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TETRAHEDRON

A Facile Synthesis of Diastereoisomeric 1,4-Diionic Organophosphorus Compounds

Issa Yavari* , Mohammad Reza Islami and Hamid Reza Bijanzadeh

Department of Chemistry, University of Tarbiat Modarres, P. O. Box 14155-4838, Tehran, Iran

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Abstract: The addition of dialkyl acetylenedicarboxylates to strong CH-acids in the presence of triphenylphosphine leading to highly functionalized 1,4-diionic organophosphorus compounds is reported. These betaines possess two vicinal stereogenic centers and exist as a mixture of two diastereoisomers. Interconversion between the two diastereoisomeric forms of these 1,4-diionic compounds *via* C-H proton exchange reactions of the $(Ph)_3P^+$-CH moieties, preclude their separation. The assignments of the two diastereoisomeric forms of these systems are based on the high-field ^1H, ^{13}C and ^{31}P NMR data.

INTRODUCTION

In recent years there has been increasing interest in the synthesis of organophosphorus compounds, *i.e.* those bearing a carbon atom bound directly to a phosphorus atom [1-5]. This interest has resulted from the recognition of the value of such compounds for a variety of industrial and chemical synthetic uses. As a result, a large number of methods have appeared describing novel synthesis of organophosphorus compounds. A number of reactions have been observed which involve 1,4-diionic phosphorus compounds as elusive transient species [5,6]. In all of the reactions in which this diionic system is postulated, the betaine cannot be isolated but appears to occur as an intermediate on the pathway to an observed product.

We have recently described [7] the synthesis of stable 1,4-diionic phosphorus compounds **1** from the reaction of triphenylphosphine and ethyl propiolate in presence of strong CH-acids. With the purpose of preparation of betaines having two vicinal stereogenic centers, such as **2**, we performed the reaction of Meldrum's acid (**3a**) or 1,3-dimethylbarbituric acid (**3b**) with triphenylphosphine and dialkyl acetylenedicarboxylates **4**. Thus, reaction of CH-acids **3** with acetylenic esters **4** in presence of triphenylphosphine leads to the corresponding 1,4-diionic compounds **2** as a diastereoisomeric mixture.

*Fax: (98)21-8006544

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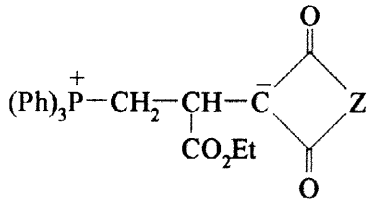

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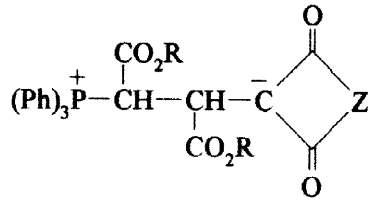

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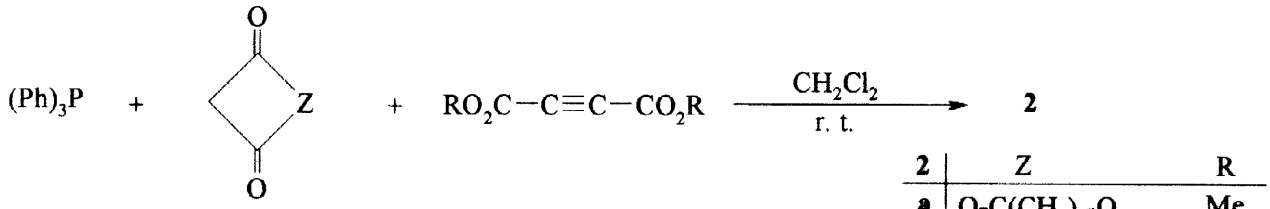
Z = O-C(CH$_3$)$_2$-O or CH$_3$N-CO-NCH$_3$



