Short communication

Synthesis of Functionalized Stable Phosphorus Ylides. New Synthesis of Dimethyl (Z)-2-[2-(ethoxycarbonyl)-1-cyclopentenyl]-2-butenedioates

Sakineh Asghari,* Zahra Sobhaninia and Zahra Naderi

Department of Chemistry, University of Mazandaran, P. O. BOX 453, Babolsar, Iran

** Corresponding author: E-mail: s.asghari@umz.ac.ir, Fax: 00981125233702*

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Abstract

Ethyl 2-oxo-1-cyclopentanecarboxylate undergoes a reaction with dialkyl acetylenedicarboxylate in the presence of triphenyphosphine to produce stable phosphorus ylides in good yields. These ylides undergo intramolecular Wittig reaction in boiling toluene to produce cyclobutene derivatives, which undergo ring-opening reactions to produce dialkyl (*Z*)-2-[2-(ethoxycarbonyl)-1-cyclopentenyl]-2-butenedioates.

Keywords: Ethyl 2-oxo-1-cyclopentanecarboxylate, dialkyl acetylenedicarboxylate, triphenylphosphine, intramolecular Wittig reaction.

1. Introduction

Organophosphorus compounds, those bearing a carbon atom directly bonded to a phosphorus atom are synthetic targets of interest, at least because of their value for a variety of industrial, biological, and chemical synthetic uses.[1–3] Phosphorus ylides are reactive systems, which take part in many valuable reactions in the synthesis of organic products.[4–6] We previously reported the synthesis of cyclobutene derivatives by intramolecular Wittig reaction, which were converted to electron-deficient 1,3-dienes.[7–9] In continuation of studies in introducing the new methods on synthesis of phosphorus ylide and electron-deficient compounds, we wish to report the reaction between ethyl 2-oxo-1-cyclopentanecarboxylate **2** and dialkyl acetylenedicarboxylates in the presence of triphenylphosphine. Thus, reaction of triphenylphosphine with electron-deficient acetylenic ester **1** in the presene of a CH-acid such as **2** leads to ylide **3** in good yields.

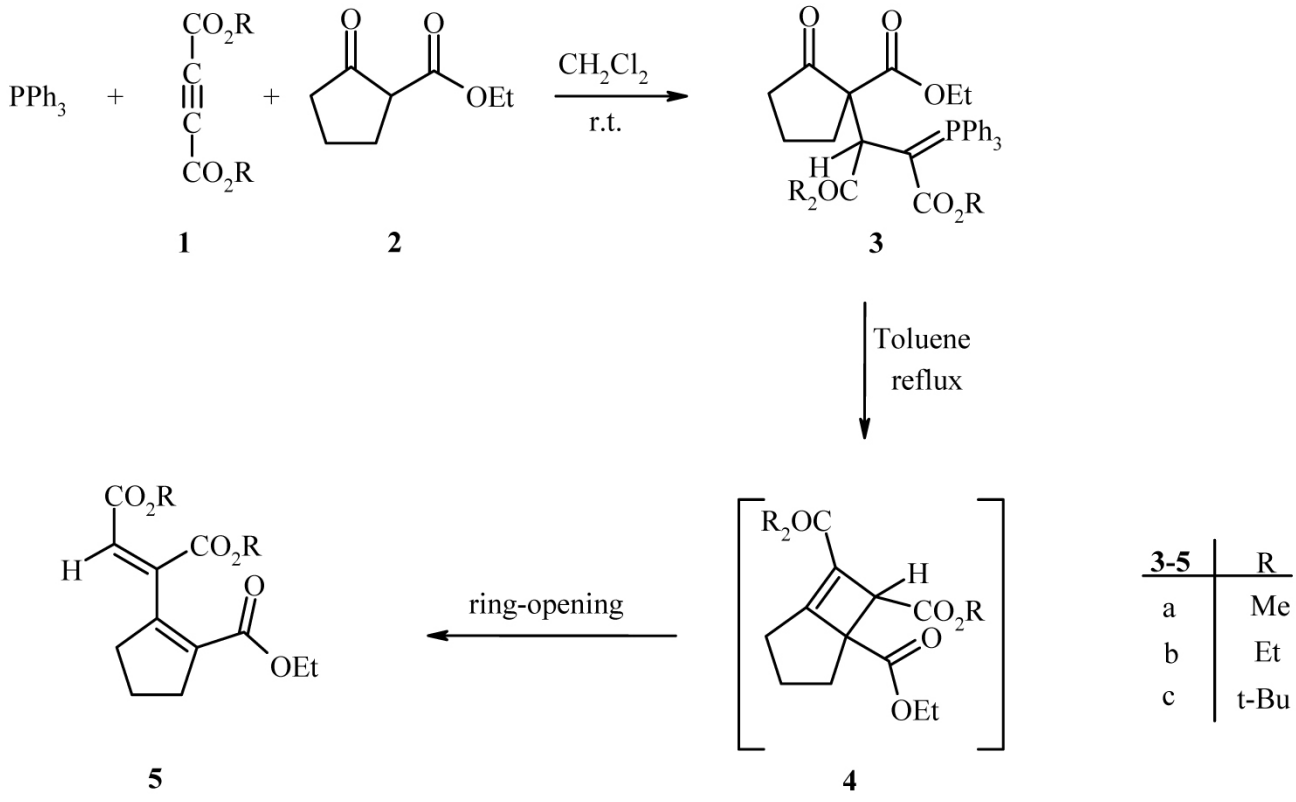
These compounds then undergo intramolecular Wittig reaction in boiling toluene to produce cyclobutene derivatives **4**, which undergoes electrocyclic ring-opening reaction to generate highly functionalized 1,3-dienes **5** (Scheme 1).

