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Molecular structures and preferred conformations of stabilized keto diester phosphonium ylides

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ABSTRACT

Triphenylphosphonium ylidic keto diesters with a nonylidic ester group, $Ph_3P=C(CO_2CH_2CH_3)-CO-CO_2CH_2CH_3$, **1**, and $Ph_3P=C(CO_2CH_2CH_3)CO-CH_2-CO_2CH_2CH_3$, **2**, have the keto group *syn* and the ylidic ester acyl group *anti* to phosphorus. Conformation of **2** is assigned by X-ray crystallography, while conformations of **1** and **2** are based on ¹H and ¹³C NMR spectroscopy, and comparisons of acyl stretching frequencies with predicted values from HF and DFT methods. Thermolyses of **1** and **2** gave the expected acetylene derivatives in high yield, consistent with the *syn* keto conformation and in agreement with earlier observations of thermolyses of stabilized phosphonium ylides. Results from the X-ray spectrum of **2** confirm the proposed structure.

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1. Introduction

For triphenylphosphonium ylides with one keto or carboxylic ester group in the ylidic moiety the acyl oxygen can be oriented *syn* or *anti* with respect to phosphorus [1,2] and conformation is defined in terms of this orientation. There is electronic delocalization between phosphorus and the ylidic acyl groups, consistent with extensive physical evidence [3], and in monoketo ylides, with R an alkyl group, there are favorable interactions between anionoid oxygen and cationoid phosphorus in a *syn* conformer, confirmed by X-ray crystallography, NMR spectroscopy and theoretical computation [4]. This generalization does not apply to all mono esters, because although simple monoester ylides have the *syn* conformation [1,2,5] those with a bulky nonylidic substituent group, *e.g.*, t-butyl, have the *anti* conformation which is not predicted by the usual theoretical treatments [6].

Schemes 1 and 2 are as Supplementary data. In ylidic keto esters the keto group is generally *syn*, and the ester group is *anti* [7], and in diesters, with few exceptions, one group is *syn* and the other *anti* [8]. In diester ylides with different sized alkoxy groups the smaller group is *syn* and the other *anti* [9]. We are unaware of any evidence for the existence of *syn–syn* alkyl diesters or keto esters in the crystal or in solution. Conformations in solid and in solution are generally the same for triphenylphosphonium ylides with aliphatic keto or ester groups. The *anti* conformations of ylidic alkyl ester groups in solution can often be established by ¹H NMR spectroscopy from observation of π shielding due to orientation of a terminal alkyl group towards the face of a phosphonium phenyl group [7a,7b,9b]. It has been suggested that these interactions with phenyl groups may be modestly stabilizing [10]. The short time scale of IR spectroscopy allows determination of acyl stretching frequencies, which are sensitive to conformation, and can be compared with calculated values [11]. This treatment can be applied to mixtures of ylides, but involves reliance on empirical Scale Factors, SF, [12] and lacks the quantitative nature of NMR spectroscopy or the rigor of X-ray spectroscopy. Conformations from these different methods are generally in agreement [11], but some ylides are monomers in the crystal [5], but mixtures in solution.

We examined conformations of two keto diesters, **1** and **2**, with only one carboxylic ester group bonded to the ylidic carbon noting that nonylidic groups sometimes affect conformations [6]. The ylidic keto group was expected to have the *syn* conformation [4] and thermolyses of such triphenyl phosphonium ylides are useful in preparing substituted acetylenes [13] and establishing conformations. The keto ester **2**, but not **1**, forms crystals suitable for use of X-ray crystallography, but for both compounds we examined NMR and IR spectra and used HF and DFT methods to predict geometries and acyl stretching frequencies. These ylides differ in the bonding to the nonylidic ester group and the methylene tether group in **2** allows flexibility to that group and affects interactions between keto and ester groups. The IR spectra of these ylides are complex, but signals of ester groups are readily assigned by observation of ¹H NMR interactions between an alkyl ester group and a



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phosphonium phenyl in an *anti* ester ylide. [7a,7b,9b] Acyl stretching frequencies can be compared with predicted values [11], and are higher for ester than keto groups in aliphatic keto esters.

Scott and Radom estimated Scale Factors, SF, for various computational methods by examination of many organic and inorganic compounds, often with simple structures, and critically discussed uses of the methods [12]. The DFT functional BLYP/6-31G(d) gave satisfactory agreement between observed and predicted acyl stretching frequencies for a range of ylidic diesters, keto esters and diketones [11].

Atomic charges were estimated with the Natural Population Analysis (NPA) method because although the significance of numerical charge values is uncertain, depending on the method of calculation [12b,14] the charge sequence is structurally useful. For **1** and **2**, the nonylidic ester groups may affect generalizations regarding expected conformations, as for some mono ylides [6] and also affect thermolyses.

