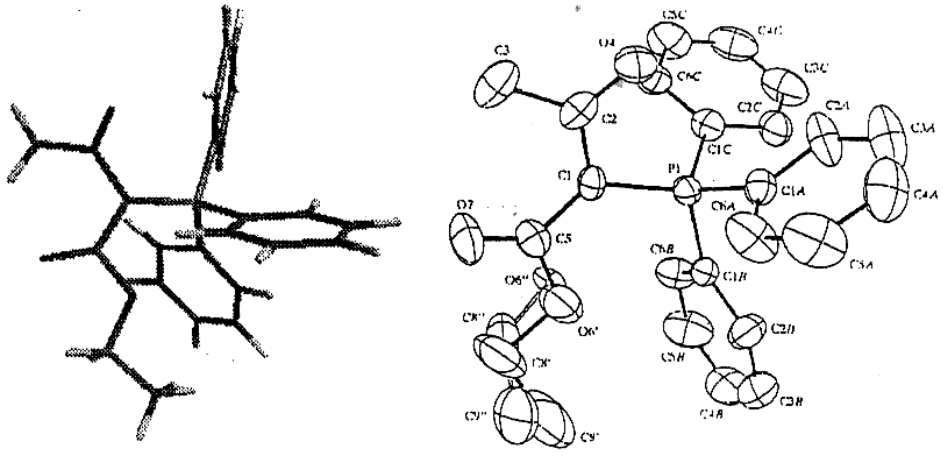
Calculated geometries of **2** and **3** are similar to those in the crystal, and bond angles and lengths are compared in Tables III and IV. The numbering of the atoms in the calculated structures, as shown in Figures 1 and 2, corresponds to those used in describing crystal structures.[5] In comparing computed geometries with those in the crystal, we round off computed lengths and distances with the second decimal place and angles to the nearest degree, because of computational limitations, and contact distances C8(H)···Ph and C9(H)···Ph, are approximate and are based on computed distances to phenyl carbon atoms.

The ^{1}H NMR spectra of **1–5**, with the upfield shifts of CH_3 of the alkoxylic groups and the essentially constant chemical shifts of the keto CH_3 in various conditions, are consistent with the crystal structures, although they do not provide evidence regarding values of the P1–C1–C2–O4 torsional angles. The close proximities of CH_3 of the alkoxylic groups to phenyl and the π-shielding agree with the results of Nishio et al.,[8,9] although they may be directed by the electronic delocalization and interactions of the keto and ester groups with phosphorus rather than by C–H/π interactions. There should be a favorable interaction between a keto oxygen and a phosphonium ion



Calculated structure of **2** Crystal structure of 2[5]

FIGURE 1 The molecular structure of methyl 2-triphenylphosphoranylidene-3-oxobutyrate (**2**) showing calculated and crystal geometries. For the crystal structure hydrogen atoms have been omitted for clarity. (Reproduced by permission from the International Union of Crystallography.)



Calculated structure of **3** Crystal structure of 3[5]

FIGURE 2 The molecular structure of ethyl 2-triphenylphosphoranylidene-3-oxobutyrate (**3**) showing calculated and crystal geometry. For the crystal structure hydrogen atoms have been omitted for clarity. (Reproduced by permission from the International Union of Crystallography.)

in **1** (refer to Scheme 1) where, in the crystal, the P···O distance is 2.9 Å.[4]

In the crystal, the ester C=O bond (C5-O7) is consistently shorter than the keto C=O bond (C2—O4) (by 0.023–0.051 Å),[5] and this shortening, although not its magnitude, is predicted by calculations (see Tables III and IV). Bond angles at the ylidic C1 deviate from the strictly trigonal 120° due to a balance between steric compressions involving phenyl and alkoxy groups, and C3 and O7, and favorable interactions between P1 and O4 and O6, where interatomic distances are ca. 2.8 Å.[5] These variations are predicted qualitatively for **2**, but the calculated C5—C1—P1 bond angle of **3** is low (see Table IV). We note a problem in refining the geometry of the ethoxy residue in crystalline **3**.[5] Predicted distances of the methyl hydrogen of an alkoxylic group to the face of a phenyl group (ca. 3.6 Å) are consistent with the observed upfield NMR shifts (see Tables I, III and IV).