2. Results and Discussion

On the basis of the chemistry of trivalent phosphorus nucleophiles,[10,11] it is reasonable to assume that ylide **3** results from initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by **2**, followed by attack of the carbon atom of the anion of **2** to vinyltriphenylphosphonium cation **6** to generate the stable ylide **3**. This compound undergoes intramolecular Wittig reaction in boiling toluene to produce strained cyclobutene derivative **4**, which is finally converted to electron-deficient 1,3 – dienes **5** via a ring-opening reaction (Scheme 2).

The structures of compounds **3a–c** were deduced from IR, ^{1}H and ^{13}C NMR spectra. The mass spectra of these ylides are fairly similar and display the molecular ion peaks. Other fragmentations involved the loss of the ester moieties or PPh_3 from the ion molecule. Although compounds **3** possesses two stereogenic centers, and two diastereomers are expected, the ^{1}H NMR spectrum of the reaction mixture shows only one diastereoisomer.

The ^{1}H and ^{13}C NMR spectra of **3a–c** are also consistent with the presence of two isomers (see experimental section). The ylide moiety of these compounds is strongly conjugated to the adjacent carbonyl group and its rotation



Scheme 1

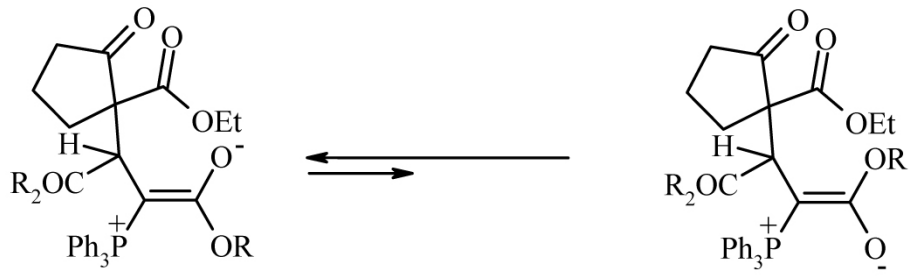
about the partial double bound in (*E*)-**3** and (*Z*)-**3** geometrical isomers is slow on the NMR timescale at ambient temperature.

The assignment of the configuration (*Z*) to the major geometrical isomer of **3** is based on the ^{1}H NMR chemical shift of the OR moiety, which is expected to be shielded as a result of the anisotropic effect of the phenyl groups (Scheme 3).

