

Full Paper

A Facile Route to Diastereomeric Phosphorus Ylides. Chemoselective Synthesis of Dialkyl (*E*)-2-[1-(2-Oxocyclopentylidene)ethyl]-2-butenedioates

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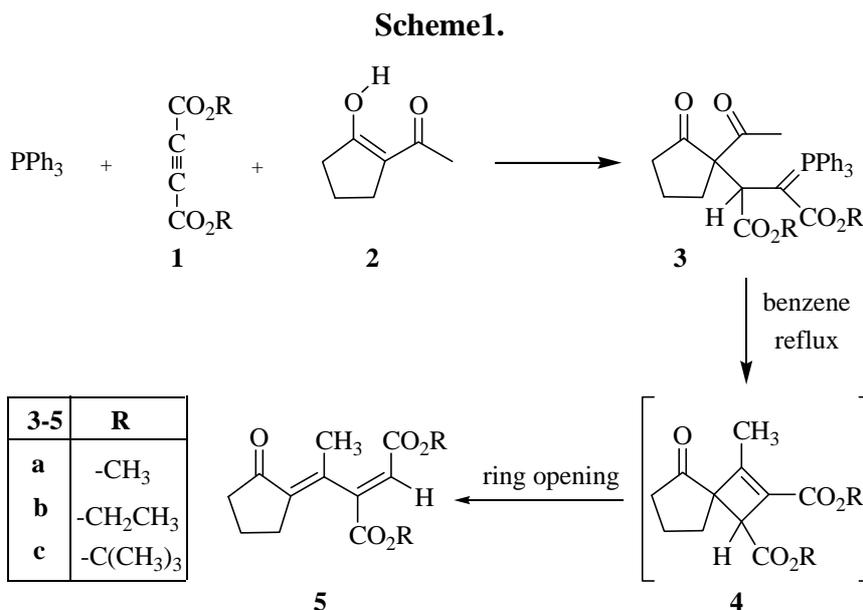
Abstract: 2-Acetylcyclopentanone undergoes a smooth reaction with triphenylphosphine and dialkyl acetylenedicarboxylates to produce dialkyl 2-(1-acetyl-2-oxocyclopentyl)-3-(1,1,1-triphenyl- λ^5 -phosphanylidene)succinates. These compounds undergo intramolecular Wittig reactions in boiling benzene to produce highly strained spirocyclobutene derivatives, which spontaneously undergo ring-opening reactions to produce dialkyl (*E*)-2-[1-(2-oxocyclopentylidene)ethyl]-2-butenedioates.

Keywords: 2-Acetylcyclopentanone, phosphorus ylides, spirocompounds, intramolecular Wittig reaction.

Introduction

Phosphorus ylides are reactive compounds which participate in many valuable syntheses of organic products [1-4]. Phosphorus ylides are interesting synthetic targets because of their importance in a variety of industrial, biological and chemical synthetic usages [5-9]. These ylides are usually prepared by treatment of a phosphonium salt with a base, and the phosphonium salts are usually obtained from the phosphine and an alkyl halide and also Michael addition of phosphorus nucleophiles to activated olefins.

In recent years the three-component reactions of triphenylphosphine, electron-deficient derivatives and *ZH*-acids ($Z=C, O, N, S$) that leads to phosphorus ylides have been reported by Yavari *et al.* [10-15]. We here report the reaction of 2-acetylcyclopentanone (**2**, acting as a *CH*-acid) and dialkyl acetylenedicarboxylates **1** in the presence of triphenylphosphine. These reactions lead to diastereomeric phosphorus ylides **3**. These compounds undergo intramolecular Wittig reactions in boiling benzene to produce spirocompounds **4**, which spontaneously undergo ring-opening reactions to produce dialkyl (*E*)-2-[1-(2-oxopentylidene)ethyl]-2-butenedioates **5** (Scheme 1).