3	Z
a	O-C(CH$_3$)$_2$-O
b	CH$_3$N-CO-NCH$_3$

4	R
a	Me
b	Et
c	*t*-Bu

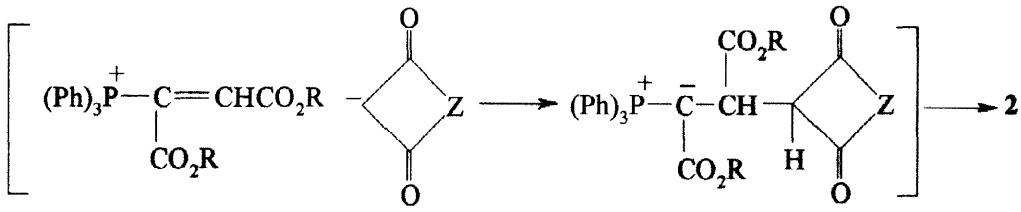
2	Z	R
a	O-C(CH$_3$)$_2$-O	Me
b	O-C(CH$_3$)$_2$-O	Et
c	O-C(CH$_3$)$_2$-O	*t*-Bu
d	CH$_3$N-CO-NCH$_3$	Me
e	CH$_3$N-CO-NCH$_3$	Et

RESULTS AND DISCUSSION

This three component reaction produces the hitherto unknown butanedioates **2a-e** in 90-98% yields. All the compounds are stable crystalline solids whose structure is fully supported by elemental analyses and IR, high-field ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopy and mass spectrometry data. The mass spectra of these 1:1:1 adducts displayed fairly weak molecular ion peaks. Any initial fragmentation involved the loss of ester moieties and scission of the ring.

A cyclic six-membered ring structure for compound **2** is unlikely because it requires several chemical shift coincidences in the ^{1}H and ^{13}C NMR spectra. If compound **2** had a cyclic structure, then we were to expect a doublet at about δ 160 for the C-O-P moiety in the ^{13}C NMR spectra. Structure **2** was further confirmed by the ^{31}P NMR spectroscopic data (δ 24-25) which is in agreement with the presence of a (Ph)$_3$P$^+$-C grouping [8,9].

On the basis of the chemistry of trivalent phosphorus nucleophiles [1-5] it is reasonable to assume that compound **3** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by CH-acid **3**. Then, the positively charged ion is attacked by the enolate anion of the CH-acid to generate ylide **6**. Compound **6** apparently isomerizes, under the reaction conditions, to produce the 1,4-diionic compound **2**.



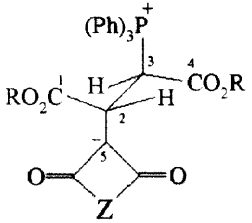
5 6

Meldrum's acid (**3a**) and 1,3-dimethylbarbituric acid (**3b**) have considerably higher acidities (pK_a 7.3-7.7) than acyclic analogues such as dimethylmalonate (pK_a 15.9) or even the diketone analogue 5,5-dimethylcyclohexane-1,3-dione (pK_a 11.2) [10]. Thus, the second acidic C-H of **3a** or **3b** can undergo proton-transfer reactions to convert the stable ylide **6** to betaine **2**. The origin of the anomalously high acidity of Meldrum's acid has been the subject of recent theoretical studies [11-13].

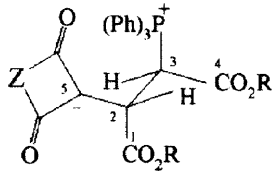
Since betaine **2** possesses two stereogenic centers, two diastereoisomers are possible. Compounds **2a-e** are, in fact, a mixture of two diastereoisomers. All attempts to separate these diastereoisomers were unsuccessful, perhaps because of the presence of a labile $(Ph)_3P^+$-C*H* proton in these isomers. The ^1H NMR spectroscopic signal for this proton disappears on addition of a small drop of D_2O to the $CDCl_3$ solution of **2**.