Predicted bond lengths and angles are similar to those in the crystal and differences in torsional angles of the phenyls and contact distances are due to limitations in the calculations or to packing forces in the crystal. The sharp signals in the NMR spectra indicate that structures are mobile in solution, with free rotation about P—C and C—CH_3 bonds on the NMR timescale. Thus structures in the crystal and averaged structures in solution could differ provided that conformational barriers are low in solution (see Tables I and II).[2–4] The situation is different for monoacyl ylides where barriers are high.[10]

Carbonyl Stretching Vibrations

The IR carbonyl stretching frequencies of the ester and keto residues are relatively insensitive to substituents (see Table I). Ylides undergo a large number of stretching and bending vibrations, and, for simplicity, we examined those of the carbonyl groups of **2** and **3** by taking the structures obtained by using the 3-21 (G*) or 6-31 (G*) basis sets and identifying the motions by using PM3 semiempirical parameters,[12,13,17] which give for **2**, ν = 1980 and 1873 cm^{-1} for the ester and keto carbonyl groups respectively. The corresponding values for **3** are 1974 and 1875 cm^{-1}. This procedure indicates that stretch of the keto carbonyl groups is not strongly coupled with other motions, except for bending of the bonds to the carbonyl carbon, but that of the ester carbonyl groups is coupled strongly with bending of the O=C—OR residues. This procedure predicts frequencies which are too high by factors of 1.19–1.22,[12] and the factors are approximately 1.32 if we use the AM1 rather than the PM3 basis set in identifying motions.

CONCLUSIONS

In the crystal and in solution ylides **1–5** adopt conformations with the alkoxylic group, but not the keto methyl group, oriented toward phosphorus. The near planarity of the ylidic moiety in the crystal permits extensive electronic delocalization and favorable interactions between cationoid phosphorus and the keto and alkoxylic oxygens. These structures allow π-shielding of CH_3 of the alkoxylic groups due to their directed orientations, with the possibility of mildly favorable C—H/π interactions.[8,9]

Interactions with solvents used in crystallizations appear not to affect conformations in the crystal[3,4] or in solution (see Tables III and IV), although $CHCl_3$ is a hydrogen-bond donor and DMSO interacts with cationoid centers.[15]

Structures of **2** and **3** optimized by using the HF 3-21 (G*) and 6-31 (G*) basis sets are similar to those in the crystal. However, but molecular mechanics and semiempirical treatments fail by giving structures in which either the keto or ester group is twisted out of plane.

EXPERIMENTAL

Synthesis

The acylalkoxycarbonyl-ylides **2–5** were prepared by conventional transylidation methods.[1,5] The phosphonium-ylide salt **1** was obtained by reaction of ethoxycarbonylmethylenetriphenyl phosphorane with ethoxycarbonylmethyltriphenylphosphonium bromide.[18] Commercially available solvents for NMR measurements were used without further purification except that where as necessary trace acid in $CDCl_3$ was removed by Al_2O_3 or $NaHCO_3$. The phosphorus-carbon coupling constants are very similar to those seen earlier in other phosphorus ylides.[19]

A solution of acyl chloride (20 mmol) in 5 cm^3 of dry C_6H_6 was added slowly to the alkoxycarbonylmethylenetriphenylphosphorane (40 mmol) and 100 cm^3 of dry C_6H_6 under a dry atmosphere. The stirred solution was maintained at room temperature for 30 min to allow a white crystalline solid to separate. After filtration of alkoxycarbonylmethyltriphenylphosphonium chloride, the solvent was evaporated to give the alkyl-2-triphenylphosphoranylidene-3-oxobutyrates, **2–5**, as oils which were crystallized from ethyl acetate.

