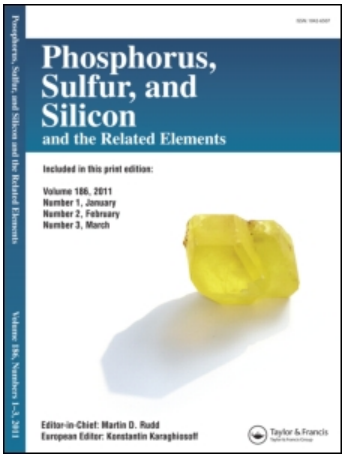

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TRIPHENYLPHOSPHINE CATALIZED REACTION BETWEEN 1,3-DICARBONYL COMPOUNDS AND ACETYLENIC ESTERS

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Reaction of triphenylphosphine with dialkyl acetylenedicarboxylates in the presence of strong CH-acids such as acetylacetone, methyl acetoacetate, cyclopentane-1,3-dione, or 5,5-dimethylcyclohexane-1,3-dione (dimedone) have been studied. In some cases, stable phosphorus ylides are obtained in excellent yields. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in (E) and (Z) geometrical isomers is slow on the NMR time scale at ambient temperature. Thus, these ylides exist as a mixture of geometrical isomers. From the reaction of dimedone with dimethyl acetylenedicarboxylate (DMAD) in the presence of triphenylphosphine, a chromene derivative is obtained. A Michael addition product was obtained from the reaction of cyclopentane-1,3-dione and DMAD.

Keywords: 1,3-Diketone; acetylenic ester; CH-acid; triphenylphosphine

There are many studies on the reaction between trivalent phosphorus nucleophiles and acetylenic esters in the presenc of OH, NH, or CH acids.[1–3] In some cases ylide products are stable, but in other cases they cannot be isolated and appear to occur as an intermediate on the pathway to an observed product. We describe the reaction of cyclic and acyclic 1,3-dicarbonyl compounds with acetylenic esters in the presence of triphenylphosphine, which leads to stable phosphorus ylides or chromene derivatives.

RESULTS AND DISCUSSION

The reaction of dialkyl acetylendicarboxylates **1** with acetylacetone or methyl acetoacetate in the presence of triphenylphosphine proceeded at

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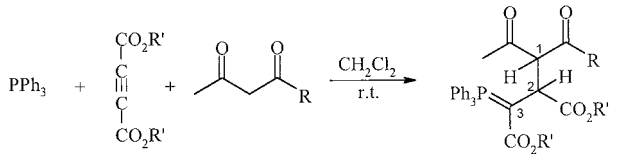
room temperature in dichloromethane, and was complete within a few hours. The ^{1}H and ^{13}C NMR spectra of the crude products clearly indicated the formation of the stable ylides **3** (Scheme 1). No other products other than **3** could be detected. The structures of compounds **3a–3d** were deduced from their elemental analyses and IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The mass spectra of these stable ylides displayed molecular ion peaks at appropriate *m/z* value. Any initial fragmantation involves loss from, or complet loss of the side chains and scission of the heterocyclic ring system.

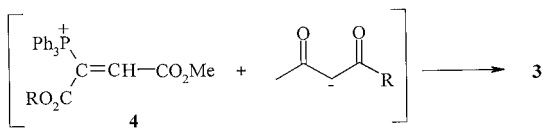


R'	R
1a : Me	**2a** : Me
1b : ^{t}Bu	**2b** : OMe

R	R'	% Ylide
3a : Me	Me	98
3b : Me	^{t}Bu	98
3c : OMe	Me	98
3d : OMe	^{t}Bu	97

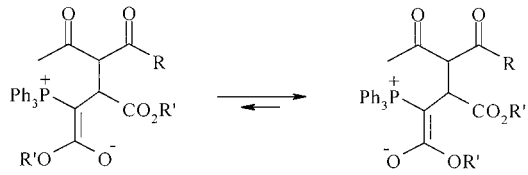
SCHEME 1

On the basis of the well established chemistry of trivalent phosphorus nucleophiles,[4–8] it is reasonable to assume that phosphorus ylide **3** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct followed by attack of the carbon moiety of the enolate anion of the CH-acid to the vinylphosphonium cation **4** to generate ylide **3** (Scheme 2).



SCHEME 2

^{1}H, ^{13}C, and ^{31}P NMR spectra of the stable ylides **3a** and **3b** are consistent with the presence of two diastereoisomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in the (*E*)-**3** and (*Z*)-**3** geometrical isomers (Scheme 3) is slow on the NMR time scale at ambient temperature. Due to the presence of two chirality centers in ylides **3c** and **3d**, the situation is more complex. The NMR spectra of these phosphoranes are consistent with the presence of four diastereoisomers.