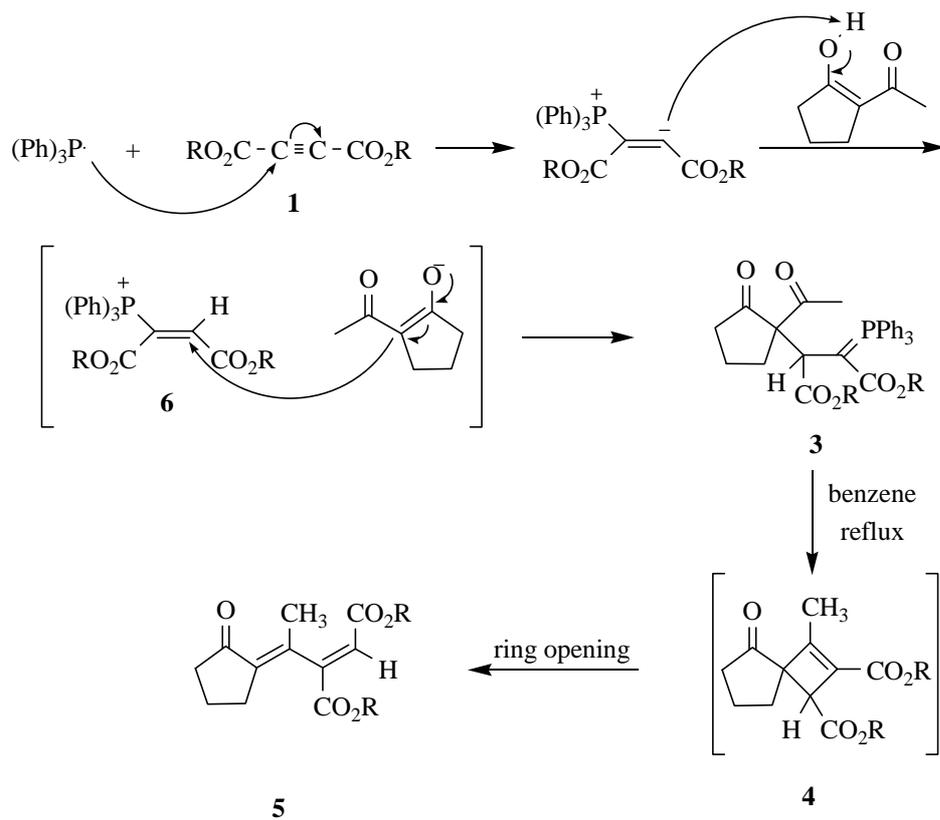
Results and Discussion

We have not established a mechanism for the formation of **5a-c** experimentally, but a reasonable possibility is indicated in Scheme 2. On the basis of the well established chemistry of trivalent phosphorus nucleophiles [1, 5, 6], it is reasonable to assume that the initial addition of triphenylphosphine to the acetylenic ester and subsequently the protonation of the 1:1 adduct was followed by attack of the carbon moiety of the enolate of *CH*-acid to the vinylphosphonium cation **6** to generate ylide **3**.

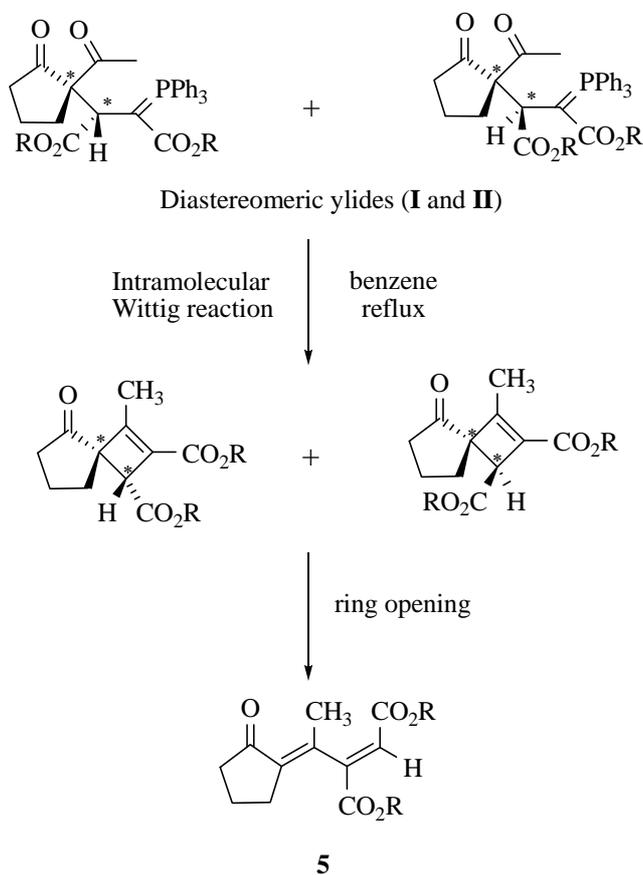
Phosphorus ylides **3a-c** then undergo smooth reactions in boiling benzene to produce triphenylphosphine oxide and spirocompounds **4a-c**. These compounds were unstable and were not isolated, but rather they are spontaneously converted to functionalized 1,3-dienes **5a-c**. (Scheme 2).

Compounds **3a-c** possess two stereogenic centers, and two diastereomers are expected (**I** and **II**) to form (Scheme 3), and indeed two diastereomers were isolated from the reaction mixtures. It should be pointed out that both diastereomeric ylides (**I** and **II**) were converted to 1,3-dienes with the same geometry, indicating that the ring opening reactions did not take place as a concerted reaction.