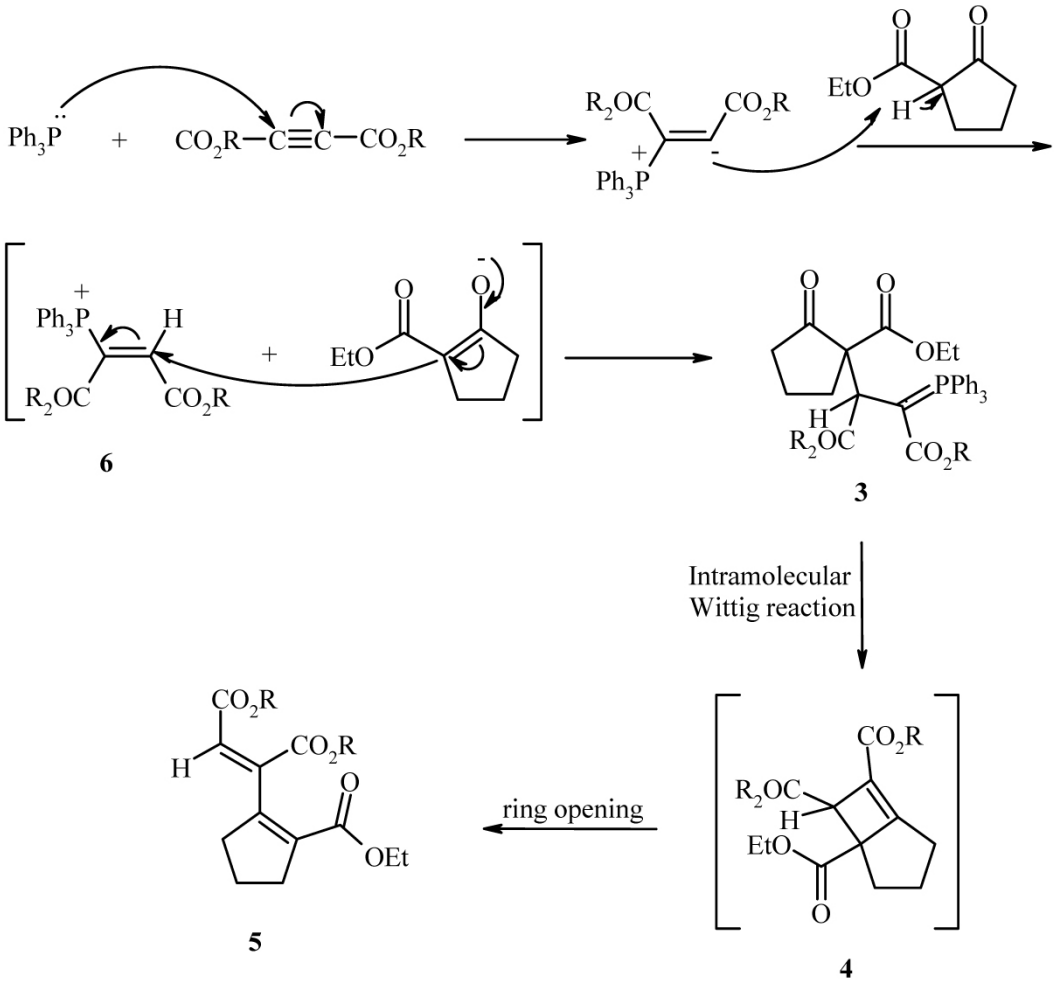
The ^{1}H NMR spectrum of **3a** in $CDCl_3$ at 25°C exhibits two sharp singlets at about 2.8 and 3.64 ppm for the methoxy groups of the *Z*– isomer, and two sharp singlets at about 3.46 and 3.60 ppm for the methoxy groups of the *E*-isomers. The diastereotopic protons of the CH_2 groups appear as multiplet signals in ^{1}H NMR spectrum as a result of the presence of chiral centers in compound **3**.

The presence of the ^{31}P nucleus in compound **3** helps to assign the signals by long-range couplings with ^{1}H and ^{13}C nuclei (see experimental section). The ^{13}C NMR spectrum of **3a** displays two signals at about 48.4 and 51.7 ppm for two methoxy groups and a doublet at about 39.0 ppm ($^1J_{PC}$ = 125.8 Hz) for P=C group of *Z*-isomer and two signals at about 49.5 and 51.6 ppm for two methoxy groups and also a doublet at about 39.6 ppm ($^1J_{PC}$ = 125.5 Hz) for P=C group of *E*-isomer. Other signals exhibited characteristic resonance with appropriate chemical shifts for two geometrical isomers. The ^{1}H and ^{13}C NMR spectra of **3b** and **3c** are similar to those of **3a**, except that for the ester groups, which exhibited characteristic resonances.