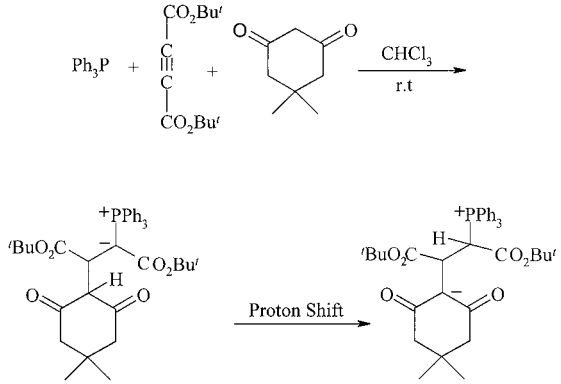


(*E*)-**3**; Major (*Z*)-**3**; Minor

SCHEME 3

Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts and coupling constants in various geometrical isomers of compounds **3a–3d** are shown in Table I.

The reaction of di-*tert*-butyl acetylendicarboxylate with dimedone in the presenc of triphenylphospine leads to stable 1,4-diionic compound **6**. This compound results from the proton transfer reaction in the initial ylide **5** (Scheme 4).



5 **6**

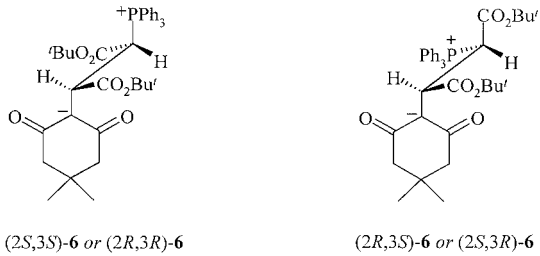
SCHEME 4

The presence of the ^{31}P nucleus in compound **6** helps in the assinment of the signals by long-renge couplings with ^{1}H and ^{13}C nuclei (see Experimental section). The vicinal proton-proton coupling constant ($^{3}J_{HH}$) as a function of torsion angle can be obtained from the Karplus equation.[9,10] Typically, J_{gauche} varies between 1.5 and 5 Hz and J_{anti} between 10 and 14 Hz. Observation of $^{3}J_{HH} = 10.8$ Hz for the vicinal protons in compound **6** indicates an anti arrangement for these centers. Since compound **6** possesses two chirality centers

TABLE I Selected ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shift (δ in ppm) and Coupling Constants (J in Hz) for H-2, OR, CO_2R, C-2, and C-3 in Diastereoisomers of Compounds **3a–3d**

		^{1}H NMR data				^{13}C NMR data		
Compound	Isomer (%)	H-2 ($^{3}J_{PH}$)	OR′	CO_2R'	C-1 ($^{3}J_{PC}$)	C-2 ($^{2}J_{PC}$)	C-3 ($^{1}J_{PC}$)	^{31}P NMR
3a	M (60)	3.46 (–)	3.00	3.54	63.07 (–)	40.58 (13)	35.61 (125)	23.78
	m (40)	2.90 (–)	3.54	3.54	64.35 (–)	39.42 (13)	35.24 (132)	23.78
3b	M (65)	3.19 (18)	0.95	1.40	66.40 (6)	45.20 (14)	38.60 (125)	23.00
	m (35)	3.13 (19)	1.39	1.48	68.40 (6)	44.52 (14)	40.50 (132)	24.17
3c	1 (45)	3.31–3.37 (–)	3.05	3.52	60.02 (–)	44.00 (14)	39.40 (127)	24.00–24.20
	2 (24)	3.31–3.37 (–)	3.57	3.59	60.00 (–)	42.80 (14)	40.00 (135)	24.00–24.20
	3 (19)	3.31–3.37 (–)	3.05	3.46	61.80 (–)	43.20 (14)	39.10 (125)	24.00–24.20
	4 (12)	3.31–3.37 (–)	3.60	3.62	61.70 (–)	42.50 (13)	39.80 (133)	24.00–24.20
3d	1 (32)	3.13 (18)	0.92	1.40	61.84 (4)	43.90 (14)	40.70 (135)	24.21
	2 (30)	3.11 (18)	1.43	1.45	61.80 (4)	45.00 (14)	38.40 (133)	23.04
	3 (23)	3.07 (18)	1.49	1.50	60.20 (4)	44.30 (14)	40.40 (135)	24.59
	4 (15)	3.05 (17)	0.94	1.47	57.30 (4)	43.50 (14)	38.50 (133)	23.38

two diasteroisomers with anti H—C—C—H arrangements are possible (Scheme 5).