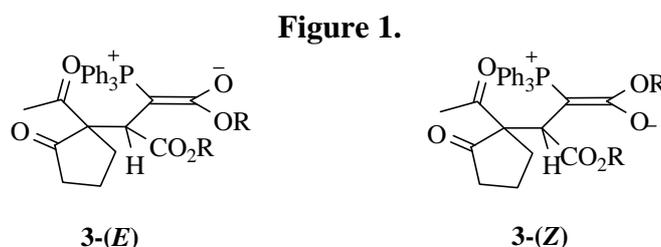
Scheme 2.



Scheme 3.



The structures of the compounds **3a-c** were deduced from their elemental analyses, high field ^1H - and ^{13}C -NMR as well as IR spectra data. The ^1H - and ^{13}C -NMR spectra of diastereomeric ylides **3a-c** were consistent with the presence of two geometric isomers. The ylide moiety of these compounds is strongly conjugated to the adjacent carbonyl group and a rotation around the partial double bond in the **3-(E)** and **3-(Z)** geometric isomers (Figure 1) is relatively slow on the NMR time scale at ambient temperature.



The geometries of the double bonds in compound **5** were established using ^1H -NMR data. For the double bond bearing two ester groups, we considered the chemical shift of the vinylic proton. If the vinylic proton is in a *cis* position relative to the ester group on the adjacent carbon atom, an anisotropy effect is imposed by the carbonyl of the *cis* ester group which causes a deshielding effect on this proton, so this proton usually appears at a frequency higher than 6.5 ppm [16], as it was clearly observed in our ^1H -NMR spectra of compounds **5a-c**. Therefore, it can be concluded that the vinylic proton is located in the *cis* position with respect to the vicinal ester group. We also investigated the stereochemistry of the compound **5** by using a NOE experiment. In the decoupling process of the methyl protons, the NOE difference spectrum did not show a nuclear Overhauser enhancement of the CH_2 protons of the cyclopentanone moiety nor the vinylic proton. The irradiation of the CH_2 protons also the vinylic proton lead to no enhancement of the intensity of the CH_3 protons. On the basis of these results, the geometry for the compound **5** is as indicated in Scheme 3.

Conclusions

In conclusion, the present method may be considered as a practical route for the synthesis of the stable phosphorus ylides and electron deficient 1,3-butadienes. This procedure has advantages of high yield, mild reaction conditions, and simple experimental and work-up conditions.

Experimental

General

Triphenylphosphine, dialkyl acetylenedicarboxylate and 2-acetyl cyclopentanone were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^1H - and ^{13}C -NMR spectra were measured with a Bruker DRX-500 AVANCE spectrometer at 500 and 125.8 MHz, respectively.

Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were recorded on a Shimadzu IR-470 spectrometer.

General procedure for preparation of

*dialkyl 2-(1-acetyl-2-oxocyclopentyl)-3-[1,1,1-triphenyl- λ^5 -phosphanylidene]succinates (exemplified by **3a**)*

A mixture of dimethyl acetylenedicarboxylate (0.245 mL, 2 mmol) in CH_2Cl_2 (4 mL) was added dropwise at -10°C over 10 min. to a magnetically stirred solution of 2-acetylcyclopentanone (**2**, 0.252 g, 2 mmol) and triphenyl phosphine (0.524 g, 2 mmol) in CH_2Cl_2 (10 mL). The mixture was allowed to stand at room temperature along with stirring for 24 hours. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (Merck silica gel 60, 230-400 mesh) using ethyl acetate-hexane (30:70) as eluent. Two diastereomers were isolated. The solvents were removed under reduced pressure to give ylides **3a-I** and **3a-II** as white powders.

*Dimethyl 2-(1-acetyl-2-oxocyclopentyl)-3-[1,1,1-triphenyl- λ^5 -phosphanylidene] succinate (**3a**)*