The structures of **5a–c** were deduced from their ^{1}H,



Scheme 3



Scheme 2

^{13}C NMR and IR spectral data. The strong carbonyl absorption bands at 1722–1735 cm^{-1} for all the compounds were observed. The ^{1}H NMR spectrum of **5a** displays characteristic signals at about 6.75 ppm for the CH group and appropriate chemical shifts in the olefinic region. Because of loss of the chiral center during the conversion of compound **3** to **5**, the proton signals of CH_2 groups were simplified in **5**. The ^{13}C NMR spectrum of **5a** exhibits four signals at about 126.1, 132.0, 144.1 and 149.7 ppm for olefinic carbons. The partial assignment of these signals is given in experimental section. The mass spectra of the compound **5a** displayed molecular ion peak at *m/z* = 282. Initial fragmentations involve loss of the alkoxy and esteric groups.

3. Experimental

Ethyl 2-oxo-1-cyclopentanecarboxylate, dialkyl acetylenedicarboxylate and triphenyl phosphine were obtained from Fluka (Buchs, Switzerland) and used without further purifications. Melting points were measured with an Electrothermal 9100 apparatus. ^{1}H, ^{13}C and ^{31}P NMR spectra were measured at 500.1, 125.8, and 202.5 MHz, respectively, with a Bruker DRX-500 Avance instrument. $CDCl_3$ was used as solvent. IR spectra were recorded on a Shimadzu FT-IR Bruker Vector 22 spectrometer. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

General procedure for preparation of dialkyl 2-[1-(ethoxycarbonyl)-2-oxocyclopentyl]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate compounds (exampli-fied by 3a).

To a magnetically stirred solusion of ethyl 2-oxo-1-cyclopentane carboxylate (0.31 g, 2 mmol) and triphenylphosphine (0.52 g, 2 mmol) in CH_2Cl_2 (10 ml) was added, dropwise, a mixture of dimethyl acetylenedicarboxylate (0.28 g, 2 mmol) in CH_2Cl_2 (3 ml) at –10 °C over 10 min. The mixture was allowed to stand at room temperature for 24 hours. The solvent was removed under reduced pressure and the residue was purified by silica gel (Merck silica gel, 230–400 mesh) column chromatography using hexane:ethyl acetate (1:5) as eluent. The solvent was removed under reduced pressure and ylide **3a** was obtained.

Dimethyl 2-[1-(ethoxycarbonyl)-2-oxocyclopentyl]-3-(1,1,1-triphenyl-λ^5-phosphanylidene) succinate (3a): White powder; m.p. 170 –172 °C, yield 0.9 g (80%); IR (KBr) ($\nu_{max,}$ cm^{-1}): 3050 (CH), 2985 (CH), 1735, 1725 (C=O), 1640 (C=C); MS, *m/z* (%): 279 ($OPPh_3^+$+1, 3), 262 ($^+PPh_3$, 5), 180 [M$^+$–(PPh_3+2CO_2Me), 19], 83 [M$^+$–(CO_2Et+PPh_3+$Me_2OCC{\equiv}CCO_2Me$)+1, 45], 57 ($CH_3CH_2O^+$, 100); Anal. Calcd for $C_{32}H_{33}O_7P$ (560.59): C, 68.56; H, 5.93; Found: C, 68.49; H, 5.89.

