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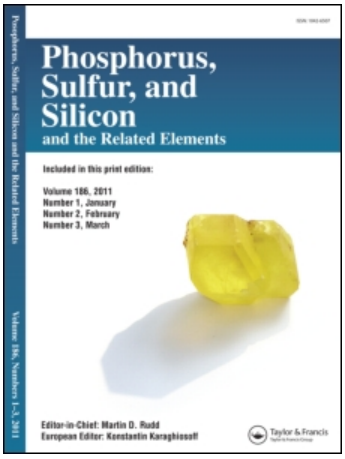

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VINYL TRIPHENYLPHOSPHONIUM SALT–MEDIATED SYNTHESIS OF FUNCTIONALIZED ALKENES

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Deoxybenzoin undergoes a smooth reaction with acetylenic esters in the presence of triphenylphosphine to produce phosphorus ylides. Only the* tert*-butyl phosphorus ylide undergoes an intramolecular Wittig reaction to produce highly strained cyclobutenes in boiling toluene, which spontaneously undergoes ring-opening reactions to produce highly functionalized 1,3-dienes. The unstable ylides undergo a 1,2-proton transfer and the loss of PPh_3 to produce functionalized alkenes.

Keywords Alkyl propiolates; deoxybenzoin; dialkyl acetylenedicarboxylate; triphenylphosphine; Wittig reaction

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INTRODUCTION

Phosphorus ylides are reactive systems that take part in many valuable reactions in organic chemistry.[1–8] These ylides have found use in a wide variety of reactions interesting to synthesis chemists, especially in the synthesis of naturally occurring products, and compounds with biological and pharmacological activities.[2,9–13] These ylides are usually prepared by treatment of a phosphonium salt with a base, and the salts are usually prepared from the phosphine and an alkyl halide.[14] Phosphonium salts can also be prepared by Michael addition of phosphorus (III) compounds such as triphenylphosphine to acetylenic esters, leading to zwitterionic intermediates, which are not detected even at low temperatures. These unstable intermediates can be trapped by a proton donor such as methanol, amide, imide, strong *CH*-acid, and a variety of electrophiles to produce various compounds such as ylides.[15]

We have recently described the synthesis of 2*H*-oxetes[16] **1** from the reaction of phenacylchloride as an electron-deficient ketone with dialkyl acetylenedicarboxylate and triphenylphosphine. With the purpose of preparing 2*H*-oxetes having phenyl and benzyl group at C-2, such as **2**, we performed the reaction of deoxybenzoin **4** with triphenylphosphine and dialkyl acetylenedicarboxylates **3**. This reaction did not afford the corresponding 2*H*-oxetes **2**, but yielded phosphorus ylide **5** (Scheme 1).

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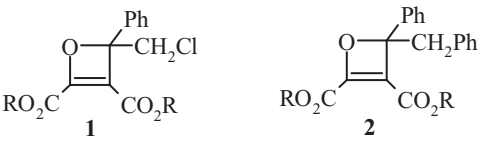
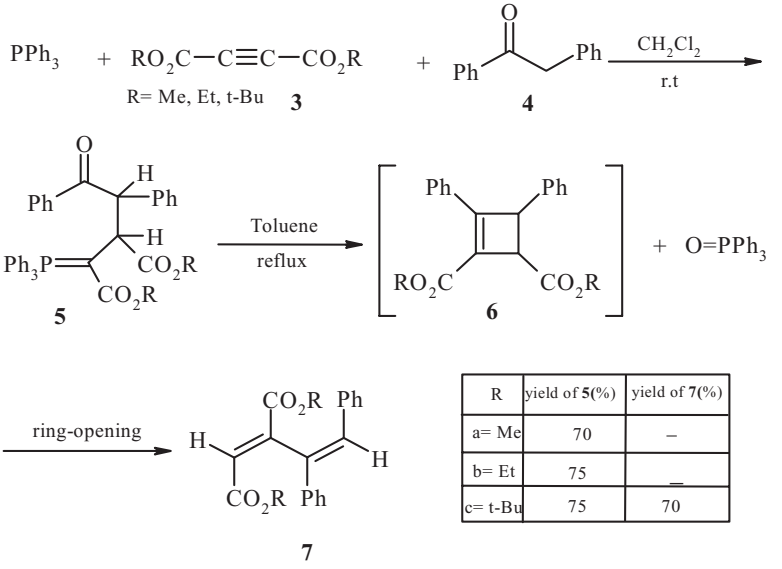


Scheme 1

Only compound **5c-I** undergoes an intramolecular Wittig reaction to produce highly strained cyclobutene **6** in boiling toluene, which spontaneously undergoes a ring opening reaction to produce highly functionalized 1,3-diene **7** (Scheme 2).