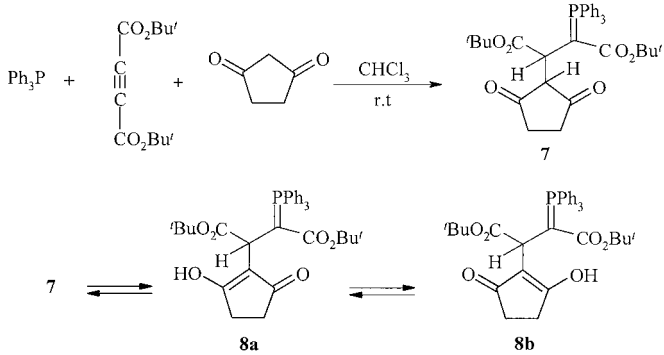


(2*S*,3*S*)-**6** *or* (2*R*,3*R*)-**6** (2*R*,3*S*)-**6** *or* (2*S*,3*R*)-**6**

SCHEME 5

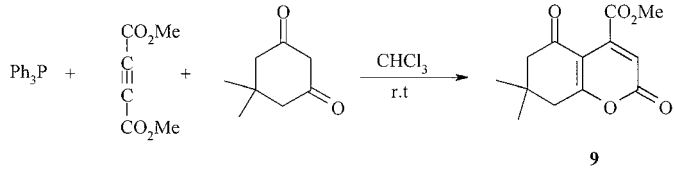
The three-bond carbon-phosphorus coupling, $^3J_{PC}$, depends on configuration, as expected, transoid couplings being larger than cisoid ones. The Karplus relation can be derived from the data for organophosphorus compounds with tetra- and penta-coordinate phosphorus.[11] The observation for $^3J_{PC}$ of 12 Hz for the P—C—C—C moiety (Experimental section), is in agreement with the anti arrangment. The $^3J_{PC}$ for the P—C—C—C(O) moiety is less than 2 Hz, which corresponds to (2*S*,3*S*)-**6** and its mirror image (2*R*,3*R*)-**6** geometries.

The reaction of di-*tert*-butyl acetylenedicarboxylate with cyclopentane-1,3-dione in the presence of triphenylphosphine leads to stable ylide **7**. Compound **7** is in equilibrium with the enol forms **8a** and **8b** (Scheme 6).



SCHEME 6

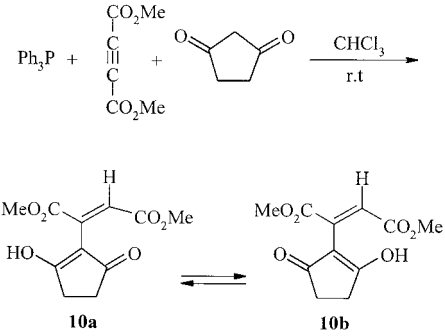
The reaction of DMAD with dimedone in the presence of triphenylphosphine leads to a chromene derivative **9** (Scheme 7).



9

SCHEME 7

From the reaction of cyclopentane-1,3-dione with DMAD in the presence of triphenylphosphine the addition product **10** was obtained (Scheme 8). Assignment of the (*E*) canfiguration to the carbon-carbon double bond in **10** is based on the chemical shift of the olefinic proton.[12]



10a 10b

SCHEME 8

In summary, we have described a one-pot reaction of acetylenic esters with cyclic and acyclic 1,3-diketones in the presence of triphenylphosphine. From the reaction of acyclic 1,3-dicarbonyl compounds with acetylenic esters in the presence of triphenylphosphine, stable phosphorus ylides **3a–3d** have been obtained. From the reaction of di-*tert*-butyl acetylenedicarboxylate with dimedone or cyclopentane-1,3-dione in the presence of triphenylphosphine, 1,4-diionic compound **6** and ylide **7** were obtained respectively.

The reaction of DMAD with dimedone or cyclopentane-1,3-dione in the presence of triphenylphosphine, leads to chromene derivative **9** and addition product **10** respectively. The present method carries the advantage that, not only is the reaction performed under neutral conditions, but also the substances can be mixed without any activation or modification.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses 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 on a BRUKER DRX-500 AVANCE instrument with $CDCl_3$ as solvent at 500.1, 125.8, and 202.4 MHz, respectively. The mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. 1,3-Dicarbonyl compounds **1**, dialkyl acetylendicarboxylates **2**, and triphenylphosphine were obtained from Fluka (Buchs, Switzerland) and used without further purification.

Preparation of Dimethyl 2-(1-Acetyl-2-oxopropyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (3a)

General Procedure

To a magnetically stirred solution of 0.52 g triphenylphosphine (2 mmol) and 0.2 g acetylacetone (2 mmol) in 5 mL dry CH_2Cl_2 was added, dropwise, a mixture of 0.28 g DMAD (2 mmol) in 3 mL dry CH_2Cl_2 at 0°C over 5 min. The reaction mixture was then allowed to warm up to room temperature. After 8 h stirring at room temperature, the white solid product was filtered, washed with diethyl ether (2 × 5 ml), and recrystallized from ethanol. White powder, 0.99 g, yield 98%, m.p. 173–175°C. IR 1714, 1613 (C=O). MS (*m/z*, %): 504 (M^+, 3), 446 (6), 406 (20), 183 (100), 181 (30), 151 (18), 108 (32), 67 (17), 56 (24).