Major isomer, **3a**–(*Z*) (68%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 1.03 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 1.99–2.05 (2H, m, CH_2), 2.14–2.20 (2H, m, CH_2), 2.64–2.68 and 2.90–2.95 (2H, 2m, CH_2), 2.8 (3H, s, OCH_3), 3.58 (1H, d, $^3J_{PH}$ 18.8 Hz, CH), 3.64 (3H, s, OCH_3), 3.76–3.83 (2H, m, OCH_2), 7.43–7.53 (15H, m, arom); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 13.9 (CH_3), 20.3, 30.6 and 36.8 ($3CH_2$), 39.0 (d, $^1J_{PC}$ 125.8 Hz, P=C), 48.4 and 51.7 ($2OCH_3$), 49.1 (d, $^2J_{PC}$ 13.7 Hz, CH), 60.9 (OCH_2), 67.5 (quaternary carbon of cyclopentanone), 127.0 (d, $^1J_{PC}$ 92.7 Hz, C_{ipso}), 128.3 (d, $^3J_{PC}$ 11.9 Hz, C_{meta}), 131.7 (C_{para}), 133.9 (d, $^2J_{PC}$ 9.6 Hz, C_{ortho}), 169.2 (C=O, ester), 170.0 (d, $^2J_{PC}$ 13.8 Hz, C=O ester), 174.6 (d, $^3J_{PC}$ 6.5 Hz, C=O ester), 213.5 (C=O, ketone); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 26.23.

Minor isomer, **3a**–(*E*) (32%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 1.17 (3H, t, $^3J_{HH}$ 7 Hz, CH_3), 1.74–1.84 (4H, m, $2CH_2$), 2.32–2.4 and 2.55–2.62 (2H, 2m, CH_2), 3.46 (3H, s, OCH_3), 3.56 (1H, d, $^3J_{PH}$ 17.9 Hz, CH), 3.54–3.57 (2H, m, OCH_2), 3.60 (3H, s, OCH_3), 7.66–7.72 (15H, m, arom); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 13.9 (CH_3), 20.3, 30.6 and 36.7 ($3CH_2$), 39.6 (d, $^1J_{PC}$ 125.5 Hz, P=C), 48.2 (d, $^2J_{PC}$ 14.1 Hz, CH), 49.5 and 51.6 ($2OCH_3$), 61.1 (OCH_2), 67.1 (quaternary carbon of cyclopentanone), 127.1 (d, $^1J_{PC}$ 93.4 Hz, C_{ipso}), 128.4 (d, $^3J_{PC}$ 11 Hz, C_{meta}), 132.0 (C_{para}), 134.0 (d, $^2J_{PC}$ 9.6 Hz, C_{ortho}), 169.1

(C=O, ester), 171.1 (d, $^2J_{PC}$ 14.8 Hz, C=O ester), 174.6 (d, $^3J_{PC}$ 6.5 Hz, C=O ester), 212.8 (C=O, ketone). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 25.94.

Diethyl 2-[1-(ethoxycarbonyl)-2-oxocyclopentyl]-3-(1,1,1-triphenyl-λ^5-phospha nylidene)succinate (3b): White powder, m.p. 160–162 °C, yield 1.1 g (90%); IR (KBr) (ν_{max}, cm^{-1}): 3040 (CH), 2982 (CH), 1745, 1726 (C=O), 1645 (C=C); MS, *m/z* (%): 279 ($OPPh_3^+$+1, 10), 262 ($^+PPh_3$, 2), 180 [M$^+$–(PPh_3+2CO_2Et), 100], 86 ($CHCO_2Et^+$, 100), 57 ($CH_3CH_2CO^+$, 36); Anal. Calcd. for $C_{34}H_{37}O_7P$ (588.64): C, 69.38; H, 6.34; Found: C, 69.32; H, 6.30.

Major isomer, **3b**–(*Z*) (69%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 0.32 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 0.97 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 1.26 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 1.96–2.01 (2H, m, CH_2), 2.11–2.21 (2H m, CH_2), 2.85–2.89 and 3.12–3.16 (2H, 2m, CH_2), 3.49 (1H, d, $^3J_{HP}$ 18.6 Hz, CH), 3.69–3.7 (2H, m, OCH_2), 3.85–3.88 (2H, m, OCH_2), 3.95–4.18 (2H, m, OCH_2), 7.44–7.54 (15H, m, arom); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 13.6, 13.8 and 13.9 ($3CH_3$), 20.4, 30.7 and 36.8 ($3CH_2$), 38.5 (d, $^1J_{PC}$ 125.8 Hz, P=C), 48.1 (d, $^2J_{PC}$ 14 Hz, CH), 60.4, 60.8 and 60.8 ($3OCH_2$), 67.6 (d, $^3J_{PC}$ 4 Hz, quaternary carbon of cyclopentanone), 127.2 (d, $^1J_{PC}$ 92.1 Hz, C_{ipso}), 128.2 (d, $^3J_{PC}$ 12 Hz, C_{meta}), 131.6 (d, $^4J_{PC}$ 2.4 Hz, C_{para}), 134.0 (d, $^2J_{PC}$ 9.6 Hz, C_{ortho}), 170.0 (d, $^2J_{PC}$ 13.1 Hz, C=O ester), 170.2 (C=O ester), 174.1 (d, $^3J_{PC}$ 7 Hz, C=O ester), 214.9 (C=O, ketone); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 26.14.