R	yield of **5**(%)	yield of **7**(%)
a= Me	70	–
b= Et	75	–
c= t-Bu	75	70

Scheme 2

When the reaction of deoxybenzoin was carried out with alkyl acetylenedicarboxylate **8** (a mono acetylenic ester) in the presence of PPh_3, the phosphorus ylide **10** was not obtained, but the functionalized alkene **9** was isolated (Scheme 3).

RESULTS AND DISCUSSON

On the basis of the chemistry of trivalent phosphorus nucleophiles,[1,2,9,13] it is reasonable to assume that phosphorus ylide **5** results from the initial addition of triphenylphosphine to dialkyl acetylenedicarboxylate and subsequent protonation of the zwitterionic intermediate by the deoxybenzoin. Then the positively charged ion is attacked by the enolate of deoxybenzoin to form the stable ylides **5a–c**. These compounds possess two stereogenic centers, and two diastereomers are expected (**I** and **II**). We could only isolate diastereomeric ylides of **5c** from its reaction mixture as yellow (**5c-I**) and white (**5c-II**) powders, respectively, but we could not isolate diastereomers of **5a** and **5b** (Scheme 4).

Both diastereomers of **5c** were refluxed separately in toluene. First the diastereomer of **5c** (yellow powder) only underwent an intramolecular Wittig reaction to produce unstable

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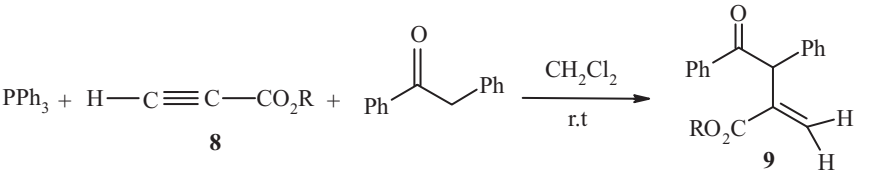
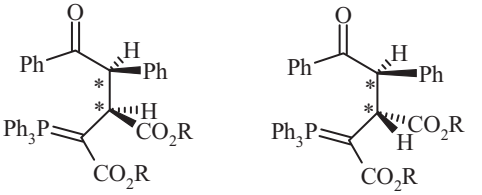


R	yield of **9**
a= Me	8
b= Et	7

Scheme 3



Scheme 4

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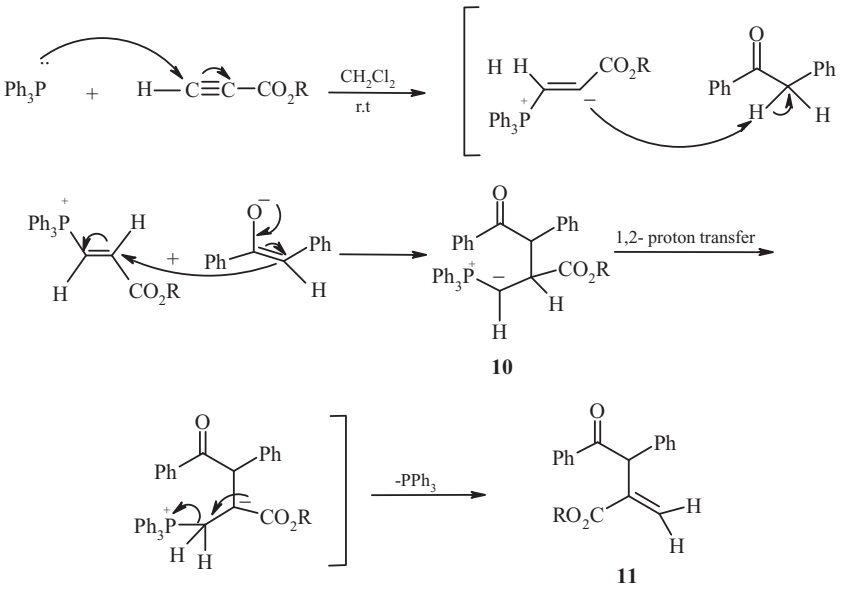
cyclobutene **6**, which spontaneously was converted to functionalized 1,3-diene **7** by a ring-opening reaction.