The 500 MHz ^1H NMR spectra of compounds **2a-e** displayed signals for vicinal methine protons at δ 4.79-5.90, which appear as two sets of double doublets for the major (M) and minor (m) diastereoisomers. The vicinal proton-proton coupling constant ($^3J_{HH}$) as a function of torsion angle can be obtained from the Karplus equation [14]. Typically, J_{gauche} varies between 1.5 and 5 Hz and J_{anti} between 9 and 14 Hz. Observation of $^3J_{HH}$ 9.8-12.0 Hz for the vicinal protons in major and minor diastereoisomers of compounds **2a-e** (see Table 1) indicates an *anti* arrangement for these protons. The assignments of the (2*S*, 3*S*)-**2** and (2*R*, 3*S*)-**2** cofigurations of **2a-e** are based on the three-bond carbon-phosphorus coupling, $^3J_{CP}$. Vicinal carbon-phosphorus coupling depends on configuration, as expected, *transoid* couplings being larger than *cisoid* ones. The Karplus relation can be derived from the data for organophosphorus compounds with tetra- and penta-valent phosphorus [16]. The observation of $^3J_{CP}$ of 16-18 Hz for the $C(CO)_2$ group (see Table 1), is in agreement with the (2*R*, 3*R*)-**2** for the major diastereoisomer. On the other hand, measuerement of $^3J_{CP}$ of 18-20 Hz for the ester C=O group, is in accord with the (2*R*, 3*S*)-**2** for the minor diastereoisomer.

To check whether the above conclusions regarding the nature of diastereoisomers of **2a-e** are reasonable, we turned to ^{31}P NMR spectroscopy. Two ^{31}P signals are observed at about 24 ppm (downfield from 85% H_3PO_4) for compounds **2a** and **2e**. These shifts are similar to those observed for alkyl-triphenylphosphonium iodide [8,9]. The ^{31}P chemical shift for a cyclic six-membered ring structure having a P-O bond is expected to be 80-90 ppm more shielded [8,15].



M (2*R*,3*R*)-**2**



m (2*R*,3*S*)-**2**

Table 1 Selected ^{1}H and ^{13}C NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for H-2, H-3, C-1, C-2, C-3, C-4 and C-5 in the major (M) and minor (m) diastereoisomers of compounds **2a-e**

Compound	Isomer (%)	^{1}H NMR spectroscopic data		^{13}C NMR spectroscopic data				
		H-2 ($^{3}J_{PH}$, $^{3}J_{HH}$)	H-3 ($^{2}J_{PH}$, $^{3}J_{HH}$)	C1 ($^{3}J_{PC}$)	C2 ($^{2}J_{PC}$)	C3 ($^{1}J_{PC}$)	C4 ($^{2}J_{PC}$)	C5 ($^{3}J_{PC}$)
2a	M (72)	4.79	5.70	174.32	44.21	44.62	167.79	71.49
		(4.4, 10.7)	(10.8,10.7)	(~0)	(4.6)	(39.6)	(~0)	(14.6)
2a	m (28)	4.89	5.84	174.17	42.72	43.38	168.43	71.02
		(3.9, 12.0)	(13.9, 12.0)	(18.2)	(~0)	(50.8)	(~0)	(1.5)
2b	M (70)	4.78	5.65	173.99	44.76	44.72	167.55	71.69
		(3.5, 10.7)	(11.4, 10.70)	(~0)	(4.9)	(39.4)	(~0)	(13.0)
2b	m (30)	4.85	5.85	173.60	42.48	43.06	167.64	71.82
		(6.9, 11.4)	(15.1, 11.4)	(18.2)	(~0)	(49.6)	(~0)	(2.2)
2c	M (73)	4.49	4.74	173.45	45.86	45.53	166.34	71.92
		(3.5, 11.4)	(11.6, 11.4)	(~0)	(4.8)	(39.5)	(~0)	(13.3)
2c	m (27)	4.71	5.74	172.72	43.04	42.59	165.88	72.52
		(4.4, 12.3)	(16.7, 12.3)	(19.1)	(~0)	(48.2)	(~0)	(2.2)
2d	M (56)	5.02	5.93	174.22	43.82	43.59	167.47	82.63
		(5.7, 10.7)	(10.8, 10.7)	(~0)	(4.5)	(40.2)	(~0)	(12.0)
2d	m (44)	5.10	5.95	173.87	41.67	42.54	167.68	83.39
		(6.3, 11.3)	(10.7, 11.3)	(17.4)	(~0)	(49.8)	(~0)	(2.2)
2e	M (55)	4.97	5.79	173.94	44.45	43.44	167.02	82.62
		(5.3, 10.4)	(10.7, 10.4)	(~0)	(4.5)	(40.7)	(~0)	(12.0)
2e	m (45)	5.02	5.89	173.15	41.78	42.28	167.03	83.35
		(6.3, 11.4)	(15.4, 11.4)	(18.0)	(~0)	(49.0)	(~0)	(2.1)