2. Experimental

2.1. IR spectroscopy

Spectra were examined on a Bruker IFS 56 FT spectrometer with a KBr disk or in $CHCl_3$ with allowance for solvent signals, in the range of 400–4000 cm⁻¹ although only acyl stretching frequencies are considered.

2.2. NMR spectroscopy

NMR spectra were monitored on Bruker DRX 300 or Varian Inova 500 spectrometers in acid free $CDCl_3$ and are referred to TMS or 85% H₃PO₄. ¹³C NMR spectra were obtained with and without ¹H decoupling.

2.3. Elemental analysis and mass spectra

Elemental analysis as on a Fison EA 1108 analyzer and mass spectra were obtained on a MAT 95 XP Thermo Finnigan Spectrometer at 70 eV.

2.4. Synthesis – general procedure for preparation of keto diester triphenylphosphonium ylides **1** and **2**

A solution of monoethyl oxalyl chloride or ethyl malonyl chloride (40 mmol) in dry benzene (16 ml) was added slowly to (carbethoxymethylene) triphenylphosphorane, $Ph_3=CH-CO_2Et$ (80 mmol), in dry benzene (200 ml) under a dry atmosphere. After stirring at room temperature, reaction was complete in 8hr. and a white solid, (carbethoxymethyl) triphenylphosphonium chloride, $Ph_3P^+-CH_2-CO_2EtCl^-$, separated. After filtration the solvent was removed by rotary evaporation giving a solid. Recrystallization from ethyl acetate-hexane (1:1) gave the keto diester ylides **1** or **2**.

2.5. Diethyl 2-triphenylphosphoranylidene-3-oxosuccinate, 1

Yield 97%, mp. 124–126 °C, ¹H NMR (CDCl₃) δ_{ppm} : 0.71 (t, 3H, CH₃, *J* = 7.1 Hz); 1.29 (t, 3H, CH₃, *J* = 7.1 Hz); 3.77 (q, 2H, O—CH₂, *J* = 7.1 Hz); 4.25 (q, 2H, O—CH₂, *J* = 7.1 Hz); 7.7–7.4 (m, 15H). ¹³C NMR (CDCl₃) δ_{ppm} : 13.6 (CH₃); 14.04 (CH₃); 59.0 (O—CH₂); 60.8 (O—CH₂); 67.6 (d, P=C, ¹*J*_{P-C} = 110.6 Hz); 124.2 (d); 128.7 (d); 132.4 (d); 133.6 (d); 167.1 (d, CO₂, ³*J*_{P-C} = 13.1 Hz); 167.4 (d, CO₂, ²*J*_{P-C} = 14.8 Hz); 184.6 (d, C=O keto, ²*J*_{P-C} = 6.1 Hz). ³¹ P NMR (CDCl₃) δ_{ppm} : 16.4. IR (KBr): 1539, 1673,1739 cm⁻¹. HR-MS: *m/z* for C₂₆ H₂₅O₅P [M+H]⁺: 448.1439, found 448.1430.

2.6. Diethyl 2-triphenylphosphoranylidene-3-oxoglutarate, 2

Yield 68%, mp. 106 °C, ¹H NMR (CDCl₃) δ_{ppm} : 0.66 (t, 3H, *CH*₃, *J* = 7.1 Hz); 1.28 (t, 3H, *CH*₃, *J* = 7.1 Hz); 3.72 (q, 2H, O—*CH*₂, *J* = 7.1 Hz); 3.85 (s, 2H, CO—*CH*₂); 4.19 (q, 2H, O—*CH*₂, *J* = 7.1 Hz); 7.42–7.74 (m, 15H). ³¹P NMR (CD Cl₃) δ_{ppm} : 15.4; ¹³C NMR (CDCl₃) δ_{ppm} : 13.8 (*CH*₃); 14.4 (*CH*₃); 48.1 (d, CO—*CH*₂—*CO*₂); 58.6 (O—*CH*₂); 60.5 (O—*CH*₂); 71.5 (d, P=*C*, ¹*J*_{P-C} = 111.2 Hz); 126.4 (d); 128.7 (d); 131.8 (d); 133.4 (d); 167.9 (d, CO₂, ²*J*_{P-C} = 15.5 Hz); 170.4 (d, CO₂, ⁴*J*_{P-C} = 1.2 Hz); 189.6 (d, *C*=O keto, ²*J*_{P-C} = 5.2 Hz). ³¹(KBr): 1538, 1666, 1726 cm⁻¹. HR-MS: *m*/*z*. for C₂₇H₂₇O₅P [M+H]⁺: 462.1596, found 462.1591.