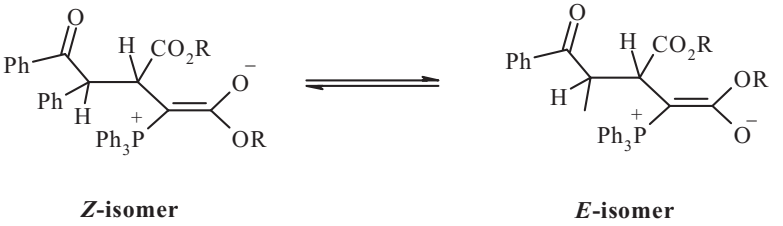
It seems that when the reaction of deoxybenzoin was carried out with alkyl propiolate in the presence of PPh_3, phosphorus ylide **10** was formed. These ylides are less stable than **5** and spontaneously undergo a 1,2-proton transfer and then loss of triphenylphosphine to produce functionalized alkenes **11** (Scheme 5).

The structures of **5a–c** (**I** and **II**) were deduced from ^1H, ^{13}C, ^{31}P NMR, IR, and mass spectra. The ^1H NMR spectrum of stable ylide **5c-I** (yellow powder, first diastereomer) exhibited four singlets at about 0.80, 1.26, 1.27, and 1.43 ppm for four *tert*-butyl groups, two doublets of doublet at about 3.21 ppm ($^3J_{PH}$ 17.8 Hz, $^3J_{HH}$ 11.1 Hz) and 3.20 ppm ($^3J_{PH}$ 17.8 Hz, $^3J_{HH}$ 11.1 Hz) for two methine protons of $CHCO_2Bu^t$ groups, and two doublets at about 6.55 ppm ($^3J_{HH}$ 11.1 Hz) and 6.25 ppm ($^3J_{HH}$ 11.1 Hz) for two methine protons of CHPh groups with unequal intensity ratio for their (*Z*) and (*E*) isomers, respectively. As the temperature was increased, these signals collapsed; for example, two doublets at about 6.25 and 6.55 ppm for CHPh converted to a broad doublet at 333 K. This observation is attributed to the temperature-dependent equilibrium between the geometric (rotational) isomers, *E* and *Z*, i.e., the result of a restricted rotation (Scheme 6).

The ^{13}C NMR spectrum of **5c-I** displayed two unequal doublets at about 39.66 ppm ($^1J_{PC}$ 123.8 Hz) and 42.63 ppm ($^1J_{PC}$ 131.9 Hz) for two P=C groups, two unequal doublets at about 48.13 ppm ($^2J_{PC}$ 12.9 Hz) and 47.58 ppm ($^2J_{PC}$ 12. Hz) for two *C*HCO_2Bu^t groups, and two unequal doublets at about 51.38 ppm ($^3J_{PC}$ 4.9 Hz) and 52.66 ppm ($^3J_{PC}$ 5.4 Hz) for two *C*HPh groups, respectively. The ^{31}P NMR spectrum of **5c-I** exhibited two unequal signals at about 23.72 and 24.51 ppm for their *Z*- and *E*-isomers.