Methyl 2-Triphenylphosphoranylidene-3-oxobutyrate (2). 68% from methoxy carbonylmethylenetriphenylphosphorane and acetyl chloride,

m.p. 151–152 C, lit. 151–152°C[20]; ν_{max} (KBr)/cm^{-1} 1681 (CO_2CH_3) and 1560 ($COCH_3$)). ^{1}H-NMR δ_{ppm} (300 MHz; $CDCl_3$): 2.49 (3H, s, CO—C*H*$_3$), 3.10 (3H, s, O—C*H*$_3$), 7.4–7.75 (15H, m, aromatic); ^{13}C-NMR δ_{ppm} (75.4 MHz; $CDCl_3$): 29.2 (d, $^3J_{P-C}$6.6, CO—*C*H$_3$), 49.5 (O—*C*H$_3$), 71.2 (d, $^1J_{P-C}$111.9, *P*=*C*), 126.6 (d, $^1J_{P-C}$ 93.3, *C*$_6$H$_5$), 128.5 (d, $^3J_{P-C}$ 12.1, *C*$_6$H$_5$), 131.6 (d, $^4J_{P-C}$ 3.2, *C*$_6$H$_5$), 133.1 (d, $^2J_{P-C}$ 9.9, *C*$_6$H$_5$), 168.5 (d, $^2J_{P-C}$ 15.3, *C*O$_2$Me), 195.4 (d, $^2J_{P-C}$ 3.3, *C*OMe). ^{31}P-NMR δ_{ppm} (121.4 MHz; $CDCl_3$): 17.9.

Ethyl 2-Triphenylphosphoranylidene-3-oxobutyrate (3). 79%, m.p. 169–171°C, lit. 169–171°C;[21] ν_{max} (KBr)/cm^{-1} 1654 (CO_2Et) and 1555 ($COCH_3$)). ^{1}H-NMR δ_{ppm} (300 MHz; $CDCl_3$): 0.63 (3H, t, *J* 7.1, O—CH$_2$—C*H*$_3$), 2.46 (3H, s, COC*H*$_3$), 3.7 (2H, q, *J* 7.1, O—C*H*$_2$—CH$_3$), 7.5 (15H, m, aromatic). ^{13}C-NMR δ_{ppm} (75.4 MHz; $CDCl_3$): 14.1 (O—CH$_2$—*C*H$_3$), 29.7 (d, $^3J_{P-C}$ 6.85, CO—*C*H$_3$), 58.7 (O—*C*H$_2$—CH$_3$), 70.9 (d, $^1J_{P-C}$111.6, *P*=*C*), 126.8 (d, $^1J_{P-C}$ 93.65, *C*$_6$H$_5$), 128.4 (d, $^3J_{P-C}$ 12.45, *C*$_6$H$_5$), 131.4 (d, $^4J_{P-C}$ 2.9, *C*$_6$H$_5$), 133.0 (d, $^2J_{P-C}$ 9.8, *C*$_6$H$_5$), 168.1 (d, $^2J_{P-C}$ 15, *C*O$_2$Et), 195.4 (d, $^2J_{P-C}$ 4.1, *C*OMe). ^{31}P-NMR δ_{PPM} (121.4 MHz; $CDCl_3$): 17.6.

i-*Propyl-2-triphenylphosphoranylidene-3-oxobutyrate (4).* 89% from *i*-propoxy carbonylmethylenetriphenylphosphorane and acetyl chloride, m.p. 186–187°C; ν_{max} (KBr)/cm^{-1} 1652 (CO_2Pr^i) and 1552 (COMe)). ^{1}H-NMR δ_{ppm} (300 MHz; $CDCl_3$): 0.75 (6H, d, *J* 6.2, O—CH(C*H*$_3$)$_2$), 2.50 (3H, s, COC*H*$_3$), 4.6–5.1 (1H, m, *J* 6.2, O—C*H*(CH$_3$)$_2$), 7.4–8.0 (15H, m, aromatic). ^{13}C-NMR δ_{ppm} (75.4 MHz; $CDCl_3$): 21.5 ($CO_2CH(CH_3)_2$), 29.1 (d, $^3J_{P-C}$ 6.6, *C*OCH$_3$), 65.6 ($CO_2CH(CH_3)_2$), 71.7 (d, $^1J_{P-C}$ 111.9, *P*=*C*), 126.7 (d, $^1J_{P-C}$ 93.9, *C*$_6$H$_5$), 128.5 (d, $^3J_{P-C}$ 12.1, *C*$_6$H$_5$), 131.6 (d, $^4J_{P-C}$ 3.3, *C*$_6$H$_5$), 133.2 (d, $^2J_{P-C}$ 9.8, *C*$_6$H$_5$). 167.5 (d, $^2J_{P-C}$15.3, *C*O$_2$Pr^i), 195.2 (d, $^2J_{P-C}$ 3.3, *C*OMe). Anal. Calcd. for $C_{25}H_{25}O_3P$: C, 74.24; H, 6.23. Found: C, 74.36; H, 6.32.