2.7. Characterization of ylide 2 acid solvate is as Supplementary data

See Supplementary data.

2.8. Thermolysis – general procedure for keto diester ylides, 1 and 2

The keto diester ylides (20 mmol) were heated in a round bottom flask fitted with a condenser and external and internal temperature controls. The vertical condenser was modified to allow collection of condensates. The solid was heated to 150–200 °C, external temperature, giving a viscous melt and thermolysis produced a liquid which was distilled under vacuum giving the acetylenic ester. The nonvolatile residue is triphenylphosphine oxide, mp. 150–154 °C. Thermolysis was also made in solid state diluted conditions using pure sand (Riedel) in 97% excess, showing almost the same results.

2.9. Thermolysis of 1

Thermolysis of 1, gave EtO₂C—CC=C—CO₂Et, (82%), bp 82–84 °C/ 4.5 mm Hg [15]. ¹H NMR (CDCl₃) δ_{ppm} : 1.3 (t, 6H, *J* = 7.1 Hz); 4.3 (q, 4H, *J* = 7.1 Hz).

2.10. Thermolysis of 2

Thermolysis of 2 gave EtO₂C—C=C—CH₂—CO₂Et, (74%), bp 60–64 °C/2.6 mm Hg. ¹H NMR (CDCl₃) δ_{ppm} : 1.2 (t, 6H, *J* = 7 Hz); 3.2 (s, 4H); 4.2 (q, 4H, *J* = 7 HZ); Anal. Calcd. For C₉ H₁₂ O₄ (%): C, 58.69; H, 6.57. Found (%): C, 59.03; H, 6.88.

Examples of thermolysis of other ylidic keto esters are as Supporting data.

2.11. Computation

Structures were optimized by HF/6-31G(d) and DFT methods, and acyl stretching frequencies were estimated with unconstrained structures. Calculations were made with Spartan '06 or '08 for Windows and convergence conditions as described [9]. Frequencies are rounded off to the nearest whole number. The literature SF = 0.9945 [12a] was used with BLYP/6-31G(d) but with HF/ 6-31G(d) we used SF = 0.866 for ester acyl groups and SF = 0.834 for keto acyl groups [11]. The B3LYP/6-31G(d) method with SF = 0.9614 [12a] was also used. Comparison of geometries of **2** (Tables 5 and 6) involves X-ray crystallography [16]. Structures for **1** and **2** from the BLYP/6-31G(d) method are in Chart 1. Computed and observed acyl stretching frequencies for keto diester ylides are in Table 2. Fractional charges (NPA) from B3LYP/6-31G(d) are in Table 3.



Chart 1. (a) Computed structures of *anti*-ester syn-keto 1 and 2 from the BLYP/6-31G(d) method. (b) Structures of 1 and 2 and atom-numbering from X-ray crystallography [16].

3. Results and discussion

The conformation of crystalline keto diester, **2**, is given by X-ray crystallography [16] and it forms 1:1 crystals with acetic acid without affecting conformations of the ylidic syn keto and anti ester groups, but we have no X-ray evidence for keto diester, 1. Orientations of ylidic ester groups with respect to phosphorus were established by ¹H NMR chemical shifts of the terminal CH₃ of ester alkoxy groups where π -shielding in the signal indicates orientation of the CH₃ group towards the face of a phenyl group [7,9b], and comparison of ¹³C NMR signals with and without ¹H decoupling, together with ³¹P coupling, is useful in establishing locations of some functional groups and signal assignments [17]. The NMR signals show that these keto esters have conformations similar to those of the simpler derivatives [7] with the keto acyl groups syn to phosphorus, consistent with the thermolytic evidence, and ylidic anti ester acyl groups. Comparisons of observed and predicted IR signals of the keto and ester acyl groups provide information on their locations. The nonylidic ester groups are linked to the ylidic keto group by a single bond and NMR signals indicate that in solution rotation is free about this bond.

3.1. Ph₃P=C(CO₂CH₂CH₃)CO-CO₂CH₂CH₃,1

The ¹H NMR signals of the keto diester, **1**, are simple in that there is a CH₃ triplet at 0.71 ppm of the ylidic *anti* ester ethoxy group with π -shielding and a second triplet at 1.29 ppm, of the terminal CH₃ nonylidic ethoxy ester group (Table 1). The two quartets of the ester methylene groups have ¹H chemical shifts in the ex-

pected region. Atom-numbering is as in Chart 1 and structures of **1** (and **2**) estimated with the BLYP/6-31G(d) method are shown in this Chart. The ¹³C signals were obtained without and with ¹H coupling which assists assignment (Table 1). Multiplicities of some of these signals, are sensitive to ¹H coupling which simplifies assignments (Table 1). Without ¹H coupling there are two doublets of the ylidic and nonylidic ester acyl groups at *ca.* 167.2 ppm, Table 1, with very similar chemical shifts and slightly different ³¹P coupling. With ¹H coupling there is further long range coupling, and the higher chemical shift signal of one of the two ester acyl group (Table 1), which as shown later is consistent with NPA values [12b,14].