Scheme 5



Scheme 6

The ^{1}H NMR spectrum of **5c-II** (white powder, second diastereomer) exhibited four singlets at about 0.92, 1.30, 1.31, and 1.60 ppm for four *tert*-butyl groups, two doublet of doublets at about 3.35 ppm ($^{3}J_{PH}$ 18.4 Hz, $^{3}J_{HH}$ 10.8 Hz) and 3.36 ppm ($^{3}J_{PH}$ 18.3 Hz, $^{3}J_{HH}$ 10.7 Hz) for two methine protons of $CHCO_2Bu^t$ groups, and two doublets at about 6.32 ppm ($^{3}J_{HH}$ 10.7 Hz) and 5.98 ppm ($^{3}J_{HH}$ 10.8 Hz) for two methine protons of *C*HPh groups with unequal intensities, respectively. The ^{13}C NMR spectra of **5c-II** displayed two unequal doublets at about 38.66 ppm ($^{1}J_{PC}$ 126.6 Hz) and 41.12 ppm ($^{1}J_{PC}$ 133.7 Hz) for two P=C groups, two unequal doublets at about 47.86 ppm ($^{2}J_{PC}$ 12.9 Hz) and 47.12 ppm ($^{2}J_{PC}$ 12.4 Hz) for two $CHCO_2Bu^t$ groups, and two unequal doublets at about 51.86 ppm ($^{3}J_{PC}$ 4.9 Hz) and 52.80 ppm ($^{3}J_{PC}$ 5.5 Hz) for two CHPh groups, for their *Z*- and *E*-isomers, respectively. The ^{31}P NMR spectrum of **5c-II** exhibited two unequal signals at 23.72 and 24.10 ppm. The mass spectrum of **5c** displayed a molecular ion peak at *m/z* 684. Fragmentations involve the loss of one of the side chains (C_4H_7, OC_4H_7, CO_2Bu^t, and PPh_3). The structural assignment made on the basis of ^{1}H and ^{13}C NMR spectra for compound **5c** was supported by a measurement of its IR spectrum.

The ^{1}H and ^{13}C NMR spectra of the mixture of diastereomeric ylides **5a** and **5b** are similar to those of **5c**, except for the esteric groups, which exhibited characteristic

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resonances with appropriate chemical shifts. The mass spectra of **5a** and **5b** exhibited molecular ion peaks at *m/z* 600 and 628 for methyl and ethyl derivatives, respectively.

Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts and coupling constants in diastereomeric ylides **5a–c** are shown in Table I. Partial assignments of IR and mass spectra are given in the Experimental section.

The structure of **7** was deduced from its ^{1}H, ^{13}C NMR, IR, and mass spectra. The ^{1}H NMR of **7** exhibited two singlets at about 1.45 and 1.65 ppm for two *tert*-butyl groups, and two singlets at about 5.40 and 6.92 ppm for two olefinic protons. The ^{13}C NMR spectrum of **7** displayed two signals at about 28.10 and 28.15 ppm for two *tert*-butyl groups, two signals at about 80.70 and 82.56 ppm for two quaternary carbons of *tert*-butoxy groups, and two signals at about 120.68 and 151.19 ppm for olefinic carbons. The mass spectrum of **7** displayed a molecular ion peak at *m/z* 406. Fragmentations involve the loss of one of the side chains. The structure of **7** was supported by measurements of its IR spectrum. ^{1}H, ^{13}C NMR, IR, and mass spectra of **7** are given in the Experimental section.

The structures of **11a** and **11b** were deduced from their ^{1}H, ^{13}C NMR, IR, and mass spectra. The ^{1}H NMR spectrum of **11a** exhibited a signal at about 3.75 ppm for methoxy group, a singlet at about 5.30 ppm for methine proton of CHPh group, and two signals at about 5.89 and 6.48 ppm for two geminal vinylic protons. The ^{13}C NMR spectrum of **11a** displayed a signal at about 52.2 ppm for methoxy group, a signal at 55.39 ppm for CHPh, and two signals at 132.96 and 140.23 ppm for olefinic carbons. The mass spectrum of **11a** exhibited a molecular ion peak at *m/z* 280. The IR spectrum of **11a** displayed strong carbonyl absorption bands at 1709 and the C=C absorption band at 1636 cm^{-1}. The ^{1}H and ^{13}C NMR spectra of **11b** are similar to those of **11a**, except for the esteric group, which exhibited characteristic resonances with appropriate chemical shifts. The mass spectrum of **11b** exhibited a molecular ion peak at *m/z* 294.