In conclusion, we have found that the reaction of strong CH-acids, such as Meldrum's acid or 1,3-dimethylbarbituric acid, with dialkyl acetylenedicarboxylates in the presence of triphenylphosphine leads to a facile synthesis of higly functionalized 1,4-diionic organophosphorus compounds **2a-e** in excellent yields.

EXPERIMENTAL SECTION

Dialkyl acetylenedicarboxylates, Meldrum's acid and 1,3-dimethylbarbituric acid were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500, 125.77 and 202.46 MHz, respectively. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

Preparation of dimethyl 2-(2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-yl-5-yid)-3-triphenylphosphoniobutane-1,4-dioate (2a). General procedure

To a magnetically stirred solution of triphenylphosphine (0.26 g, 1 mmol) and Meldrum's acid (0.14 g, 1 mmol) in acetone (5 ml) was added, dropwise, a mixture of dimethyl acetylenedicarboxylate (0.12 ml, 1 mmol) in acetone (2 ml) over 2 min. After 20 min stirring at room temperature, the product was filtered and recrystallized from ethanol. Colourless crystals, 0.61 g, m.p. 180-184 °C decomp., yield 98%. IR (KBr) (ν_{max}, cm^{-1}): 1731 and 1738 (C=O). MS, *m/z* (%): 548 (M^+, 1), 334 (18), 303 (10), 262 (10), 183 (100). Anal. Calcd. for $C_{30}H_{29}O_8P$ (548.53): C, 65.69; H, 5.33%. Found: C, 65.8; H, 5.4%. ^{1}H, ^{13}C and ^{31}P NMR data for the major isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.60 (6 H, s, 2 CH_3), 3.23, 3.27 (6 H, 2 s, 2 OMe), 4.79 (1 H, dd, $^{3}J_{HH}$ 10.7 Hz and $^{3}J_{PH}$ 4.4 Hz), 5.70 (1 H, dd, $^{3}J_{HH}$ 10.7 Hz and $^{2}J_{PH}$ 10.8 Hz), 7.6 - 8.0 (15 H, m, arom); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 26.02 [C(CH_3)$_2$], 44.21 (d, $^{2}J_{PC}$ 4.6 Hz, P-CH-CH), 44.62 (d, $^{1}J_{PC}$ 39.6 Hz, P-CH), 52.89, 53.23 (2 OMe), 71.49 [d, $^{3}J_{PC}$ 14.6 Hz, C(CO)$_2$], 101.90 (CMe_2), 121.47 (d, $^{1}J_{PC}$ 88.2 Hz, C_{ipso}), 129.83 (d, $^{3}J_{PC}$ 12.8 Hz, C_{meta}), 134.32 (d, $^{4}J_{PC}$ 2.3 Hz, C_{para}), 134.54 (d, $^{2}J_{PC}$ 9.68 Hz, C_{ortho}) 166.56 (O=*C*-C-*C*=O), 167.79, 174.32 (2 C=O, ester). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 23.80 [$(Ph)_3P^+$-C]. ^{1}H, ^{13}C and ^{31}P NMR data for the minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (6 H, s, 2 CH_3), 3.28, 3.60 (6 H, 2 s, 2 OMe), 4.90 (1 H, dd, $^{3}J_{HH}$ 12.0 Hz and $^{3}J_{PH}$ 3.90 Hz), 5.84 (1 H, dd, $^{3}J_{HH}$ 12.0 Hz and $^{2}J_{PH}$ 13.88 Hz), 7.6-8.0 (15H, m, arom); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 26.12 [C(CH_3)$_2$], 42.72 (P-CH-CH), 43.38 (d, $^{1}J_{PC}$ 50.8 Hz, P-CH), 52.67, 52.90 (2 OMe), 71.02 [d, $^{3}J_{PC}$ 1.5 Hz, C(CO)$_2$], 101.14 (CMe_2), 118.16 (d, $^{1}J_{PC}$ 87.4 Hz, C_{ipso}), 130.03 (d, $^{3}J_{PC}$ 13.0 Hz, C_{meta}), 134.55 (d, $^{2}J_{PC}$ 9.68 Hz, C_{ortho}), 134.93 (C_{para}), 166.63