The doublet of the ylidic keto group at *ca*. 185 ppm and that of the ylidic carbon at 67.6 ppm are split by ³¹P coupling. Chemical shifts and coupling constants are in Table 1.

3.2. Ph₃P=C(CO₂CH₂CH₃)CO-CH₂-CO₂CH₂CH₃, 2

X-ray observations of **2** and the 1:1 mixture with acetic acid show that the ylidic ester group has the *anti* conformation [16], as in solution from observation of π -shielding of the ¹H NMR signal of the terminal methyl of the ethoxy ester group (Table 1). The keto diester **2**-solvate was prepared because acetic acid promotes formation of good mono crystals for X-ray crystallography [7a] and limits disorder in the nonylidic ester group [16]. This solvate showed hydrogen bond intermolecular interactions and the *anti*ester conformation with Π shielding was as observed with ylide **2**, [16]. The other ¹H signals for **2**, do not provide much useful

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Fable 1	
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¹ H-NMR	1	2
² 1 4 5 COO-CH ₂ -C <u>H</u> ₃	0.71 t	0.66 t
² ¹ ⁴ ⁵ COO-C <u>H</u> ₂ -CH ₃	3.77 q	3,72 q
⁷ ⁶ ⁸ ⁹ COO-CH ₂ -C <u>H</u> ₃	1.29 t	1.28 t
⁷ ⁶ ⁸ ⁹ COO-C <u>H</u> ₂ -CH ₃	4.25 q	4.19 q
³ ¹⁰ ⁷ CO-C <u>H</u> ₂ -COO		3.85 s
¹³ C-NMR (¹ H decoupling)		
P=C- <u>C</u> OO-	167.4 d (² J _{P-C} = 14.8 Hz)	167.9 d (² J _{P-C} = 15.5 Hz)
1 1 3 7 6 P=C-CO- <u>C</u> OO-	167.1 d (³ J _{P-C} = 13.1 Hz)	
1 1 3 7 P=C- <u>C</u> O-COO-	184.6 d (² J _{P-C} = 6.1 Hz)	
1 1 P= <u>C</u> -	67.6 d (${}^{1}J_{P-C} = 110.6 \text{ Hz}$)	71.5 d (¹ J _{P-C} = 111.2 Hz)
1 1 3 10 P=C- <u>C</u> O-CH ₂ -		189.6 d (² J _{P-C} = 5.2 Hz)
¹ 1 3 10 7 P=C-CO-CH ₂ - <u>C</u> OO-		170.4 d (⁴ J _{p-c} =1.2 Hz)
1 1 3 10 P=C-CO- <u>C</u> H ₂ -		48.1 d (³ J _{P-C} = 7.8 Hz)
¹³ C-NMR (¹ H coupling)		
P=C- <u>C</u> OO-CH ₂ -	167.6 dt (² J _{P-C} = 15.1 Hz)	167.9 dt (² J _{P-C} = 14.7 Hz)
1 1 3 7 8 P=C-CO- <u>C</u> OO-CH ₂ -	167.3 dt (³ J _{P-C} = 13.4 Hz)	
1 1 3 7 P=C- <u>C</u> O-COO-	184.6 d ($^{2}J_{P-C} = 6.1 \text{ Hz}$)	
1 1 P= <u>C</u> -	67.7 d (¹ J _{P-C} = 110.4 Hz)	71.5 d (¹ J _{P-C} = 112.1 Hz)
1 1 3 10 P=C- <u>C</u> O-CH ₂ -		189.6 dt (² J _{P-C} = 5.18 Hz)
1 1 3 10 7 P=C-CO-CH ₂ - <u>C</u> OO-CH ₂ -		170.4 m
1 1 3 10 7 P=C-CO-CH ₂ -COO-CH ₂ -		48.1 dt (³ J _{P-C} = 7.3 Hz)

¹H- and ¹³C- (with and without ¹H decoupling) data for keto diester ylides 1, Ph₃P=C(CO₂Et)CO-CO₂Et, and 2, Ph₃P=C(CO₂Et)CO-CH₂-CO₂Et.

information on conformation, and we observed only one signal at 3.85 ppm of the CH_2 linkage between the nonylidic ester and keto groups in the ylidic residue, indicating equivalence of the two hydrogens with weak ³¹P coupling, unlike the situation with **1**

and due to different locations relative to the phosphonium group. The structure with numbering of positions is in Chart 1.