*First diastereomer (**3a-I**):* M.p. $126\text{--}128.5^\circ\text{C}$; yield 50 %; IR (KBr, ν_{max} , cm^{-1}): 1755, 1730 and 1705 (C=O), 1629 (C=C); MS m/z (%): 530 (M^+ , 10), 499 ($\text{M}^+\text{-OCH}_3$, 14), 471 ($\text{M}^+\text{-CO}_2\text{Me}$, 25), 487 ($\text{M}^+\text{-CH}_3\text{CO}$, 18), 268 ($\text{M}^+\text{-PPh}_3$, 25), 209 [$\text{M}^+\text{- (PPh}_3\text{+CO}_2\text{Me)}$, 37], 43 (CH_3CO^+ , 100); Anal. calcd. for $\text{C}_{31}\text{H}_{31}\text{O}_6\text{P}$ (530.56); C, 70.18; H, 5.89%. Found: C 70.06; H, 5.83%; $^1\text{H-NMR}$ (CDCl_3) **3a-I (Z)**: δ_{H} 1.42-1.50 (2H, m, CH_2), 1.60 (3H, s, CH_3), 1.97-2.13 (2H, m, CH_2), 2.58-2.82 (2H, m, CH_2), 2.92 and 3.70 (6H, 2s, 2OCH₃), 3.56 (1H, d, $^3J_{\text{PH}}=18.4$ Hz, CH), 7.4-7.7 (15H, m, -Ph); $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 20.12 (CH_2), 27.64 (CH_3), 29.81 (CH_2), 37.31 (CH_2), 39.38 (d, $^1J_{\text{PC}}=122.5$ Hz, P=C), 40.09 (d, $^2J_{\text{PC}}=13.4$ Hz, CH), 48.71 and 51.83 (2OCH₃), 73.94 (cyclopentanone quaternary carbon), 127.61 (d, $^1J_{\text{PC}}=91.4$ Hz, C_{ipso}), 128.58 (d, $^3J_{\text{PC}}=11.7$ Hz, C_{meta}), 131.9 (C_{para}), 133.97 (d, $^2J_{\text{PC}}=9.4$ Hz, C_{ortho}), 169.94 (d, $^2J_{\text{PC}}=13.1$ Hz, C=O ester), 174.24 (d, $^3J_{\text{PC}}=5.3$ Hz, C=O ester), 203.70 and 216.22 (2C=O, ketones). **3a-I (E)** (31 %) $^1\text{H-NMR}$ (CDCl_3): δ_{H} 1.55 (3H, s, CH_3), 1.62-1.65 (2H, m, CH_2), 2.2-2.40 (2H, m, CH_2), 2.48-2.53 (2H, m, CH_2), 3.43 and 3.68 (2OCH₃), 3.59 (1H, d, $^3J_{\text{PH}}=18.5$ Hz, CH), 7.4-7.67 (15H, m, -Ph); $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 21.5 (CH_2), 25.44 (CH_3), 29.14 (CH_2), 37.5 (d, $^1J_{\text{PC}}=127.5$ Hz, P=C), 38.70 (CH_2), 48.12 (d, $^2J_{\text{PC}}=13.2$ Hz, CH), 49.65 and 52.34 (2OCH₃), 73.26 (cyclopentanone quaternary carbon), 126.7 (d, $^1J_{\text{PC}}=91.7$ Hz, C_{ipso}), 128.2 (d, $^3J_{\text{PC}}=11.5$ Hz, C_{meta}), 131.6 (C_{para}), 132.13 (d, $^2J_{\text{PC}}=9.9$ Hz, C_{ortho}), 168.5 (d, $^2J_{\text{PC}}=12.8$ Hz, C=O ester), 174.8 (d, $^3J_{\text{PC}}=5.2$ Hz, C=O ester), 203.65 and 215.02 (2C=O, ketones).

*Second diastereomer (**3a-II**):* M.p. $151\text{--}152^\circ\text{C}$; yield 45 %; IR (KBr, ν_{max} , cm^{-1}): 3059 and 2987 (CH), 1751, 1726 and 1689 (C=O), 1629 (C=C); MS m/z (%): 530 (M^+ , 8), 471 ($\text{M}^+\text{-CO}_2\text{Me}$, 18), 487 ($\text{M}^+\text{-CH}_3\text{CO}$, 30), 268 ($\text{M}^+\text{-PPh}_3$, 21), 209 ($\text{M}^+\text{- (PPh}_3\text{+CO}_2\text{Me)}$, 28), 43 (CH_3CO^+ , 100); Anal. calcd. for $\text{C}_{31}\text{H}_{31}\text{O}_6\text{P}$ (530.56); C, 70.18; H, 5.89%; Found C 70.05, H 5.78 %; **3a-II (Z)** (68 %) $^1\text{H-NMR}$ (CDCl_3): δ_{H} 1.64 (3H, s, CH_3), 1.82-1.95 (2H, m, CH_2), 2.09-2.18 (2H, m, CH_2), 2.88-2.96 (2H, m, CH_2), 2.80 and 3.69 (6H, 2s, 2OCH₃), 3.49 (1H, d, $^3J_{\text{PH}}=18.8$ Hz, CH), 7.45-7.64 (15H, m, -Ph); $^{13}\text{C-NMR}$ (CDCl_3): δ_{C} 20.33 (CH_2), 25.45 (CH_3), 29.12 (CH_2), 39.84 (d, $^1J_{\text{PC}}=121.9$ Hz, CH), 40.07