(O=*C*-C-*C*=O), 168.43 (C=O, ester), 174.17 (d, $^3J_{PC}$ 18.2 Hz, C=O, ester). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 24.15 [$(Ph)_3P^+$-C].

Diethyl 2-(2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-yl-5-yid)-3-triphenylphosphoniobutane-1,4-dioate (2b)

Colourless crystals,0.55 g, m.p 163-166 °C decomp., yield 95%. IR (KBr) (ν_{max}, cm^{-1}): 1729 and 1735 (C=O). MS, *m/z*, (%): 576 (M^+, 2), 503 (16), 348 (2), 401 (3) 262 (30), 183 (100). Anal. Calcd. for $C_{32}H_{33}O_8P$ (576.60): C, 66.66; H, 5.77%. Found: C, 65.2; H, 5.8%. ^{1}H and ^{13}C NMR data for the major isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87 (3H, t, $^3J_{HH}$ 7.3 Hz, CH_3), 0.99 (3 H, t, $^3J_{HH}$ 7.3 Hz, CH_3), 1.65 (6 H, 2 s, 2 CH_3), 3.6, 3.78 (4 H, m, 2 OCH_2), 4.78 (1 H, dd, $^3J_{HH}$ 10.7 Hz and $^3J_{PH}$ 3.5 Hz), 5.65 (1 H, dd, $^3J_{HH}$ 10.7 Hz and $^2J_{PH}$ 11.4 Hz), 7.3- 8.1 (15 H, m, arom); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 13.85, 14.13 (2 CH_3), 26.17 [$C(CH_3)_2$], 44.72 (d, $^1J_{PC}$ 39.4 Hz, P-*C*H), 44.76 (d, $^2J_{PC}$ 4.9 Hz, P-CH-*C*H), 61.95, 63.13 (2 OCH_2), 71.69 [d, $^3J_{PC}$ 13.0 Hz, *C*$(CO)_2$], 101.92 (*C*Me_2), 122.16 (d, $^1J_{PC}$ 88.4 Hz, C_{ipso}), 129.77 (d, $^3J_{PC}$ 13.0 Hz, C_{meta}), 134.13 (d, $^4J_{PC}$ 2.3 Hz, C_{para}), 134.59 (d, $^2J_{PC}$ 9.8 Hz, C_{ortho}) 166.50 (O=*C*-C-*C*=O), 167.55, 173.99 (2 C=O, ester). ^{1}H and ^{13}C NMR data for the minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88 (3 H, t, $^3J_{HH}$ 7.3 Hz, CH_3), 1.18 (3 H, t, $^3J_{HH}$ 6.9 Hz, CH_3), 1.35 (6 H, s, 2 CH_3), 4.05, 4.19 (4 H, m, 2 OCH_2), 4.85 (1 H, dd, $^3J_{HH}$ 11.4 Hz and $^3J_{PH}$ 6.9 Hz), 5.85 (1 H, dd, $^3J_{HH}$ 11.4 Hz and $^2J_{PH}$ 15.1 Hz), 7.3- 8.1 (15 H, m, arom); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 13.67, 14.53 (2 CH_3), 26.11 [$C(CH_3)_2$], 42.48 (P-CH-*C*H), 43.06 (d, $^2J_{PC}$ 49.6 Hz, P-*C*H), 61.53, 62.47 (2 OCH_2), 71.82 [d, $^3J_{PC}$ 2.2 Hz, *C*$(CO)_2$], 101.19 (*C*Me_2), 118.51 (d, $^1J_{PC}$ 86.5 Hz, C_{ipso}), 129.92 (d, $^3J_{PC}$ 12.8 Hz, C_{meta}), 134.68 (d, $^2J_{PC}$ 6.3 Hz, C_{ortho}),134.73 (C_{para}) 166.54 (O=*C*-C-*C*=O), 167.64 (C=O, ester), 173.60 (d, $^3J_{PC}$ 18.2 Hz, C=O, ester).