Ester CH_2 signals were assigned by coupling with CH_3 groups and ^{13}C signals were monitored without and with 1H coupling

Table 2

Computed and observed acyl stretching frequencies for keto diester ylides 1 Ph₃P=C(CO₂Et)CO-CO₂Et, and 2, Ph₃P=C(CO₂Et)CO-CH₂-CO₂Et.

	HF			BLYP			Observed (cm ⁻¹)	
1. No CH ₂ tether group Syn-keto anti-ester	1596	1661	1740	1582	1665	1718 ^a	1550 ^c (1560	1673 ^d 1663	1734 ^e 1730)
Syn-keto syn ester Anti-keto anti-ester	1555 -	1647	1739 -	1585 1609	1615 1668	1706 1707	-	- -	- -
2. With CH ₂ tether group Syn-keto anti ester	1571	1645	1721	1604	1654	1711 ^b	1577 ^c (1558	1661 ^d 1659	1734 ^e 1727)
Anti-keto anti-ester	-	-	-	1632	1690	1707	_	-	-

Observed values in parentheses were in $\mbox{CHCl}_3.$

^a 1618, 1688, 1750 with B3LYP/6-31G(d).

^b 1634, 1690, 1708 with B3LYP/6-31G(d) stretching frequencies assignment:

^c Syn keto.

^d Anti ester.

^e Nonylidic ester.

Table 3

Natural population analysis for syn-keto anti-ester ylides, $Ph_3P=C(CO_2Et)CO-CO_2Et$, 1, and $Ph_3P=C(CO_2Et)CO-CH_2-CO_2Et$, 2.

	Ylide 1	Ylide 2		Ylide 1	Ylide 2
P^1	1.651	1.657	C ³	0.422	0.514
C ¹	-0.738	-0.740	O^4	-0.577	-0.588
C^2	0.741	0.737	C ⁷	0.739	0.808
0^{2}	-0.585	-0.609	O ⁵	-0.556	-0.598
0^1	-0.564	-0.568	O^6	-0.524	-0.530
			C ¹⁰	-	-0.614

Atoms are numbered as in Tables 4-6 and Chart 1. Fractional charges are from B3LYP/6-31G(d).

allowing assignment of alkyl group signals. Without ¹H coupling there is a doublet at *ca*. 168 ppm, with ³¹P coupling of the ylidic acyl carbon of the ester group, and with ¹H coupling it becomes a doublet of triplets. The ¹³C doublet of the nonylidic ester acyl group at *ca*.170 ppm, without ¹H coupling, shows weak ³¹P coupling, and with ¹H coupling it becomes a multiplet. The doublet ylidic keto acyl signal at *ca*. 189.6 ppm, without ¹H coupling. The linking **C**H₂ signal at 48.1 ppm is a doublet due to coupling with ³¹P and with ¹H coupling it becomes a doublet of triplets. The doublet give of the ylidic carbon at *ca*. 71 ppm shows strong ³¹P coupling and is unaffected by ¹H coupling. The phenyl ¹H and ¹³C signals are similar to those of **1**.

3.3. Acyl stretching frequencies and predictions of conformations

The NMR spectra of the keto diester ylides provide considerable but incomplete structural evidence. Acyl stretching frequencies were calculated by the HF/6-31G(d) method with SF values of 0.866 and 0.834, estimated earlier for ylidic ester and keto acyl groups, respectively [11] and from BLYP/6-31G(d) with the literature SF value of 0.9945, [12], Table 2. The B3LYP/6-31G(d) method, with the literature SF value of 0.9614 [12a], was also used to estimate acvl stretching frequencies and structures. Fits to experiment by the HF and BLYP methods were generally satisfactory for triphenylphosphonium ylidic esters and ketones with small (methyl, ethyl) alkyl groups [11], but, with the literature SF [12a], IR fits were less satisfactory with B3LYP/6-31G(d). The calculations involve structural optimization and some preliminary IR calculations were made for conformers which were excluded on structural evidence. Partial NPA atomic charges [12,14] were also estimated, and complement the spectral evidence (Table 3). The BLYP/6-31G(d) method, which does not depend significantly on an SF value, is useful in estimating stretching frequencies but it gives slightly longer bonds, especially with polar groups, and the HF/6-31G(d) method is probably more reliable in this respect, although over estimation of force constants and reliance on the considerable empirical corrections limit its use in predicting frequencies [12b]. Acyl stretching frequencies are consistent with ylidic resonance and for syn keto anti ester ylides the keto acyl group has the lower frequency [11a] (Table 2). There is no evidence for a conformation with both acyl groups syn with respect to phosphorus and it is unusual except in some diketo ylides with phenyl or very bulky groups in the ylidic moiety [6b]. Assignments of *syn–anti* conformations fit those from the BLYP/6-31G(d) method and evidence noted earlier [11]. The SF values for HF/6-31G(d) used with the triphenylphosphonium ylides are lower than the literature value, [11,12a] but that for ester acyl groups is reasonably satisfactory for the nonylidic ester acyl groups $C^7 O^5$ at the end of the tethers. The B3LYP/6-31G(d) method, with SF = 0.9614 [12a], was used in comparisons of some observed and predicted acyl stretching frequencies. Results for ester acyl groups were satisfactory, but not those for the keto acyl groups, as for simpler ketones and keto esters [11].