(CH₂), 48.37 (d, ²J_{PC} = 13.4 Hz, CH), 51.82 and 52.22 (2OCH₃), 73.97 (cyclopentanone quaternary carbon), 127.5 (d, ¹J_{PC} = 91.5 Hz, C_{ipso}), 128.43 (d, ³J_{PC} = 12.20 Hz, C_{meta}), 131.92 (d, ⁴J_{PC} = 2.9 Hz, C_{para}), 134.02 (d, ²J_{PC} = 9.5 Hz, C_{ortho}), 170.39 (d, ²J_{PC} = 13.3 Hz, C=O ester), 175 (d, ³J_{PC} = 6.5 Hz, C=O ester), 202.8 and 215 (2C=O, ketones). **3a-II (E)** (32 %) ¹H-NMR (CDCl₃): δ_H 1.65 (3H, s, CH₃), 1.82-1.95 (2H, m, CH₂), 2.09-2.18 (2H, m, CH₂), 2.88-2.96 (2H, m, CH₂), 3.47 and 3.69 (6H, 2s, 2OCH₃), 3.64 (1H, d, ³J_{PH} = 19.5 Hz, CH), 7.45-7.64 (15H, m, -Ph); ¹³C-NMR (CDCl₃): δ_C 21.07 (CH₂), 25.84 (CH₃), 28.55 (CH₂), 39.71 (CH₂), 40.58 (d, ¹J_{PC} = 129.4 Hz, P=C), 48.37 (d, ²J_{PC} = 13.4 Hz, CH), 51.82 and 52.22 (2OCH₃), 73.97 (cyclopentanone quaternary carbon), 127.3 (d, ¹J_{PC} = 90.8 Hz, C_{ipso}), 128.33 (d, ³J_{PC} = 12.07 Hz, C_{meta}), 131.97 (d, ⁴J_{PC} = 2.83 Hz, C_{para}), 132.12 (d, ²J_{PC} = 9.3 Hz, C_{ortho}), 171.07 (d, ²J_{PC} = 13.5 Hz, C=O ester), 172.5 (d, ³J_{PC} = 6.9 Hz, C=O ester), 202.3 and 214.8 (2C=O, ketones).

Diethyl 2-(1-acetyl-2-oxocyclopentyl)-3-[1,1,1-triphenyl-λ⁵-phosphanylidene] succinate (3b)

First diastereomer (3b-I): M.p. 157.5-159 °C; yield 53 %; IR (KBr, ν_{max}, cm⁻¹): 1745, 1730 and 1705 (C=O), 1632 (C=C); MS *m/z* (%): 558 (M⁺, 7), 530 (M⁺-C₂H₅, 14), 515 (M⁺-CH₃CO, 31), 485 (M⁺-CO₂Et, 18), 296 (M⁺-PPh₃, 20), 223 [M⁺- (PPh₃+CO₂Et), 37], 43 (CH₃CO⁺, 100); Anal. calcd. for C₃₃H₃₅O₆P (530.56); C, 70.96; H, 6.32%; Found: C 70.88; H, 6.25%; **3b-I (Z)** (64 %) ¹H-NMR (CDCl₃): δ_H 1.18 (3H, t, ³J_{HH} = 7 Hz, CH₃), 1.25 (3H, t, ³J_{HH} = 7.2 Hz, CH₃), 1.51-1.55 (2H, m, CH₂), 1.57 (3H, s, CH₃), 1.85-1.97 (2H, m, CH₂), 2.75-2.78 (2H, m, CH₂), 3.56 (1H, d, ³J_{PH} = 18.5 Hz, CH), 3.66-3.68 (2H, m, OCH₂), 4.12-4.15 (2H, m, OCH₂), 7.46-7.81 (15H, m, -Ph); ¹³C-NMR (CDCl₃): δ_C 14.13 and 14.34 (2CH₃), 20.17 and 27.70 (2CH₂), 29.69 (CH₃), 37.38 (d, ¹J_{PC} = 122.78 Hz, P=C), 37.78 (CH₂), 49.12 (d, ²J_{PC} = 12.96 Hz, CH), 57.54 and 61.35 (2OCH₂), 74.17 (cyclopentanone quaternary carbon), 128.16 (d, ¹J_{PC} = 92.98 Hz, C_{ipso}), 128.53 (d, ³J_{PC} = 11.82 Hz, C_{meta}), 131.86 (C_{para}), 134.07 (d, ²J_{PC} = 9.4 Hz, C_{ortho}), 166.03 (d, ²J_{PC} = 12.8 Hz, C=O ester), 173.87 (d, ³J_{PC} = 6.3 Hz, C=O ester), 204.51 and 216.40 (2C=O, ketones). **3b-I (E)** (36 %) ¹H-NMR (CDCl₃): δ_H 1.21 (3H, t, ³J_{HH} = 7.1 Hz, CH₃), 1.25 (3H, t, ³J_{HH} = 7.2 Hz, CH₃), 1.41-1.46 (2H, m, CH₂), 1.62 (3H, s, CH₃CO), 2.07-2.12 (2H, m, CH₂), 2.44-2.52 (2H, m, CH₂), 3.37-3.39 (2H, m, OCH₂), 3.47 (1H, d, ³J_{PH} = 19.8 Hz, CHCO₂Et), 4.12-4.15 (2H, m, OCH₂), 7.46-7.81 (15H, m, -Ph); ¹³C-NMR (CDCl₃): δ_C 13.10 and 13.60 (2CH₃), 19.28 and 25.86 (2CH₂), 29.05 (CH₃CO), 37.1 (d, ¹J_{PC} = 125.8 Hz, P=C), 37.26 (CH₂CO), 48.5 (d, ²J_{PC} = 12.6 Hz, CHCO₂Et), 60.97 and 62.15 (2OCH₂), 71.5 (cyclopentanone quaternary carbon), 127.8 (d, ¹J_{PC} = 90.8 Hz, C_{ipso}), 129.89 (³J_{PC} = 12.4 Hz, C_{meta}), 132.13 (²J_{PC} = 9.81 Hz, C_{ortho}), 134.83 (C_{para}), 165.04 (d, ²J_{PC} = 13.1 Hz, C=O ester), 170.72 (d, ³J_{PC} = 6.7 Hz, C=O ester), 203.84 and 215.01 (2C=O, ketones).