Di-t-butyl 2-(2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-yl-5-yid)-3-triphenylphosphoniobutane-1,4-dioate (2c)

Colourless crystals, 0.59 g, m.p. 180-184 °C decomp., yield 94%. IR (KBr) (ν_{max}, cm^{-1}): 1706 and 1727 (C=O). MS, *m/z* (%): 632 (M^+, 1), 376 (2), 319 (7), 262 (17), 183 (40), 57 (100). Anal. Calcd. for $C_{36}H_{41}O_8P$ (632.69): C, 68.34; H, 6.48%. Found: C, 68.0; H, 6.6%. ^{1}H and ^{13}C NMR data for the major isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03, 1.10 (18 H, s, 2 CMe_3), 1.65 (6 H, s, 2 CH_3), 4.49 (1 H, dd, $^3J_{HH}$ 11.4 Hz and $^2J_{PH}$ 11.4 Hz), 4.74 (1 H, dd, $^3J_{HH}$ 11.4 Hz and $^3J_{PH}$ 3.5 Hz), 7.5 -8.1 (15 H, m, arom); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 26.31 [$C(CH_3)_2$], 27.72 [2 $C(CH_3)_3$], 45.53 (d, $^1J_{PC}$ 39.5 Hz, P-*C*H), 45.86 (d, $^2J_{PC}$ 4.9 Hz, P-CH-*C*H), 71.92 [d, $^3J_{PC}$ 13.3 Hz, *C*$(CO)_2$], 81.77, 84.72 [2 *C*$(CH_3)_3$], 101.59 [*C*$(CH_3)_2$], 123.56 (d, $^1J_{PC}$ 89.0 Hz, C_{ipso}), 129.48 (d, $^3J_{PC}$ 12.8 Hz, C_{meta}), 133.62 (d, $^4J_{PC}$ 2.6 Hz, C_{para}),134.57 (d, $^2J_{PC}$ 9.7 Hz, C_{ortho}) 166.13 (O=^{13}C-C-^{13}C=O), 166.34, 173.45 (2 C=O, ester). ^{1}H and ^{13}C NMR data for the minor isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.05, 1.38 (18 H, s, 2 CMe_3), 1.35 (6 H, s, 2 CH_3), 4.71 (1 H, dd, $^3J_{HH}$ 12.3 Hz and $^3J_{PH}$ 4.4 Hz), 5.74 (1 H, dd, $^3J_{HH}$ 12.3 Hz and $^2J_{PH}$ 16.71 Hz), 7.5-8.1 (15 H, m, arom); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 27.47 [2 $C(CH_3)_3$], 28.36 [$C(CH_3)_2$], 42.59 (d, $^1J_{PC}$ 48.2 Hz, P-*C*H), 43.04 (P-CH-*C*H), 72.52 [d, $^3J_{PC}$ 2.2 Hz, *C*$(CO)_2$], 80.90, 83.71 (2 *C*Me_3), 100.72 (*C*Me_2), 119.08 (d, $^1J_{PC}$ 86.4 Hz, C_{ipso}), 129.68 (d, $^3J_{PC}$

12.8 Hz, C_{meta}), 134.37 (d, $^4J_{PC}$ 2.5 Hz, C_{para}), 134.79 (d, $^2J_{PC}$ 10.2 Hz, C_{ortho}), 165.88 (C=O, ester), 166.16 (O=*C*-C-*C*=O), 172.72 (d, $^3J_{PC}$ 19.1 Hz, C=O, ester).