Examples of geometries are in Tables 4–6 and bond lengths and angles are similar to those of other diester [8,9a,18] or keto ester triphenylphosphonium ylides [7a,c]. We have no X-ray evidence on the keto diester ylide, **1**, but the ylidic ester group is *anti* (Table 1), and the ylidic keto group is *syn*, with the acyl oxygen oriented between two phenyl groups, as is typical of *syn* keto groups in keto esters [7]. Estimated and observed frequencies for the *syn* keto-*anti* ester conformer **1** are generally in reasonable agreement, eliminating the existence of *syn*-*syn* or *anti*-*anti* conformers. Frequencies of the nonylidic ester acyl groups are not reliable indicators of conformation, because of the flexibility of the

Table 4

Selected computed geometric parameters (Å, °) for syn-keto anti-ester ylide $Ph_3P=C$ (CO₂Et) CO-CO₂Et, 1.

	HF	BLYP	B3LYP		HF	BLYP	B3LYP	
Bond lengths	: (Å)							
$P^{1}-C^{1}$	1.75	1.78	1.76	$C^{3}-0^{4}$	1.21	1.25	1.24	
$C^{1}-C^{2}$	1.45	1.46	1.45	C ³ C ⁷	1.53	1.55	1.55	
C ¹ C ³	1.44	1.45	1.44	C ⁷ -O ⁵	1.19	1.22	1.21	
$C^2 - O^2$	1.20	1.23	1.22	C ⁷ -O ⁶	1.32	1.36	1.34	
$C^2 - O^1$	1.34	1.34	1.37					
Bond angles	(°)							
$P^1 - C^1 - C^2$	122	123	122	$C^1 - C^3 - O^4$	126	125	125	
$P^1 - C^1 - C^3$	120	117	118	$C^{1}-C^{3}-C^{7}$	119	119	118	
$C^1 - C^2 - O^2$	125	124	126	O ⁴ -C ³ -C ⁷	116	116	116	
$C^1 - C^2 - O^1$	113	113	113	$C^{3}-C^{7}-O^{5}$	122	123	123	
$0^{2}-C^{2}-0^{1}$	121	122	121	$C^{3}-C^{7}-O^{6}$	119	119	119	
$C^2 - C^1 - C^3$	118	120	120	$0^{5}-C^{7}-0^{6}$	125	125	125	

Numbering as in Chart 1. Ylide 1 did not give suitable crystals for X-ray crystallography.

Table 5 Selected computed and observed Bond Lengths (Å) for 2, $Ph_3P=C(CO_2Et)-CO-CH_2-CO_2Et$.

	Calculated	Observed		
	HF	BLYP	B3LYP	
P^1-C^1	1.75	1.77	1.76	(1.75)
$C^{1}-C^{2}$	1.44	1.46	1.45	(1.45)
$C^{1}-C^{3}$	1.45	1.46	1.45	(1.43)
$C^2 - O^2$	1.20	1.24	1.23	(1.22)
$C^2 - O^1$	1.34	1.40	1.38	(1.36)
$C^{3}-0^{4}$	1.21	1.25	1.24	(1.24)
C ⁷ O ⁵	1.19	1.23	1.21	(1.21)
C ⁷ -C ¹⁰	1.51	1.53	1.52	(1.51)
C ⁷ -O ⁶	1.32	1.37	1.35	(1.33)
C ³ -C ¹⁰	1.52	1.54	1.53	(1.53)

Numbering as in Chart 1. Observed values are in parentheses [16].

Table 6

Selected computed and observed bond angles (°) for 2, $Ph_3P\!\!=\!\!C(CO_2Et)\!-\!CO\!-CH_2\!-\!CO_2Et$.