In conclusion, the present method may be considered as a practical synthesis of stable diastereomeric phosphorus ylides, which can be converted to functionalized alkenes under neutral conditions in good yields.

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EXPERIMENTAL

Deoxybenzoin, triphenylphosphine, dialkyl acetylenedicarboxylates, and alkyl propiolate were obtained from Fluka (Buche, Switzerland) and were used without further purification. IR spectra were recorded on a 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. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured with a Bruker DRX-300 AVANCE spectrometer at 300.1, 75.5, and 121.5 MHz, respectively. Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses were performed using a Heraeus CHN-O rapid analyzer.

Preparation of Dialkyl 2-(2-Oxo-1,2-diphenyl ethyl)-3-(triphenylphosphoran yliden)succinate (5): General Procedure

A solution of dialkyl acetylenedicarboxylate (2 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a magnetically stirred solution of deoxybenzoin (0.39 g, 2 mmol) and triphenylphosphine (0.52 g, 2 mmol) in CH_2Cl_2 (10 mL) at $-10^{\circ}C$ over 10 min. The mixture was allowed to stand at room temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by silica gel (Merck silica gel, 230–400 mesh)

Table I Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for ylides **5a–c**

Ylides **5**	^{1}H, ^{13}C, and ^{31}P NMR: δ (ppm) ($CDCl_3$, TMS)
5a-I (*Z*-isomer)	δ_H: 2.89 and 3.46 ($2OCH_3$), 3.35 (1H, dd, $^{3}J_{PH}$ 17.3 Hz, $^{3}J_{HH}$ 11.1 Hz, CH), 6.42 (1H, d, $^{3}J_{HH}$ 11.1 Hz, CH)
	δ_C: 40.91 (d, $^{1}J_{PC}$ 124.6 Hz, P=C), 47.60 (d, $^{2}J_{PC}$ 12.5 Hz, CH), 48.46 and 51.44 ($2OCH_3$), 51.88 (d, $^{3}J_{PC}$ 5.0 Hz, CH), 201.08 (C=O, Ketone)
	δ_p: 23.63
(*E*-isomer)	δ_H: 3.46 and 3.56 ($2OCH_3$), 3.33 (1H, dd, $^{3}J_{PH}$ 17.1 Hz, $^{3}J_{HH}$ 11.1 Hz, CH), 6.22 (1H, d, $^{3}J_{HH}$ 11.1 Hz, CH)
	δ_C: 41.88 (d, $^{1}J_{PC}$ 133.4 Hz, P=C), 46.96 (d, $^{2}J_{PC}$ 12.6 Hz, CH), 49.85 and 50.06 ($2OCH_3$), 52.25 (d, $^{3}J_{PC}$ 5.2 Hz, CH), 200.62 (C=O, Ketone)
	δ_p: 24.16
5a-II (*Z*-isomer)	δ_H: 3.01 and 3.55 ($2OCH_3$), 3.5 (1H, dd, $^{3}J_{PH}$ 17.0 Hz, $^{3}J_{HH}$ 10.7 Hz, CH), 6.27 (1H, d, $^{3}J_{HH}$ 10.7 Hz, CH)
	δ_C: 39.37 (d, $^{1}J_{PC}$ 126.1 Hz, P=C), 47.26 (d, $^{2}J_{PC}$ 12.5 Hz, CH), 48.61 and 51.46 ($2OCH_3$), 51.77 (d, $^{3}J_{PC}$ 4.9 Hz, CH), 201.08 (C=O, Ketone)
	δ_p: 24.22
(*E*-isomer)	δ_H: 3.44 and 3.74 ($2OCH_3$), 3.61 (1H, dd, $^{3}J_{PH}$ 18.6 Hz, $^{3}J_{HH}$ 10.6 Hz, CH), 5.81 (1H, d, $^{3}J_{HH}$ 10.6 Hz, CH)