Di-tert-butyl 2-(1-acetyl-2-oxocyclopentyl)-3-[1,1,1-triphenyl-λ⁵-phosphanylidene] succinate (3c)

First diastereomer (3c-I): M.p. 149-149.5 °C; yield 53 %; IR (KBr, ν_{max}, cm⁻¹): 1752, 1733 and 1705 (C=O), 1620 (C=C); MS *m/z* (%): 614 (M⁺, 5), 571 (M⁺-CH₃CO, 25), 558 (M⁺-C₄H₈, 16), 513 (M⁺-CO₂^tBu, 28), 456 [M⁺-(CO₂^tBu+C₄H₉), 38], 352 (M⁺-PPh₃, 14), 251 [M⁺- (PPh₃+CO₂^tBu), 37], 43 (CH₃CO⁺, 100); Anal. calcd. for C₃₇H₄₃O₆P (614.73): C 72.29, H 7.05 %; Found C 72.15, H 6.95 %; **3c-I (Z)** (59 %) ¹H-NMR (CDCl₃): δ_H 0.84 (9H, s, CMe₃), 1.47 (9H, s, CMe₃), 1.49 (3H, s, CH₃), 1.87-

1.88 (2H, m, CH₂), 2.01-2.06 (2H, m, CH₂), 2.78-2.83 (2H, m, CH₂), 3.37 (1H, d, ³J_{PH} = 16.8 Hz, CH), 7.4-7.55 (15H, m, -Ph); ¹³C-NMR (CDCl₃): δ_C 20.28 and 25.83 (2CH₂), 28 and 28.44 (2CMe₃), 28.21 (CH₃), 37.58 (d, ¹J_{PC} = 120.79 Hz, P=C), 38.76 (CH₂), 44.92 (d, ²J_{PC} = 14.28 Hz, CH), 74.49 (cyclopentanone quaternary carbon), 80.65 and 81.67 (2CMe₃), 125.8 (d, ¹J_{PC} = 85.6 Hz, C_{ipso}), 128.52 (d, ³J_{PC} = 12.1 Hz, C_{meta}), 131.96 (C_{para}), 132.1 (d, ²J_{PC} = 9.94 Hz, C_{ortho}), 169.47 (d, ³J_{PC} = 12.8 Hz, C=O ester), 175.73 (d, ³J_{PC} = 6.5 Hz, C=O ester), 204.19 and 216.98 (2C=O, ketones). **3c-I (E)** (41 %) ¹H-NMR (CDCl₃): δ_H 1.36 (9H, s, CMe₃), 1.40 (9H, s, CMe₃), 1.54 (CH₃CO), 2.01-2.06 (2H, m, CH₂), 2.51-2.56 (2H, m, CH₂), 2.90-2.94 (2H, m, CH₂), 3.35 (1H, d, ³J_{PH} = 16.8 Hz, CH), 7.65-7.78 (15H, m, -Ph); ¹³C-NMR (CDCl₃): δ_C 20.28 and 25.16 (2CH₂), 28 and 28.04 (2CMe₃), 28.13 (CH₃), 38.3 (d, ¹J_{PC} = 122 Hz, P=C), 38.29 (CH₂), 49.1 (d, ²J_{PC} = 14.1 Hz, CH), 74.11 (cyclopentanone quaternary carbon), 81.18 and 81.79 (2CMe₃), 126.2 (d, ¹J_{PC} = 84.5 Hz, C_{ipso}), 128.30 (d, ³J_{PC} = 11.95 Hz, C_{meta}), 131.66 (C_{para}), 135.38 (d, ²J_{PC} = 10.1 Hz, C_{ortho}), 168.80 (d, ²J_{PC} = 13 Hz, C=O ester), 172.56 (d, ³J_{PC} = 6.5 Hz, C=O ester), 202.41 and 212.82 (2C=O, ketones).