Major isomer **3a**-(***E***) , (60%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 2.10 and 2.22 (6H, 2 s, 2 CH_3), 3.00 and 3.54 (6H, 2 s, 2 OMe), 3.46 (1H, br, P–C–CH), 5.42 (1H, br, CH), 7.41–7.57 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 26.72 and 28.99 (2 CH_3), 35.61 (d, $^{1}J_{PC}$ 125 Hz, P–C), 40.58 (d, $^{2}J_{PC}$ 13 Hz, P–C–*C*H), 45.04 and 47.98 (2 OMe), 63.07 (CH), 123.24 (d, $^{1}J_{PC}$ 89 Hz, C_{ipso}), 124.72 (d, $^{3}J_{PC}$ 12 Hz, C_{meta}), 128.27 (C_{para}), 130.17 (d, $^{2}J_{PC}$ 7 Hz, C_{ortho}), 165.84 (d, $^{2}J_{PC}$ 18 Hz, P–C=C). 171.35 (d, $^{3}J_{PC}$ 12 Hz, C=O), 198.22 and 200.01 (2 C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 23.78 (Ph_3P^+–C).

Minor isomer **3a**-(***Z***), (40%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 2.03 and 2.14 (6H, 2 s, 2 CH_3), 2.90 (1H, br, P–C–CH), 3.54 (6H, 2 OMe), 5.05 (1H, br, CH), 7.41–7.57 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 26.09 and 26.72 (2 CH_3), 35.24 (d, $^{1}J_{PC}$ 132 Hz, P–C), 39.42 (d, $^{2}J_{PC}$ 13 Hz, P–C–*C*H), 46.37 and 47.98 (2 OMe), 64.35 (CH), 122.66 (d, $^{1}J_{PC}$ 83 Hz, C_{ipso}), 124.87 (d, $^{3}J_{PC}$ 11 Hz, C_{meta}), 128.27 (C_{para}), 130.17 (d, $^{2}J_{PC}$ 7 Hz, C_{ortho}), 167.00 (d, $^{2}J_{PC}$ 18 Hz, P–C=*C*). 171.35 (d, $^{3}J_{PC}$

12 Hz, C=O), 198.20 and 200.16 (2 C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 23.78 (Ph_3P^+–C).

Di(*tert*-butyl) 2-(1-Acetyl-2-oxopropyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)-succinate (3b)

White powder, 1.15 g, yield 98%, m.p. 147–149°C. IR (KBr) (ν_{max}, cm^{-1}): 1712 (C=O), 1592 (C=C). MS (*m/z*, %): 588 (M^+, 2), 488 (10), 432 (22), 263 (81), 261 (78), 183 (100), 108 (78), 54 (20).

Major isomer **3b**-(***E***) (65%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 0.95 and 1.40 (18H, 2 s, 2 CMe_3), 2.06 and 2.34 (6H, 2 s, 2 CH_3), 3.19 (1H, dd, $^3J_{HH}$ 11 Hz, $^3J_{PH}$ 18 Hz, P–C–CH), 5.52 (1H, d, $^3J_{HH}$ 11 Hz, CH), 7.40–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 28.14 and 28.30 (2 C*Me*$_3$), 30.14 and 33.28 (2 CH_3), 38.60 (d, $^1J_{PC}$ 125 Hz, P–C), 45.20 (d, $^2J_{PC}$ 14 Hz, P–C–*C*H), 66.40 (d, $^3J_{PC}$ 6 Hz, CH), 76.94 and 80.23 (2 *C*Me$_3$), 128.10–128.40 (C_{ipso}), 128.30 (d, $^3J_{PC}$ 12 Hz, C_{meta}), 131.80 (C_{para}), 134.14 (d, $^2J_{PC}$ 8 Hz, C_{ortho}), 168.85 (d, $^2J_{PC}$ 13 Hz, P–C=*C*), 173.80 (d, $^3J_{PC}$ 5 Hz, C=O). 201.80 and 204.95 (2 C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 23.00 (Ph^3P^+–C).

Minor isomer, **3b**-(*Z*), (35%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 1.39 and 1.48 (18H, 2 s, 2 CMe_3), 2.04 and 2.22 (6H, 2 s, 2 CH_3), 3.13 (1H, dd, $^3J_{HH}$ 11 Hz, $^3J_{PH}$ 19 Hz, P–C–CH), 5.11 (1H, d, $^3J_{HH}$ 11 Hz, CH), 7.40–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 28.10 and 28.95 (2 C*Me*$_3$), 29.40 and 32.60 (2 CH_3), 40.50 (d, $^1J_{PC}$ 132 Hz, P–C), 44.52 (d, $^2J_{PC}$ 14 Hz, P–C–*C*H), 68.40 (d, $^3J_{PC}$ 6 Hz, CH), 76.90 and 80.20 (2 *C*Me$_3$), 128.10–128.40 (C_{ipso}), 128.30 (d, $^3J_{PC}$ 12 Hz, C_{meta}), 131.80 (C_{para}), 134.14 (d, $^2J_{PC}$ 8 Hz, C_{ortho}), 170.60 (d, $^2J_{PC}$ 19 Hz, P–C=C), 173.80 (d, $^3J_{PC}$ 4 Hz, C=O), 202.14 and 204.39 (2 C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 24.17 (Ph_3P^+–C).