	Calculate	Observed		
	HF	BLYP	B3LYP	
$P^1 - C^1 - C^2$	120	120	120	(120)
$P^1 - C^1 - C^3$	119	117	118	(115)
$C^{2}-C^{1}-C^{3}$	121	123	122	(123)
$C^1 - C^2 - O^2$	127	128	127	(127)
$C^{1}-C^{2}-O^{1}$	113	112	112	(112)
$0^{2}-C^{2}-0^{1}$	120	121	121	(121)
$C^{1}-C^{3}-O^{4}$	123	123	123	(122)
C ¹ -C ³ -C ¹⁰	120	119	119	(120)
0 ⁴ -C ³ -C ¹⁰	117	118	118	(117)
C ³ -C ¹⁰ -C ⁷	114	114	114	(109)(112)
C ¹⁰ -C ⁷ -O ⁵	125	127	126	(120)
0 ⁵ -C ⁷ -O ⁶	123	123	123	(123)
C ¹⁰ -C ⁷ -O ⁶	111	112	111	(117)(115)
C7-06-C8	117	116	111	(110) (114)

Numbering as in Chart 1. Observed values are in parentheses [16].

tether group and calculated frequencies are generally lower than observed. These generalizations do not apply to the HF estimated frequency of the keto group in 1, which is adjacent to an ester group, because the empirical SF value was for alkyl keto groups [11b] and does not correct for an electronic interaction with the ester acyl group. This limitation does not apply to 2 where CH₂ separates the groups. Dependence on large, structure specific, SF corrections limits the utility of HF methods for frequency predictions e.g., the literature SF = 0.8953 [12a] for HF/6-31G(d) does not fit results for ylidic ketones and esters [11b]. Frequencies from BLYP/6-31G(d) would fit experiment slightly better without the SF correction. Values of NPA charges from BLYP/6-31G(d) and B3LYP/ 6-31G(d) for syn-keto anti-ester ylides 1 and 2, Table 3, are in ranges similar to those estimated for functional groups in diester vlides [17] with extensive charge distributions. Estimated charges from the HF/6-31G(d) method (not shown) are significantly higher than from the DFT methods, especially for polar groups, but follow the same sequence. Fractional charges and signs are qualitatively as expected in terms of charge delocalization, and alkoxy oxygens have anionoid character, although less than that of acyl oxygens. The estimated negative charges on alkoxy and acyl oxygens are consistent with orientations of anti ester and syn keto groups in keto esters [7a,c].

Relative ¹³C chemical shifts for atoms in similar groups are consistent with the NPA charges, *e.g.*, as for the lower chemical shift in a tether CH_2 group relative to those in the ester alkoxy groups. These estimated charges depend upon the method of estimation [12b], but for similar groups in a given compound signs and sequence help to identify groups and assign NMR signals. The estimated high positive charge on phosphorus fits the partial double bond between it and the ylidic carbon [19].

The ¹³C chemical shifts and coupling constants with ¹H and ³¹P of the two ester acyl carbons of **1** and **2** are similar, as are long range ¹H couplings for the two groups but ³¹P coupling should be larger for the ylidic acyl carbon, with the higher chemical shift, and this assignment fits related NPA charges. The ¹³C signals of the two ester acyl groups in **2** are well separated and the NPA charge sequence fits the assignments.

3.4. Limitations in the use of IR spectra and scale factors in conformer identification

Reliance on method and structure specific SF values in comparisons of predicted and observed acyl stretching frequencies applies to both HF and DFT methods because the near unity SF for BLYP/6-31G(d) [12a] involves an assumption, and fits with this method were poor for diesters with one bulky alkoxy group (iso Pr or t-Bu), or two such alkyl groups in keto esters [11b]. There is extensive electronic delocalization in these ylides, some interatomic distances between functional groups are within the sum of the van der Waals radii, and there are limitations in treating these noncovalent interactions and estimating bond lengths in solution. The hybrid DFT B3LYP/6-31G(d) method is widely used in structure

optimization [20b] with cancellation of errors in HF and pure DFT methods [12b] but with SF = 0.9614 IR fits are, for some vlides. worse than with BLYP/6-31G(d). The theoretical methods differ in their treatment of covalent and noncovalent interactions in that HF/6-31G(d) tends to overestimate force constants, requiring large SF corrections (12), and the pure DFT BLYP/6-31G(d) method tends to give increased bond length, especially for polar groups. Predicted carbon-oxygen bond lengths follow the sequence, BLYP > B3LYP > HF (Tables 4 and 5). The B3LYP/6-31G(d) method is preferred for estimating geometries [20b] but apparently not for calculating acyl stretching frequencies of the ylides, limiting the use of this method in predicting conformations. Acyl stretching frequencies from any given method were estimated with the geometry from the same method and the tendency of HF/6-31G(d) to give shorter and BLYP/6-31G(d) longer C=O bonds than from X-ray crystallography or B3LYP/6-31G(d), creates problems in assignment of SF values. In vlidic residues there is electron delocalization between acyl and ylidic groups, and for ester acyl groups the role of the alkoxy group has to be considered. As noted the BLYP method with SF ca. 1 is sensitive to structural changes in triphenyl phosphonium ylides with very bulky alkoxy groups and large noncovalent interactions may be important [11,20].