Minor isomer, **3b**–(*E*) (31%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 1.03 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 1.14 (3H, t, $^3J_{HH}$ 7 Hz, CH_3), 1.32 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 1.74–1.81 (2H, m, CH_2), 2.38–2.5 and 2.26–2.68 (2H, 2m, CH_2), 2.92–3.03 and 3.18–3.25 (2H, 2m, CH_2), 3.52 (1H, d, $^3J_{PH}$ 18.8 Hz, CH), 3.52–3.70 (2H, m, OCH_2), 3.76–3.83 (2H, m, OCH_2), 3.95–4.18 (2H, m, OCH_2), 7.70–7.80 (15H, m, arom); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 14.3, 14.9 and 15.1 ($3CH_3$), 20.3, 29,9 and 36.6 ($3CH_2$), 38.9 (d, $^1J_{PC}$ 121.5 Hz, P=C), 49.1 (d, $^2J_{PC}$ 14.0 Hz, CH), 60.6, 60.7 and 61.0 ($3OCH_2$), 66.0 (d, $^3J_{PC}$ 4 Hz, quaternary carbon of cyclopentanone), 127.2 (d, $^1J_{PC}$ 92.1 Hz, C_{ipso}), 128.3 (d, $^3J_{PC}$ 11.5 Hz, C_{meta}), 131.6 (d, $^4J_{PC}$ 2.4 Hz, C_{para}), 134.0 (d, $^2J_{PC}$ 9.6 Hz, C_{ortho}), 169.6 (d, $^2J_{PC}$ 14.2 Hz, C=O ester), 169.3 (C=O, ester), 174.5 (d, $^3J_{PC}$ 6.9 Hz, C=O ester), 213.5 (C=O, ketone; ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 25.82.

Di-tert-butyl 2-[1-(ethoxycarbonyl)-2-oxocyclopentyl]-3-(1,1,1-triphenyl-λ^5-phosphanyllidene) succinate (3c): White powder, m.p. 150–152 °C, yield 0.9 g (75%); IR (KBr) (ν_{max}, cm^{-1}): 3030 (CH), 2978 (CH), 1750, 1725, 1714 (C=O), 1638 (C=C); MS *m/z* (%): 279 ($OPPh_3^+$+1, 57), 180 [M$^+$–(PPh_3+2$CO_2{}^t$Bu), 30], 83 (M$^+$–(CO_2Et+PPh_3 +^{t}Bu$O_2CC{\equiv}CCO_2{}^t$Bu), 24], 57 ($C_4H_9^+$, 63), 43 (CH_3CO^+, 55); Anal. Calcd. for $C_{38}H_{45}O_7P$ (644.75): C, 70.79; H, 7.04; Found: C, 70.73; H, 7.00.

Major isomer, **3c**–(*Z*) (81%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 0.87 (9H, s, CMe_3), 0.92 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 1.50 (9H, s, CMe_3), 1.98–2.04 (2H, m, CH_2), 2.06–2.33 (2H, m, CH_2), 2.87–2.92 and 3.33–3.35 (2H, 2m, CH_2), 3.4 (d, $^3J_{PH}$ 18.2 Hz, CH), 3.80–3.85 (2H, m, OCH_2), 7.42–7.52 (15H, m, arom); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 13.7 (CH_3), 20.35 (CH_2), 28.3 (CMe_3), 28.4 (CMe_3), 31.1 (CH_2), 38.2 (d, $^1J_{PC}$ 122 Hz, P=C), 40.2 (CH_2), 48.9 (d, $^2J_{PC}$ 14.2 Hz, CH), 60.7 (OCH_2), 66.1 (d, $^3J_{PC}$ 4.1 Hz, quaternary carbon of cyclopentanone), 76.8 and 80.0 ($2OCMe_3$), 127.2 (d, $^1J_{PC}$ 93.1 Hz, C_{ipso}), 127.9 (d, $^3J_{PC}$ 12.1 Hz, C_{meta}), 131.5 (C_{para}), 134.5 (d, $^2J_{PC}$ 9.5 Hz, C_{ortho}), 169.1 (d, $^2J_{PC}$ 12.8 Hz, C=O ester), 170.6 (C=O, ester), 173.7 (d, $^3J_{PC}$ 7.2 Hz, C=O ester), 215.5 (C=O, ketone); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 26.05.