Trimethyl 4-Oxo-1-(1,1,1-triphenyl-λ^5-phosphanylidene)-1,2,3-pentanetricarboxylate (3c)

Pale orange powder, 1.02 g, yield 98%, m.p. 170–172°C. IR (KBr) (ν_{max}, cm^{-1}): 1720, 1615 (C=O). MS (*m/z*, %): 520 (M^+, 2), 462 (12), 430 (15), 406 (40), 263 (38), 183 (100), 108 (40).

3c-1, (45%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 2.28 (3H, s, CH_3), 3.05 (3H, s, OCH_3), 3.31–3.37 (1H, m, P–C–CH), 3.52 and 3.63 (6H, 2 s, 2 OCH_3), 5.16 (1H, d, $^3J_{HH}$ 11 Hz, CH), 7.40–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 30.34 (CH_3), 39.40 (d, $^1J_{PC}$ 127 Hz, P–C), 44.00 (d, $^2J_{PC}$ 14 Hz, P–C–*C*H), 48.60–52.20 (3 OMe), 60.02 (CH), 127.10 (d, $^1J_{PC}$ 84 Hz, C_{ipso}), 128.35 (d, $^3J_{PC}$ 12 Hz, C_{meta}), 131.80–132.10 (C_{para}), 133.80–134.20 (C_{ortho}), 168.54 (C=O, ester), 169.50 (d,

$^{2}J_{PC}$ 18 Hz, P–C=*C*), 174.80 (d, $^{3}J_{PC}$ 5 Hz, C=O), 202.12 (C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 24.00–24.20 (Ph_3P^+–C).

3c-2, (24%). ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 2.22 (3H, s, CH_3), 3.31–3.37 (1H, m, P–C–CH), 3.57, 3.59 and 3.60 (9H, 3 s, 3 OCH_3), 4.83 (1H, d, $^{3}J_{HH}$ 11 Hz, CH), 7.40–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 29.80 (CH_3), 40.00 (d, $^{1}J_{PC}$ 135 Hz, P–C), 42.80 (d, $^{2}J_{PC}$ 14 Hz, P–C–*C*H), 48.60–52.20 (3 OMe), 60.00 (CH), 127.10 (d, $^{1}J_{PC}$ 84 Hz, C_{ipso}), 128.35 (d, $^{3}J_{PC}$ 12 Hz, C_{meta}), 131.80–132.10 (C_{para}), 133.80–134.20 (C_{ortho}), 168.50 (C=O, ester), 170.80 (d, $^{2}J_{PC}$ 18 Hz, P–C=*C*), 175.00 (d, $^{3}J_{PC}$ 5 Hz, C=O), 201.60 (C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 24.00–24.20 (Ph_3P^+–C).

3c-3, (19%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 2.35 (3H, s, CH_3), 3.05 (3H, s, OCH_3), 3.31–3.37 (1H, m, P–C–CH), 3.46 and 3.59 (6H, 2 s, 2 OCH_3), 5.28 (1H, d, $^{3}J_{HH}$ 8 Hz, CH), 7.40–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 32.80 (CH_3), 39.10 (d, $^{1}J_{PC}$ 125 Hz, P–C), 43.20 (d, $^{2}J_{PC}$ 14 Hz, P–C–*C*H), 48.60–52.20 (3 OMe) 61.80 (CH), 127.10 (d, $^{1}J_{PC}$ 84 Hz, C_{ipso}), 128.45 (d, $^{3}J_{PC}$ 12 Hz, C_{meta}), 131.80–132.10 (C_{para}), 133.80–134.20 (C_{ortho}), 169.43 (d, $^{2}J_{PC}$ 17 Hz, P–C=*C*), 168.48 (C=O, ester), 174.70 (d, $^{3}J_{PC}$ 5 Hz, C=O), 204.30 (C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 24.00–24.20 (Ph_3P^+–C).

3c-4, (12%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 2.27 (3H, s, CH_3), 3.31–3.37 (1H, m, P–C–CH), 3.60, 3.62 and 3.63 (9H, 3 s, 3 OCH_3), 4.95 (1H, d, $^{3}J_{HH}$ 8 Hz, CH), 7.40–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 33.00 (CH_3), 39.80 (d, $^{1}J_{PC}$ 133 Hz, P–C), 42.50 (d, $^{2}J_{PC}$ 12 Hz, C_{meta}), 131.80–132.10 (C_{para}), 133.80–134.20 (C_{ortho}), 168.52 (C=O, ester), 170.60 (d, $^{2}J_{PC}$ 18 Hz, P–C=C), 174.91 (d, $^{3}J_{PC}$ 5 Hz, C=O), 203.80 (C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 24.00–24.20 (Ph_3P^+–C).