In aliphatic keto ester and diester triphenylphosphonium ylides one keto or acyl group is generally *syn* to phosphorus [7,9,11,17] and in keto diester ylides **1** and **2** the extensive ylidic resonance with phosphorus and acyl oxygens, is indicated by NPA, and crystalline bond lengths (Tables 3–5).

3.5. Thermolysis of keto diester ylides **1** and **2**, and the syn-keto conformation

Keto ester ylide thermolyses giving triphenyl phosphine oxide and the acetylene derivative in good yields are favored by electron withdrawal by adjacent carboxylic ester groups, and the proposed reaction path (Scheme 1) is similar to the Wittig reaction. The curved arrows in Scheme 1 indicate covalency changes in the reaction and have no mechanistic significance. There is no indication of these reactions with aliphatic phosphonium diesters with electron delocalization between the oxygens [13,21]. Thermolyses of keto derivatives of phosphonium ylides [13] are useful in syntheses of acetylenic intermediates which are dienophiles [22] or dipolarophiles [23] and provide evidence of *syn* conformations in keto ylides. Thermolyses of triphenyl phosphonium ylides with a variety of substituent groups have been examined and these spontaneous reactions follow first-order kinetics. Aitken et al. [13c,d] give extensive evidence of the synthetic use of these reactions.

Thermolyses of triphenylphosphonium ketones and keto esters were examined earlier [13] and electron withdrawing groups, aceto and cyano [13,21] favored reaction while steric effects appeared to be unimportant. Thermolyses of **1** and **2** and the ylides listed as Supporting Material indicate that reactions are intramolecular, consistent with computation and kinetic evidence [13c,d].





Scheme 2. Plane projection of the computed thermolysis transition state of 1.

Reactions were carried out in the gas phase or diluted in a pure sand without significantly affecting yields, typical of intramolecular reactions. The HF/3-21G method was used to simulate the transition state for thermolysis of **1** and the geometry shown in cartoon form as a plane projection (Scheme 2) is as expected for a late transition state with extensive P—C1 and C3—O4 bond breaking and making of new P…O and C1—C3 bonds. Structures of phenyl and ethyl groups (Scheme 2) are omitted for clarity and the side figures indicate bond making and breaking in an irregular rectangle. Numbering is as in Chart 1.

Estimated frequencies were corrected with SF = 0.9085 [12a]. There were weak signals with imaginary frequencies in the range 34–188 cm⁻¹ representing phenyl motion about phosphorus and extensions of P—C1 and C3—O4 bonds. There is a weak signal at 2335 cm⁻¹ with motion of the acetylenic carbons which, with the literature SF, indicates partial acetylenic bond formation. The C=O stretching frequencies are 1672 and 1769 cm⁻¹ for the acyl groups that in the ylide had been in the *syn* and nonylidic groups, respectively.

4. Conclusions

Observations of π -shielding in the ¹H NMR spectra show that in the keto diethyl ester ylides, **1** and **2**, the ylidic ester alkoxy group is oriented towards PPh₃. Assignments were for ¹H and ¹³C NMR signals, with and without ¹H coupling, and were as expected in terms of NPA charges from the B3LYP/6-31G(d) method. Acyl stretching frequencies from the BLYP/6-31G(d) and HF/6-31G(d) methods confirm that in the keto diester ylides the keto group has the syn and the ylidic ester acyl group has the anti conformation, as in other keto esters. Predicted acyl stretching frequencies of diesters, 1 and 2, agreed with experiment, and computed bond lengths and angles were typical of values for triphenyl phosphonium keto and ester ylides and for 2 agreed with results from Xray crystallography. Comparison of observed and predicted acyl stretching frequencies is useful in establishing conformations of triphenyl phosphonium esters and ketoesters when X-ray crystallographic evidence is not available, although there are limitations with use of HF/6-31G(d) for adjacent keto and ester groups involving different SF for ester and keto acyl groups. The near unity SF of 0.9945 for BLYP/6-31G(d) can often be neglected, but this assumption may not always be valid. Thermolyses of 1 and 2 give the acetylene derivatives, consistent with syn conformations of the ylidic keto groups, and the computed transition state involves extensive

formation of acetylenic and triphenylphosphine oxide bonds in an intramolecular reaction.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.08.022.

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