Second diastereomer; (3c-II): M.p. 157.5-159°C; yield 42 %; IR (KBr, ν_{max}, cm⁻¹): 1748, 1725 and 1695 (C=O), 1612 (C=C); Anal. calcd. for C₃₇H₄₃O₆P (614.72): C 72.29, H 7.05 %; Found C 72.18, H 6.97 %. **3c-II (Z)** (66 %) ¹H-NMR (CDCl₃): δ_H 0.85 and 1.50 (18H, 2s, 2CMe₃), 1.56 (3H, s, CH₃CO), 1.87-1.92 (2H, m, CH₂), 1.97-2.03 (2H, m, CH₂), 3.10-3.16 (2H, m, CH₂), 3.31 (1H, d, ³J_{PH} = 20 Hz, CH), 7.40-7.52 (15H, m, -Ph); ¹³C-NMR (CDCl₃): δ_C 20.25 and 25.03 (2CH₂), 28.26 and 28.31 (2CMe₃), 28.80 (CH₃CO), 38.47 (d, ¹J_{PC} = 122.3 Hz, P=C), 40.23 (CH₂CO), 50.03 (d, ²J_{PC} = 14.1 Hz, CH), 74.38 (d, ³J_{PC} = 3.4 Hz, cyclopentanone quaternary carbon), 77.01 and 80.71 (2CMe₃), 125.90 (d, ¹J_{PC} = 84.8 Hz, C_{ipso}), 128.1 (d, ³J_{PC} = 11.8 Hz, C_{meta}), 131.95 (C_{para}), 132.10 (d, ²J_{PC} = 9.4 Hz, C_{ortho}), 160.9 (d, ²J_{PC} = 13.1 Hz, C=O ester), 173.66 (d, ³J_{PC} = 6.8 Hz, C=O ester), 203.12 and 215.98 (2C=O, ketones). **3c-II (E)** (34 %) ¹H-NMR (CDCl₃): δ_H 1.37 and 1.50 (18H, 2s, 2CMe₃), 1.52 (3H, s, CH₃CO), 2.05-2.19 (2H, m, CH₂), 2.43-2.48 (2H, m, CH₂), 2.89-2.98 (2H, m, CH₂), 3.30 (1H, d, ³J_{PH} = 21.9 Hz, CH), 7.82-8.1 (15H, m, -Ph); ¹³C-NMR (CDCl₃): δ_C 20.40 and 24.88 (2CH₂), 27.91 and 28.48 (2CMe₃), 29.28 (CH₃CO), 40.62 (d, ¹J_{PC} = 131.33 Hz, P=C), 39.42 (CH₂CO), 49.39 (d, ²J_{PC} = 13.8 Hz, CH), 74.02 (d, ³J_{PC} = 3.5 Hz, cyclopentanone quaternary carbon), 77.78 and 80.60 (2CMe₃), 125.90 (d, ¹J_{PC} = 84.8 Hz, C_{ipso}), 128.52 (d, ³J_{PC} = 12.1 Hz, C_{meta}), 131.79 (C_{para}), 135.36 (d, ²J_{PC} = 9.9 Hz, C_{ortho}), 170.83 (d, ²J_{PC} = 13.3 Hz, C=O ester), 173.42 (d, ³J_{PC} = 7 Hz, C=O ester), 202.61 and 215.43 (2C=O, ketones).