1,2-Di-*tert*-butyl 3-Methyl-4-oxo-1-(1,1,1-triphenyl-λ^5-phosphanylidene)-1,2,3-pentanetricarboxylate (3d)

Pale orange powder, 1.17 g, yield, 97%, m.p. 118–120°C. IR (KBr) (ν_{max}, cm^{-1}): 1708 and 1610 (C=O), 1605 (C=C). MS (*m/z*, %): 604 (M^+, 3), 504 (10), 448(20), 416(20), 278 (70), 263 (80), 183 (100), 108 (40), 54 (30).

3d-1, (32%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 0.92 and 1.40 (18H, 2 s, 2 C*Me*$_3$), 2.25 (3H, s, CH_3), 3.13 (1H, dd, $^{3}J_{HH}$ 10.8 Hz, $^{3}J_{PH}$ 18 Hz, P–C–*C*H), 3.48 (3H, s, OCH_3), 5.16 (1H, d, $^{3}J_{HH}$ 10.8 Hz, CH), 7.40–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 28.20 and 28.30 (2 C*Me*$_3$), 28.80 (CH_3), 40.70 (d, $^{1}J_{PC}$ 135 Hz, P–C), 43.90 (d, $^{2}J_{PC}$ 14 Hz, P–C–*C*H), 51.86 (OMe), 61.84 (d, $^{3}J_{PC}$ 4 Hz, CH), 77.30 and 80.10 (2 *C*Me$_3$), 128.00–128.60 (C_{ipso} and C_{meta}), 131.50–1320 (C_{para}), 134.00–134.60 (C_{ortho}), 168.90 and 169.10 (C=O, ester), 173.40 (d, $^{2}J_{PC}$

6 Hz, P–C=*C*), 201.80 (C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 24.21 (Ph_3P^+–C).

3d-2, (30%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 1.43 and 1.45 (18H, 2 s, 2 CMe_3), 2.19 (3H, s, CH_3), 3.11 (1H, dd, $^3J_{HH}$ 11 Hz, $^3J_{PH}$ 18 Hz, P–C–CH), 3.40 (3H, s, OCH_3), 4.84 (1H, d, $^3J_{HH}$ 11 Hz, CH), 7.40–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 27.90 and 28.10 (2 C*Me*$_3$), 29.00 (CH_3), 38.40 (d, $^1J_{PC}$ 133 Hz, P–C), 45.00 (d, $^2J_{PC}$ 14 Hz, P–C–*C*H), 51.88 (OMe), 61.80 (d, $^3J_{PC}$ 4 Hz, CH), 77.30 and 80.10 (2 *C*Me$_3$), 128.00–128.60 (C_{ipso} and C_{meta}), 131.50-132.00 (C_{para}), 134.00–134.60 (C_{ortho}), 164.40 and 170.60 (C=O, ester), 173.63 (d, $^2J_{PC}$ 6 Hz, P–C=*C*), 203.30 (C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 23.04 (Ph_3P^+–C).

3d-3, (23%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 1.49 and 1.50 (18H, 2 s, 2 CMe_3), 2.38 (3H, s, CH_3), 3.07 (1H, dd, $^3J_{PH}$ 10.7 Hz, $^3J_{PH}$ 18 Hz, P–C–CH), 3.61 (3H, s, OCH_3), 5.33 (1H, d, $^3J_{HH}$ 10.7 Hz, CH), 7.40–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 28.00 and 28.20 (2 C*Me*$_3$), 29.80 (CH_3), 40.40 (d, $^1J_{PC}$ 135 Hz, P–C), 44.30 (d, $^2J_{PC}$ 14 Hz, P–C–*C*H), 51.90 (OMe), 60.20 (d, $^3J_{PC}$ 4 Hz, CH), 80.18 and 85.16 (2 *C*Me$_3$), 128.00–128.60 (C_{ipso} and C_{meta}), 131.50–132.00 (C_{para}), 134.00–134.60 (C_{ortho}), 169.90 and 170.50 (C=O, ester), 173.47 (d, $^2J_{PC}$ 6 Hz, P–C=*C*), 201.70 (C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 23.38 (Ph_3P^+–C).