	δ_C: 40.16 (d, $^{1}J_{PC}$ 133.5 Hz, P=C), 46.29 (d, $^{2}J_{PC}$ 12.4 Hz, CH),50.91 and 51.00 ($2OCH_3$), 53.52 (d, $^{3}J_{PC}$ 5.5 Hz, CH), 201.45 (C=O, Ketone)
	δ_p: 24.59
5b-I (*Z*-isomer)	δ_H: 0.30 (3H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 0.99 (3H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 3.33 (1H, dd, $^{3}J_{HP}$ 16.9 Hz, $^{3}J_{HH}$ 11.1 Hz, CH), 3.43–4.20 (4H, m, $2OCH_2$), 6.47 (1H, d, $^{3}J_{HH}$ 11.1 Hz, CH)
	δ_C: 13.95 and 13.98 ($2CH_3$), 40.68 (d, $^{1}J_{PC}$ 124.5 Hz, P=C), 47.36 (d, $^{2}J_{PC}$ 12.5 Hz, CH), 51.75 (d, $^{3}J_{PC}$ 4.5 Hz, CH), 57.06 and 59.86 ($2OCH_2$), 201.79 (C=O Ketone)
	δ_p: 24.09
(*E*-isomer)	δ_H: 1.23 (3H, t, $^{3}J_{HH}$ 7.0 Hz, CH_3), 1.38 (3H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 3.29 (1H, dd, $^{3}J_{HP}$ 16.9 Hz, $^{3}J_{HH}$ 11.1 Hz, CH), 3.43–4.20 (4H, m, $2OCH_2$), 6.24 (1H, d, $^{3}J_{HH}$ 11 Hz, CH)
	δ_C: 15.15 and 15.48 ($2CH_3$), 42.14 (d, $^{1}J_{PC}$ 127.6 Hz, P=C), 46.75 (d, $^{2}J_{PC}$ 12.5 Hz, CH), 52.71 (d, $^{3}J_{PC}$ 4.5 Hz, CH), 58.03 and 59.86 ($2OCH_2$), 200.67 (C=O Ketone)
	δ_p: 24.24
5b-II (*Z*-isomer)	δ_H: 0.37 (3H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 1.22 (3H, t, $^{3}J_{HH}$ 7.0 Hz, CH_3), 3.36 (1H, dd, $^{3}J_{HP}$ 16.5 Hz, $^{3}J_{HH}$ 10.7 Hz, CH), 3.43–4.20 (4H, m, $2OCH_2$), 6.32 (1H, d, $^{3}J_{HH}$ 10.7 Hz, CH)
	δ_C: 13.95 and 13.98 ($2CH_3$), 39.22 (d, $^{1}J_{PC}$ 126.3 Hz, P=C), 47.49 (d, $^{2}J_{PC}$ 12.0 Hz, CH), 51.59 (d, $^{3}J_{PC}$ 4.8 Hz, CH), 57.15 and 60.46($2OCH_2$), 201.07 (C=O Ketone)
	δ_p: 24.06
(*E*-isomer)	δ_H: 1.01 (3H, t, $^{3}J_{HH}$ 7.0 Hz, CH_3), 1.08 (3H, t, $^{3}J_{HH}$ 7.1 Hz, CH_3), 3.43 (1H, dd, $^{3}J_{HP}$ 16.5 Hz, $^{3}J_{HH}$ 10.7 Hz, CH), 3.43–4.20 (4H, m, $2OCH_2$), 5.91 (1H, d, $^{3}J_{HH}$ 10.7 Hz, CH)
	δ_C: 14.09 and 14.16 ($2CH_3$), 40.35 (d, $^{1}J_{PC}$ 127.1 Hz, P=C), 47.11 (d, $^{2}J_{PC}$ 12 Hz, CH), 53.26 (d, $^{3}J_{PC}$ 4.9 Hz, CH), 58.03 and 60.46 ($2OCH_2$), 200.76 (C=O Ketone)
	δ_p: 23.54
5c-I (*Z*-isomer)	δ_H: 0.80 and 1.27 (18H, 2s, $2CMe_3$), 3.21 (1H, dd, $^{3}J_{PH}$ 17.8 Hz, $^{3}J_{HH}$ 11.1 Hz, CH), 6.55 (1H, d, $^{3}J_{HH}$ 11.1 Hz, CH)
	δ_C: 28.02 and 28.20 ($2CMe_3$), 39.69 (d, $^{1}J_{PC}$ 123.8 Hz, P=C), 48.13 (d, $^{2}J_{PC}$ 12.9 Hz, CH), 51.38 (d, $^{3}J_{PC}$ 4.9 Hz, CH), 76.54 and 79.18 ($2CMe_3$), 202.54 (C=O Ketone)
	δ_p: 23.72
(*E*-isomer)	δ_H: 1.26 and 1.43 (18H, 2s, $2CMe_3$), 3.20 (1H, dd, $^{3}J_{PH}$ 17.8 Hz, $^{3}J_{HH}$ 11.1 Hz, CH), 6.25 (1H, d, $^{3}J_{HH}$ 11.2 Hz, CH)
	δ_C: 28.02 and 28.96 ($2CMe_3$), 42.63 (d, $^{1}J_{PC}$ 131.9 Hz, P=C), 47.58 (d, $^{2}J_{PC}$ 12.7 Hz, CH), 52.66 (d, $^{3}J_{PC}$ 5.4 Hz, CH), 77.02 and 77.04 ($2CMe_3$), 201.24 (C=O Ketone)
	δ_p:24.51