t-*Butyl-2-triphenylphosphoranylidene-3-oxobutyrate (5).* (69%) from *tert*-butoxy carbonylmethylenetriphenylphosphorane and acetyl chloride, m.p. 177–178°C; ν_{max} (KBr)/cm^{-1} 1662 (CO_2Bu^t) and 1543 ($COCH_3$)). ^{1}H-NMR δ_{ppm} (300 MHz; $CDCl_3$): 1.03 (9H, s, OC(C*H*$_3$)$_3$), 2.47 (3H, s, CO—C*H*$_3$), 7.3–8.0 (15H, m, aromatic). ^{13}C-NMR δ_{ppm} (75.4 MHz; $CDCl_3$): 28.0 ($CO_2C(CH_3)_3$), 29.75 (d, $^3J_{P-C}$ 7.5,CO—*C*H$_3$), 55.0 ($CO_2C(CH_3)_3$), 70.4 (*P*=*C*), 127.1 (d, $^1J_{P-C}$ 91.3, *C*$_6$H$_5$) 128.4 (d, $^3J_{P-C}$ 12.8, *C*$_6$H$_5$), 131.3 (d, $^4J_{P-C}$ 3.8, *C*$_6$H$_5$), 133.0 (d, $^2J_{P-C}$ 9.0, *C*$_6$H$_5$), 167.6 (d, $^2J_{P-C}$ 14.3, *C*O$_2$Bu^t), 195.0 (d, $^2J_{P-C}$ 3.8, *C*OMe). Anal. Calcd. for $C_{26}H_{27}O_3P$: C, 74.63; H, 6.50. Found: C, 74.55; H, 6.40.

Spectra

^{1}H NMR spectra were recorded on Bruker DRX 300 or Varian INOVA 500 spectrometers with tetramethylsilane (TMS) as internal reference and ^{13}C and ^{31}P NMR spectra were recorded on the Bruker spectrometer and are referred to TMS or external 85% H_3PO_4, respectively, with δ, ppm., and J, Hz. Infrared spectra were obtained with a KBr disk on a Bruker IFS 56 FT spectrometer.

Structural Optimization

Calculations were made with Spartan Plus 2.0 (Wavefunction) software.[12]

REFERENCES

[1] H. J. Cristau and F. Plenat, in *The Chemistry of Organophosphorus Compounds*, edited by F. R. Hartley (Wiley, New York, 1994), vol. 3, chap. 2.

[2] S. M. Bachrach and C. I. Nitsche, in *The Chemistry of Organophosphorus Compounds*, edited by F. R. Hartley (Wiley, New York, 1994), vol. 3, Chap. 4.

[3] a) A. D. Abell and R. A. Massy-Westropp, *Aust. J. Chem.*, **35**, 2077 (1982); b) A. D. Abell, B. M. Clark, and W. T. Robinson, *Aust. J. Chem.*, **42**, 1161 (1989); c) A. D. Abell, J. Trent, and W. T. Robinson, *Chem. Commun.*, **42**, 362 (1991); d) A. D. Abell, B. M. Clark, and W. T. Robinson, *Aust. J. Chem.*, **41**, 1243 (1988); e) A. D. Abell and R. A. Massy-Westropp, *Aust. J. Chem.*, **35**, 2277 (1982); f) M. P. Cooke and K. P. Biciunas, *Synthesis*, 283 (1981).