3d-4, (15%), ^{1}H NMR (500.1 MHz, $CDCl_3$) δ 0.94 and 1.47 (18H, 2 s, 2 CMe_3), 2.32 (3H, s, CH_3), 3.05 (1H, dd, $^3J_{HH}$ 11 Hz, $^3J_{PH}$ 17 Hz, P–C–CH), 3.60 (3H, s, OCH_3), 4.92 (1H, d, $^3J_{HH}$ 11 Hz, CH), 7.40–7.70 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 28.00 and 28.10 (2 C*Me*$_3$), 30.30 (CH_3), 38.50 (d, $^1J_{PC}$ 133 Hz, P–C), 43.50 (d, $^2J_{PC}$ 14 Hz, P–C–*C*H), 51.82 (OMe), 57.30 (d, $^3J_{PC}$ 4 Hz, CH), 80.20 and 85.20 (2 *C*Me$_3$), 128.00–128.60 (C_{ipso} and C_{meta}), 131.50–132.00 (C_{para}), 134.00–134.60 (C_{ortho}), 168.40 and 169.60 (C=O, ester), 173.30 (d, $^2J_{PC}$ 2 Hz, P–C=*C*), 202.30 (C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 24.59 (Ph_3P^+–C).

Di-*tert*-butyl-2-(4,4-Dimethyl-2,6-dioxocyclohexane-2-yl-2-ylide)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)-succinate (6)

White powder, 1.23 g, yield, 98%, m.p. 125–127°C. IR (KBr) (ν_{max}, cm^{-1}): 1701 and 1603 (C=O). MS (*m/z*, %): 628 (M^+, 2), 263 (40), 209 (42), 183 (77), 108 (65), 54 (100). ^{1}H NMR (500.1 MHz,) δ 0.91 (6H, s, 2 CMe_2), 0.94 (18H, s, 2 CMe_3), 2.06–2.18 (4H, br, 2 CH_2), 4.91 (1H, d, $^3J_{HH}$ 10.8 Hz, CH), 5.51 (1H, dd, $^3J_{HH}$ 10.8 Hz, $^3J_{PH}$ 10.5 Hz, P–CH), 7.43–7.80 (15H, m, 3 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 23.46 and 23.73

(2 C*Me*$_3$), 26.37 (br, C*Me*$_2$), 28.15 (*C*Me$_2$), 39.34 (P—C—*C*H), 40.80 (d, $^1J_{PC}$ 40 Hz, P—C), 46.62 (br, 2 CH$_2$), 77.15 and 80.01 (2 *C*Me$_3$), 107.70 (d, $^3J_{PC}$ 12 Hz, P—C—C—*C*), 120.17 (d, $^1J_{PC}$ 90 Hz, C$_{ipso}$), 125.30 (d, $^3J_{PC}$ 13 Hz, C$_{meta}$), 129.22 (C$_{para}$), 130.62 (d, $^2J_{PC}$ 9 Hz, C$_{orto}$), 162.37 and 170.11 (2d, $J_{PC} = 1.5$ Hz, 2 C=O, ester), 185.36 (2 C=O). ^{31}P NMR (202.4 MHz, CDCl$_3$) δ 23.70 (Ph$_3$P$^+$—C).

Di-*tert*-butyl 2-(2-Hydroxy-5-oxo-1-cyclopentyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (7)

White powder, 1.15 g, yield, 98%, m.p. 154–156°C. IR (KBr) (ν_{max}, cm^{-1}): 1718 and 1603 (C=O). MS (*m*/*z*, %): 586 (M$^+$, 3), 411 (5), 263 (40), 261 (78), 183 (100), 108 (45).

7 (34%), ^{1}H NMR (500.1 MHz, CDCl$_3$) δ 0.92 and 0.97 (18H, 2 s, 2 CMe$_3$), 2.25 (4H, br, 2 CH$_2$), 4.35 (1H, d, $^3J_{HH}$ 9 Hz, CH), 5.60 (1H, dd, $^3J_{HH}$ 9 Hz, $^3J_{PH}$ 10 Hz, P—C—CH), 7.40–7.80 (15H, m, 3 C$_6$H$_5$). ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 23.56 and 23.72 (2 C*Me*$_3$), 29.15 (br, 2 CH$_2$), 39.50 (d, $^2J_{PC}$ 40 Hz, P—C—*C*H), 39.72 (d, $^1J_{PC}$ 106 Hz, P—C), 77.78 and 80.37 (2 *C*Me$_3$), 112.31 (CH), 119.10 (d, $^1J_{PC}$ 90 Hz, C$_{ipso}$), 125.52 (d, $^2J_{PC}$ 12 Hz, C$_{ortho}$), 129.62 (C$_{para}$), 130.70 (d, $^3J_{PC}$ 9 Hz, C$_{meta}$), 162.53 and 168.55 (2 C=O, ester), 195.83 (2 C=O). ^{31}P NMR (202.4 MHz, CDCl$_3$) δ 23.86 (Ph$_3$P$^+$—C).