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Table I Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for ylides **5a–c** *(Continued)*

Ylides **5**	^{1}H, ^{13}C, and ^{31}P NMR: δ (ppm) ($CDCl_3$, TMS)
5c-II (*Z*-isomer)	δ_H: 0.92 and 1.30 (18H, 2s, $2CMe_3$), 3.35 (1H, dd, $^{3}J_{PH}$ 18.4 Hz, $^{3}J_{HH}$ 10.8 Hz, CH), 6.32 (1H, d, $^{3}J_{HH}$ 10.6 Hz, CH)
	δ_C: 28.06 and 28.29 ($2CMe_3$), 38.66 (d, $^{1}J_{PC}$ 126.6 Hz, P=C), 47.86 (d, $^{2}J_{PC}$ 12.9 Hz, CH), 51.86 (d, $^{3}J_{PC}$ 4.9 Hz, CH), 76.40 and 79.72 ($2CMe_3$), 200.86 (C=O Ketone)
	δ_p: 23.72
(*E*-isomer)	δ_H: 1.31 and 1.60 (18H, 2s, $2CMe_3$), 3.36 (1H, dd, $^{3}J_{PH}$ 18.3 Hz, $^{3}J_{HH}$ 10.7 Hz, CH), 5.98 (1H, d, $^{3}J_{HH}$ 10.8 Hz, CH)
	δ_C: 28.06 and 28.96 ($2CMe_3$), 41.12 (d, $^{1}J_{PC}$ 133.7 Hz, P=C), 47.12 (d, $^{2}J_{PC}$ 12.4 Hz, CH), 52.80 (d, $^{3}J_{PC}$ 5.51 Hz, CH), 76.81 and 76.84 ($2CMe_3$), 200.72 (C=O Ketone)
	δ_p:24.10

column chromatography using hexane:ethyl acetate (50:50) as an eluent. A mixture of two diastereomeric ylides was obtained for **5a** and **5b**, but for **5c**, ylides **5c-I** and **5c-II** were isolated as yellow and white powders, respectively.

Dimethyl 2-(2-oxo-1,2-diphenyl ethyl)-3-(triphenylphosphoran yliden) succinate (5a, $C_{38}H_{33}O_5P$). Mixture of diastereomeric ylide **5a**, yield 70%, IR (KBr) (υ_{max}, cm^{-1}): 1729, 1684 (C=O) and 1633 (C=C); MS, *m/z* (%): 600 (M^+) (4), 541 (8), 509 (5), 405 (100), 278 (30), 262 (53), 105 (82), 77 (60).

Diethyl 2-(2-oxo-1,2-diphenyl ethyl)-3-(triphenylphosphoran yliden) succinate (5b, $C_{40}H_{37}O_5P$). Mixture of diastereomeric ylides of **5b**, yield 75%, IR (KBr) (υ_{max}, cm^{-1}): 1724, 1679 (C=O), 1628 (C=C); MS, *m/z* (%): 628 (M^+) (3) 583 (5), 555 (18), 509 (22), 433 (100), 278 (15), 262 (93), 183 (87), 105 (78), 77 (45).