Preparation of Dimethyl (E)-2-[1-(2-oxocyclopentylidene)ethyl]-2-butenedioate (5a)

Compound **3a (I or II)** was refluxed in benzene for 24 hours. The solvent was removed under reduced pressure and the viscous residue was purified by silica gel column chromatography (Merck silica gel 60, 230-400 mesh) using ethyl acetate-hexane (30:70) as eluent. The solvents were removed under reduced pressure to give the product. White powder; m.p. 67-69 °C, yield 85 %; IR (KBr, ν_{max}, cm⁻¹): 1745, 1735 and 1710 (C=O), 1627 (C=C); ¹H-NMR (CDCl₃): δ_H 1.94 (2H, t, ³J_{HH} = 7.4 Hz, CH₂), 1.98 (3H, s, CH₃), 2.50 (2H, t, ³J_{HH} = 7.3 Hz, CH₂), 2.70 (2H, m, CH₂), 3.66 (3H, s, OCH₃), 3.73 (3H, s, OCH₃), 6.71 (1H, s, CH); ¹³C-NMR (CDCl₃): δ_C 19.58 and 22.61 (2CH₂), 28.42 (CH₃), 39.06 (CH₂), 51.78 and 52.67 (2OCH₃), 124.89, 134.74, 139.82 and 149.97 (olefinic carbons), 165.06 and

165.22 (2C=O, esters), 206.29 (C=O, ketone); MS m/z (%): 252 (M^+ , 21), 237 (M^+ - Me, 25), 221 (M^+ -OMe, 34), 193 (M^+ -CO₂Me, 42), 162 [M^+ -(CO₂Me+OMe), 48], 110 (M^+ -MeO₂CCCCO₂Me, 100); Anal. calcd. for C₁₃H₁₆O₅ (252.27): C 61.90, H 6.39 %; Found C 61.77, H 6.30 %. The following compounds were prepared similarly:

Diethyl (E)-2-[1-(2-oxocyclopentylidene)ethyl]-2-butenedioate (5b). White powder; m.p. 66-68 °C; yield 80 %; IR (KBr, ν_{\max} , cm⁻¹): 1740, 1730 and 1710 (C=O), 1620 (C=C); ¹H-NMR (CDCl₃): δ_H 1.25-1.44 (6H, m, 2CH₃), 2 (2H, t, ³J_{HH} = 7.8 Hz, CH₂), 2.04 (3H, s, CH₃), 2.30-2.40 (2H, t, ³J_{HH} = 7.7 Hz, CH₂), 2.75-2.77 (2H, m, CH₂), 4.17 (2H, q, ³J_{HH} = 7.1 Hz, OCH₂), 4.25 (2H, q, ³J_{HH} = 7.1 Hz, OCH₂), 6.77 (1H, s, CH); ¹³C-NMR (CDCl₃): δ_C 14.12 and 14.14 (2CH₃), 19.62 and 22.16 (2CH₂), 28.45 (CH₃CO), 39.08 (CH₂), 60.07 and 61.60 (2OCH₂), 125.18, 134.55, 140.1 and 149.92 (olefinic carbons), 164.57 and 164.9 (2C=O, esters), 203.5 (C=O, ketone); MS m/z (%): 280 (M^+ , 16), 265 (M^+ -Me, 22), 207 (M^+ -CO₂Et, 28), 162 [M^+ -(CO₂Et+OEt), 48], 110 (M^+ -EtO₂CCCCO₂Et, 100); Anal. calcd. for C₁₅H₂₀O₅ (280.32): C 64.27, H 7.19 %; Found C 64.15, H 7.08 %.

Di-tert-butyl (E)-2-[1-(2-oxocyclopentylidene)ethyl]-2-butenedioate (5c). White powder; m.p. 64-67 °C; yield 87 %; IR (KBr, ν_{\max} , cm⁻¹): 1738, 1730 and 1715 (C=O), 1618 (C=C); ¹H-NMR (CDCl₃): δ_H 1.40 and 1.47 (2CMe₃), 1.92 (2H, t, ³J_{HH} = 7.4 Hz, CH₂), 1.95 (3H, s, CH₃CO), 2.22-2.27 (2H, t, ³J_{HH} = 7.3 Hz, CH₂), 2.65-2.70 (2H, m, CH₂), 6.54 (1H, s, CH); ¹³C-NMR (CDCl₃): δ_C 19.62 and 22.44 (2CH₂), 27.92 and 27.98 (2CMe₃), 28.48 (CH₃), 39.10 (CH₂), 81.02 and 81.82 (2CMe₃), 126.60, 133.94, 140.63 and 149.52 (olefinic carbons), 163.86 and 164.43 (2C=O, esters), 205.71 (C=O, ketone); MS m/z (%): 336 (M^+ , 8), 280 (M^+ - C₄H₈, 22), 263 (M^+ -O^tBu, 28), 235 (M^+ -CO₂^tBu, 20), 179 [M^+ -(CO₂^tBu+C₄H₈), 35], 162 [M^+ -(CO₂^tBu+O^tBu), 42], 110 (M^+ -^tBuO₂CCCCO₂^tBu, 54); Anal. calcd. for C₁₉H₂₈O₅ (336.43): C 67.83, H 8.38 %; Found C 67.70, H 8.26 %.

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Sample Availability: Available from the authors.