8 (66%), ^{1}H NMR (500.1 MHz, CDCl$_3$) δ 0.89 and 1.38 (18H, 2 s, 2 CMe$_3$), 2.19 (4H, br, 2 CH$_2$), 3.71 (1H, d, $^3J_{PH}$ 16 Hz, P—C—CH), 7.40–7.80 (15H, m, 3 C$_6$H$_5$), 12.13 (1H, br, OH). ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 24.43 (2 C*Me*$_3$), 26.98 (br, 2 CH$_2$), 34.81 (d, $^2J_{PC}$ 11 Hz, P—C—*C*H), 41.86 (d, $^1J_{PC}$ 106 Hz, P—C), 75.95 and 76.53 (2 *C*Me$_3$), 102.35 (O—C=*C*), 121.28 (d, $^1J_{PC}$ 91 Hz, C$_{ipso}$), 125.05 (d, $^2J_{PC}$ 12 Hz, C$_{ortho}$), 128.83 (C$_{para}$), 130.26 (d, $^3J_{PC}$ 10 Hz, C$_{meta}$), 168.26 (2 C=O, ester), 192.48 (C=O$\rightleftarrows$C—OH). ^{31}P NMR (202.4 MHz, CDCl$_3$) δ 23.43 (Ph$_3$P$^+$—C).

Methyl-7,7-Dimethyl-2,5-dioxo-5,6,7,8-tetrahydro-2*H*-chromene-4-carboxylate (9)

Colorless crystals, 0.49 g, yield, 98%, m.p. 97–98°C. IR (KBr) (ν_{max}, cm^{-1}): 1756, 1724 and 1666 (C=O), 1546 (C=C). MS (*m*/*z*, %): 251 (M$^+$ + 1, 20), 194 (100), 166 (22), 138 (40), 93 (77), 52 (80), 35 (84). ^{1}H NMR (500.1 MHz, CDCl$_3$) δ 1.20 (6H, s, 2 CH$_3$), 2.40 and 2.60 (4H, 2 s, 2 CH$_2$), 3.90 (3H, s, OMe), 6.20 (1H, s, CH). ^{13}C NMR (125.8 MHz, CDCl$_3$) δ 28.13 (C*Me*$_2$), 32.45 (*C*Me$_2$), 42.02 and 50.49 (2 CH$_2$), 53.10 (OMe), 111.33 (O—C=*C*), 111.77 (CH), 145.57 (*C*—CO$_2$Me), 158.97 (O—*C*=C), 165.77 (C=O, ester), 174.00 (C=O, lactone), 192.36 (C=O).

Dimethyl (E)-2-(2-Hydroxy-5-oxo-1-cyclopentyl)-2-butendioate (10). White powder, 0, 47 g, yield, 98%, m.p. 157–158 C. (IR (KBr) (vmax, cm^{-1}): 1725 and 1720 (C=O), 1592 (C=C). MS (*m/z*, %): 240 (M^+, 38), 208 (58), 181 (100), 180 (60), 153 (42), 149 (100), 122 (40), 93 (35). ^1H NMR (500.1 MHz, $CDCl_3$) δ 2.57 (4H, br, 2 CH_2), 3.75 and 3.87 (6H, 2 s, 2 OMe), 6.91 (1H, s, CH), 11.10 (1H, br, OH). ^{13}C NMR (125.8 MHz, DMSO-d_6) δ 29.54 (2 CH_2), 46.93 and 47.61 (2 OMe), 96.64 (CH), 102.07 (O–C=*C*), 141.82 (*C*=CH), 164.46 and 165.81 (2 C=O, ester), 195.98 (C=O).

REFERENCES

[1] I. Yavari, M. Anary-Abbasinegad, and Z. Hossaini, *Org. Biomol. Chem.*, **1,** 560 (2003).
[2] I. Yavari, M. Adib, and L. Hojabri, *Tetrahedron*, **58,** 7213 (2002).
[3] I. Yavari and M. Bayat, *Tetrahedron*, **59,** 2001 (2003).
[4] H. R. Hudson, *The Chemistry of Organophosphorus Compounds: Primery Secondery and Tertiary Phosphines and Heterocyclic Organophosphorus (III) Compounds* (Wiley, New York, 1990), vol. I, pp. 386–472.
[5] R. Engel, *Synthesis of Carbon-Phosphorus Bonds* (CRC Press, Boca Raton, FL, 1998).
[6] J. I. G. Cadogan, *Organophosphorus Reagents in Organic Syntesis* (Academic Press, New York, 1979).
[7] D. E. C. Corbridge, *Phosphorus an Outline of its Chemistry, Biochemistry, and Uses* (Elsevier, Amsterdam, 1995). 5th ed.
[8] R. A. Cherkasov and M. A. Pudovic, *Russ. Chem. Rev.*, **63,** 1019 (1994).
[9] M. Karplus. *J. Am. Chem. Soc.*, **88,** 2870 (1963).
[10] C. A. G. Haasnot, F. A. A. M. de Leeuw, and C. Altona, *Tetrahedron*, **36,** 2783 (1980).
[11] E. Breitmaier and W. Voelter, *Carbon-13 NMR Spectroscopy* (VCH, New York, 1990), 3rd ed., p. 250.
[12] El. Eliel and S. H. Wilen, *Stereochemistry of Organic Compounds* (Wiley, New York, 1994), p. 570.