Minor isomer, **3c**–(*E*) (19%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 1.18 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 1.38 (9H, s, CMe_3), 1.49 (9H, s, CMe_3), 1.98–2.04 (2H, m, CH_2), 2.06–2.3 (2H, m, CH_2), 2.87–2.9 and 3.11–3.17 (2H, 2m, CH_2), 3.46 (d, $^3J_{PH}$ 16.9 Hz, CH), 3.42–3.46 (2H, m, OCH_2), 7.6–7.99 (15H, m, arom); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 15.2 (CH_3), 20.5 (CH_2), 28.5 and 28.8 (2CM-

e$_3$), 30.2 (CH_2), 39.7 (CH_2), 40.4 (d, $^1J_{PC}$ 122 Hz, P=C), 48.3 (d, $^2J_{PC}$ 14 Hz, CH), 60.8 (OCH_2), 65.7 (d, $^3J_{PC}$ 4 Hz, quaternary carbon of cyclopentanone), 77.6 and 79.9 (2$OCMe_3$), 127.2 (d, $^1J_{PC}$ 93.1 Hz, C_{ipso}), 128.1 (d, $^3J_{PC}$ 12.4 Hz, C_{meta}), 131.7 (C_{para}), 134.7 (d, $^2J_{PC}$ 9.6 Hz, C_{ortho}), 170.9 (d, $^2J_{PC}$ 13.5 Hz, C=O 170.2 (C=O ester), 172.9 (d, $^3J_{PC}$ 7.2 Hz, C=O ester), 214.9 (C=O, ketone); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ_P 25.75.

General procedure for preparetion of Dialkyl (Z)-2[2-(ethoxycarbonyl)-1-cyclopentenyl]-2-butenedioate compounds (examplified by 5a)

Compound **3a** (0.56 g, 1mmol) was refluxed in toluene for 24 hours. The solvent was removed under educed pressure and the residue was purified by silica gel (Merck gel, 230–400 mesh) column chromatography using hexane:ethyl acetate as eluent. The solvent was removed under reduced pressure and **5a** was obtained.

Dimethyl (Z)-2-[2-(ethoxycarbonyl)-1-cyclopentenyl]-2-butene dioate(5a): Yellow oil, yield 0.14 g (50%); IR (KBr) (ν_{max} cm^{-1}): 1735, 1725 (C=O), 1648(C=C); ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 1.18 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 2.02 (2H, quintet, $^3J_{HH}$ 7.4 Hz, CH_2), 2.70 (2H, t, $^3J_{HH}$ 7.4 Hz, CH_2), 2.74 (2H, t, $^3J_{HH}$ 7.4 Hz, CH_2), 3.71 (3H, s, OCH_3), 3.77 (3H, s, OCH_3), 4.07 (2H, q, $^3J_{HH}$ 7.1 Hz, OCH_2), 6.75 (1H, s, CH); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 14.1 (CH_3), 29.7, 33.2 and 38.9 (3CH_2), 51.8 and 52.7 (2OCH_3), 60.2 (OCH_2), 126.1, 132.6, 144.1 and 149.7 (olefinic carbons), 164.7, 165.1 and 165.3 (3C=O, ester); MS *m/z* (%): 282 (M^+, 2), 232 (M^+–OEt, 7), 223 (M^+–CO_2Me, 54), 209 (M^+–CO_2Et, 100), 195 [M^+–(CO_2Me+C_2H_4), 63], 176 [M^+–(CO_2Et+MeOH)+1, 22], 149 [M^+–(2OMe+CO_2+C_2H_4)+1, 27]; Anal. Calcd. for $C_{14}H_{18}O_6$ (282.29): C, 59.57; H, 6.43; Found: C, 59.53; H, 6.39.