Preparation of dimethyl 2-(1,3-dimethylbarbituric acid-5-yl-5-yid)-3-triphenylphosphoniobuta-1,4-dioate (2d). General procedure

To a magnetically stirred solution of triphenylphosphine (0.26 g, 1 mmol) and 1,3-dimethylbarbituric acid (0.15 g, 1 mmol) in acetone (5 ml) was added, dropwise, a mixture of dimethyl acetylenedicarboxylate (0.12 ml, 1 mmol) in acetone (2 ml) over 2 min. After 20 min stirring at room temperature, the product was filtered and recrystallized from ethanol. Colourless crystals, 0.55 g, m.p. 153-158 °C decomp., yield 95%. IR (KBr) (ν_{max}, cm^{-1}): 1573, 1659 and 1716 (C=O). MS, *m/z* (%): 560 (M^+, 1), 333 (50), 301 (28), 262 (32), 183 (60), 54 (100). Anal. Calcd. for $C_{30}H_{29}N_2PO_7$ (560.51): C, 64.28; H, 5.21; N, 5.0%. Found: C, 64.0; H, 5.20; N, 4.9%. ^1H and ^{13}C NMR data for the major isomer: ^1H NMR (500 MHz, $CDCl_3$): δ 3.26, 3.46 (6 H, 2 s, 2 OCH_3), 3.3 (6 H, s, 2 NMe), 5.02 (1 H, dd, $^3J_{HH}$ 10.7 Hz and $^3J_{PH}$ 5.7 Hz), 5.93 (1 H, dd, $^3J_{HH}$ 10.7 Hz and $^2J_{PH}$ 10.8 Hz), 7.5-8.0 (15 H, m, arom); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 27.33 (2 NCH_3), 43.59 (d, $^1J_{PC}$ 40.2 Hz, P *C*H), 43.82 (d, $^2J_{PC}$ 4,5 Hz, P-CH *C*H), 52.75, 53.01 (2 OMe), 82.63 [d, $^3J_{PC}$ 12.0 Hz, *C*$(CO)_2$], 121.14 (d, $^1J_{PC}$ 88.0 Hz, C_{ipso}), 129.60 (d, $^3J_{PC}$ 13.0 Hz, C_{meta}), 134.30 (d, $^4J_{PC}$ 1.5 Hz C_{para}), 134.41 (d, $^2J_{PC}$ 10.1 Hz, C_{ortho}), 153.82 (C=O, urea) 162.86 (O=*C*-C-*C*=O), 167.47, 174.22 (2 C=O, ester). ^1H and ^{13}C NMR data for the minor isomer: ^1H NMR (500 MHz, $CDCl_3$): δ 2.95 (6 H, s, 2 NMe), 3.15, 3.61 (6 H, s, 2 OCH_3), 5.10 (1 H, dd, $^3J_{HH}$ 11.3 Hz and $^3J_{PH}$ 6.3 Hz), 5.95 (1 H, dd, $^3J_{HH}$ 11.3 Hz and $^2J_{PH}$ 10.7 Hz), 7.5-8.0 (15 H, m, arom); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 27.64 (2 NCH_3), 41.67 (P-CH *C*H), 42.54 (d, $^1J_{PC}$ 49.8 Hz, P-*C*H), 52.76, 53.16 (2 OMe), 83.39 [d, $^3J_{PC}$ 2.2 Hz, *C*$(CO)_2$], 118.15 (d, $^1J_{PC}$ 86.7 Hz, C_{ipso}), 129.77 (d, $^3J_{PC}$ 13.0 Hz, C_{meta}), 134.53 (d, $^2J_{PC}$ 10.1 Hz, C_{ortho}), 134.57 (C_{para}), 152.88 (C=O, urea), 163.18 (O=*C*-C-*C*=O), 167.68 (C=O), 173.87 (d, $^3J_{PC}$ 17.4 Hz, C=O, ester).