[4] P. Barahona, V. Manriquez, R. Araya-Maturana, F. Castañeda, T. Delgado, and O. Wittke, *Bol. Soc. Chil. Quím.*, **43**, 493 (1998).

[5] F. Castañeda, C. A. Terraza, M. T. Garland, C. A. Bunton, and R. F. Baggio, *Acta Crystallogr. Sect. C*, **C57**, 180 (2001).

[6] a) C. E. Blom and H. H. Günthard, *Chem. Phys. Lett.*, **84**, 267 (1981); b) K. B. Wiberg and K. E. Laidig, *J. Am. Chem. Soc.*, **109**, 5935 (1987); c) E. L. Eliel and S. H. Wilen, *Stereochemistry of Organic Compounds* (Wiley, New York, 1994), chap. 10; d) T. B. Grindley, *Tetrahedron Lett.*, **23**, 1757 (1982).

[7] R. Bacaloglu, A. Blaskó, C. A. Bunton, G. Cerichelli, F. Castañeda, and E. Rivera, *J. Chem. Soc., Perkin Trans.* **2**, 965 (1995).

[8] a) M. Nishio, Y. Umezawa, M. Hirota, and Y. Takeuchi, *Tetrahedron*, **51**, 8665 (1995); b) M. Nishio and M. Hirota, *Tetrahedron*, **45**, 7201 (1989).

[9] H. Suezawa, T. Hashimoto, K. Tsuchinaga, et al., *J. Chem. Soc., Perkin Trans. 2*, 1243 (2000).

[10] a) I. F. Wilson and J. C. Tebby, *J. Chem. Soc., Perkin Trans. 1*, 31 (1972); b) D. M. Crouse, A. T. Wehman, and E. E. Schweizer, *Chem. Commun.*, 866 (1968); c) F. J. Randall and A. W. Johnson, *Tetrahedron Lett.*, 2841 (1968).

[11] H. I. Zeliger, J. P. Snyder, and H. J. Bestmann, *Tetrahedron Lett.*, 2199 (1969).

[12] a) W. J. Hehre and J. Yu, Abstracts 221st presented at the ACS National Meeting, New Orleans, March, 1996; b) W. J. Hehre, J. Yu, P. E. Klunzinger, and L. Lou, *A Brief Guide to Molecular Mechanics and Quantum Chemical Calculations* (Wavefunction, Irvine, 1998).

[13] a) I. N. Levine, *Quantum Chemistry* (Prentice Hall, Upper Saddle River, N.J., 2000) 5th ed., chap. 17; b) C. J. Cramer, *Essentials of Computational Chemistry* (Wiley, New York, 2002) chaps. 5 and 6.
[14] a) H. E. Gottlieb, V. Kotlyar, and A. Nudelman, *J. Org. Chem.*, **62**, 7512 (1997); b) L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance in Organic Chemistry* (Pergamon, New York, 1969), 2nd ed., p. 164.
[15] J. P. Snyder, *Tetrahedron Lett.*, 215 (1971).
[16] C. J. Cramer and D. G. Truhlar, *Chem. Rev.*, **99**, 216 (1999).
[17] J. J. P. Stewart, *J. Comput. Chem.*, 543 (1990).
[18] a) R. Araya-Maturana and F. Castañeda, *Phosphorus, Sulfur, and Silicon*, **81**, 165 (1993); b) P. A. Chopard, *J. Org. Chem.*, **31**, 107 (1966).
[19] T. A. Albright, M. D. Gordon, W. J. Freeman, and E. E. Schweizer, *J. Am. Chem. Soc.*, **98**, 6249 (1976).
[20] H. J. Bestmann and H. Schulz, *Tetrahedron Lett.*, 5 (1960).
[21] L. Horner and H. Oediger, *Chem Ber.*, **91**, 437 (1958).