Diethyl (Z)-2[2-(ethoxycarbonyl)-1-cyclopentenyl]-2-butenedioate (5b): Yellow oil, yield 0.19 (60%); IR (KBr) (ν_{max}, cm^{-1}): 1732, 1725(C=O), 1665 (C=C); ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 1.18 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 1.25 (3H, t, $^3J_{HH}$ 7.2 Hz, CH_3), 1.26 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 2.01 (2H, quintet, $^3J_{HH}$ 7.5 Hz, CH_2), 2.68–2.73 (4H, m, 2 CH_2), 4.07 (2H, q, $^3J_{HH}$ 7.1 Hz, OCH_2), 4.15 (2H, q, $^3J_{HH}$ 7.2 Hz, OCH_2), 4.22 (2H, q, $^3J_{HH}$ 7.1 Hz, OCH_2), 6.74 (1H, s, CH); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 14.1 (2CH_3), 14.1 (CH_3), 29.7, 33.2 and 39.0 (3CH_2), 60.2, 60.8 and 61.7 (3OCH_2), 126.4, 132.3, 144.0 and 149.9 (olefinic carbons), 164.7, 164.8 and 164.8 (3C=O, ester); MS *m/z* (%): 310 (M^+, 100), 237 (M^+–CO_2Et, 5), 209 [M^+–(CO_2Et+C_2H_4), 7], 149 [M^+–(2OEt+CO_2+C_2H_4)+1, 6]; Anal. Calcd. for $C_{16}H_{22}O_6$ (310.35): C, 61.92; H, 7.14; Found: C, 61.88; H, 7.09.

Di-tert-butyl(Z)-2[2-(ethoxycarbonyl)-1-cyclopentenyl]-2-butenedioate (5c): Yellow oil, yield 0.14 g (40%); IR (KBr) (ν_{max}, cm^{-1}): 1733, 1722 (C=O), 1635 (C=C); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.18 (3H, t, $^3J_{HH}$ 7.1 Hz, CH_3), 1.41 (9H, s, CMe_3), 1.44 (9H, s, CMe_3), 1.97 (2H, quintet, $^3J_{HH}$ 7.6 Hz, CH_2), 2.64–2.71 (4H, m, 2 CH_2), 4.07 (2H, q, $^3J_{HH}$ 7.1 Hz, OCH_2), 6.6 (1H, s, CH); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 14.1 (CH_3), 29.7, 33.2 and 39.2 (3 CH_2), 27.9 and 28.0 (2 CMe_3), 60.1 (OCH_2), 81.3 and 81.9 (2$OCMe_3$), 127.9, 131.6, 143.4 and 150.4 (olefinic carbons), 164.0, 164.4 and 164.9 (3 C=O, ester); MS *m/z* (%): 366 (M^+, 2), 310 (M^+–C_4H_8, 11), 265 (M^+–$CO_2{}^t$Bu, 2), 209 [M^+–($CO_2{}^t$Bu+C_4H_8), 39], 181 [M^+–($CO_2{}^t$Bu+C_2H_4+C_4H_8), 39], 57 ($C_4H_9^+$, 45); Anal. Calcd. for $C_{20}H_{30}O_6$ (366.46): C, 65.55; H, 8.25;. Found: C, 65.49; H, 8.21.

4. Conclusion

The present method may be used as a practical route for the synthesis of stable phosphorous ylides, and as convenient preparation of functionalized 1,3-dienes using intramolecular Wittig reaction under neutral conditions. This procedure has advantages of high yields, mild reaction conditions, and simple experimental and work-up conditions.

5. References

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Povzetek

Prispevek obravnava reakcijo etil 2-okso-1-cklopentan karboksilatov z acetilendikarboksilati v prisotnosti trifenilfosfina. Pri tem nastanejo stabilni fosforjevi ilidi z dobrimi izkoristki. Tako pripravljeni ilidi pri refluksu toluena v intramolekularni Wittigovi reakciji dajejo derivate ciklobutena, ki pri nadalnjih reakcijah odpiranja obroča tvorijo dialkil (*Z*)-2-[2-(etoksikarbonil)-1-ciklopentenil]-2-butendioate.