Diethyl 2-(1,3-dimethylbarbituric acid-5-yl-5-yid)-3-triphenylphosphoniobutane-1,4-dioate (2e)

Colourless crystals, 0.59 g, m.p. 151-156 °C decomp, yield 90%. IR (KBr) (ν_{max}, cm^{-1}): 1582, 1659 and 1713 (C=O). MS, *m/z* (%): 588 (M^+, 2), 347 (15), 303 (28), 275 (45), 262 (95), 183 (100). Anal. Calcd. for $C_{32}H_{33}N_2PO_7$ (588.56): C, 65.30; H, 5.65; N, 4.76%. Found: C, 65.2; H, 5.40; N, 4.7%. ^1H, ^{13}C and ^{31}P NMR data for the major isomer: ^1H NMR (500 MHz, $CDCl_3$): δ 0.72 (3 H, t, $^3J_{HH}$ 7.3Hz, CH_3), 0.82 (3 H, t, $^3J_{HH}$ 6.9 Hz, CH_3), 2.92 (6 H, s, 2 NMe), 3.66, 3.74 (4 H, m, 2 OCH_2), 4.97 (1 H, dd, $^3J_{HH}$ 10.4 Hz and $^3J_{PH}$ 5.3 Hz), 5.79 (1 H, dd, $^3J_{HH}$ 10.4 Hz and $^2J_{PH}$ 10.7 Hz), 7.5-8.0 (15 H, m, arom); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 13.67, 13.99 (2 CH_3), 27.18 (2 NCH_3), 43.44 (d, $^1J_{PC}$ 40.7 Hz, P-*C*H), 44.45 (d, $^2J_{PC}$ 4.5 Hz, P-CH-*C*H), 61.72, 62.47 (2 OCH_2), 82.62 [d, $^3J_{PC}$ 12.0 Hz, *C*$(CO)_2$], 121.68 (d, $^1J_{PC}$ 88.2 Hz, C_{ipso}), 129.64 (d, $^3J_{PC}$ 13.0 Hz, C_{meta}), 134.06 (d, $^4J_{PC}$ 1.6 Hz, C_{para}), 134.47 (d, $^2J_{PC}$ 9.4 Hz, C_{ortho}), 153.86 (C=O, urea), 162.75

(O=*C*-C-*C*=O), 167.02, 173.94 (2 C=O, ester). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 24.84 [$(Ph)_3P^+$-C]. ^{1}H, ^{13}C and^{31}P NMR data for the minor isomer: ^{1}H NMR (500 MHz,$CDCl_3$): δ 0.82 (3 H, t, $^3J_{HH}$ 6.9 Hz, CH_3), 1.07 (3 H, t, $^3J_{HH}$ 7.2 Hz, CH_3), 3.24 (6 H, s, 2 NMe), 3.45, 4.03 (4 H, m, 2 OCH_2), 5.03 (1 H, dd, $^3J_{HH}$ 11.4 Hz and $^3J_{PH}$ 6.3 Hz), 5.89 (1 H, dd, $^3J_{HH}$ 11.4 Hz and $^2J_{PH}$ 15.4 Hz), 7.5 - 8.0 (15 H, m, arom); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ 13.54, 14.35 (2 CH_3), 27.50 (2 NCH_3), 41.78 (P-CH-CH), 42.28 (d, $^1J_{PC}$ 49.0 Hz, P-*C*H), 61.26, 62.32 (2 OCH_2), 83.35 [d, $^3J_{PC}$ 2.1 Hz,, *C*$(CO)_2$], 118.43 (d, $^1J_{PC}$ 86.4 Hz, C_{ipso}), 129.47 (d, $^3J_{PC}$ 13.1 Hz, C_{meta}), 134.40 (d, $^2J_{PC}$ 8.0 Hz, C_{ortho}), 134.43 (C_{para}), 152.91 (C=O, urea), 163.00 (O=*C*-C-*C*=O), 167.03 (C=O, ester), 173.15(d, $^3J_{PC}$ 18.0 Hz, C=O, ester). ^{31}P NMR (202.46 MHz, $CDCl_3$): δ 24.79 [$(Ph)_3P^+$-C].

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