Di-tert-butyl 2-(2-oxo-1,2-diphenyl ethyl)-3-(triphenylphosphoran yliden) succinate (5c, $C_{44}H_{45}O_5P$). First diastereomer: **5c-I**, yellow powder, mp 155–157°C, yield 45%; IR (KBr) (υ_{max}, cm^{-1}): 1729 and 1710 (C=O), 1678 (C=C); MS, *m/z* (%): 684 (M^+) (5), 583 (23), 489 (81), 377 (100), 333 (48), 278 (30), 262 (25), 77 (40), 57 (60).

Second diastereomer: **5c-II**, white powder, mp 208–210°C, yield 55%; IR (KBr) (υ_{max}, cm^{-1}): 1725 and 1710 (C=O), 1678 (C=C); MS, *m/z* (%): 684 (M^+) (3), 526 (36), 489 (65), 377 (100), 333 (48), 278 (20), 262 (37), 57 (65).

Preparation of Di(*tert*–butyl) (E-2-[(Z)-1,2-Diphenyl-1-ethenyl]2-butenedioate (7, $C_{26}H_{30}O_4$)

Compound 5**c-I** was refluxed in toluene, and after 24 h, it was converted to compound **7** by loss of $OPPh_3$. The solvent was removed under reduced pressure, and viscous residue was purified by silica gel (Merck silica gel, 230–400 mesh) column chromatography using hexane:ethyl acetate (50:50). The solvent was removed under reduced pressure, and the product was obtained from recrystallization in ether.

7, white powder, mp 114–116°C, yield 70%; IR (KBr) (υ_{max}, cm^{-1}): 1720 and 1685 (C=O) and 1610 (C=C); MS, *m/z* (%): 406 (M^+) (2), 350 (4), 294 (83), 276 (62), 231 (100), 203 (34), 105 (20), 77 (6), 57 (63); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.45 (9H, s, CMe_3), 1.65 (9H, s, CMe_3), 5.40 (1H, s, olefinic proton), 6.92 (1H, s, olefinic proton), 6.85–6.89 (2H, m, aromatic protons), 7.07–7.14 (3H, m, aromatic protons), 7.20–7.23 (2H,

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m, aromatic protons), 7.38–7.44 (3H, m, aromatic protons);^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 28.10 (2C*Me*$_3$), 80.70 and 82.56 (2O*C*Me$_3$), 120.68, 151.19 (olefinic carbons), 128.08, 129.13, 129.94, 130.12, 134.84, 135.72, 136.92 and 137.70 (aromatic carbons), 164.62 and 167.27 (2C=O, ester).

Preparation of Methyl-2-[2-oxo-1,2-diphenyl ethyl)acrylate (11a, $C_{18}H_{16}O_3$)

A solution of triphenylphosphine (0.52 g, 2 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a magnetically stirred solution of deoxybenzoin (0.39 g, 2 mmol) and methyl propiolate (0.17 mL, 2 mmol) in CH_2Cl_2 (10 mL) at −10°C over 10 min. The reaction mixture then was allowed to warm up at room temperature and was stirred for 24 h. The solution 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 (80:20) as an eluent. The solvent was removed under reduced pressure, and **11a** was obtained as yellow powder.

Yellow powder, mp 62–64°C, yield 80%; IR (KBr) (υ_{max}, cm^{-1}): 1709 (C=O), 1636 (C=C); MS, *m/z* (%): 280 (M^+) (5), 249 (5), 115 (41),105 ($PhCO^+$) (100), 77 (79); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 3.75 (3H, s, OCH_3), 5.30 (1H, s, CH), 5.89 (1H, s, CH), 6.48 (1H, s, CH), 7.26–8.00 (10H, m, aromatic protons); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 52.20 (OCH_3), 55.39 (CH), 127.72, 128.55, 128.69, 128.90, 129.12, 129.58, 135.67 and 136.35 (aromatic carbons), 132.96 and 140.23 (olefinic carbons), 167.07 (C=O ester), 197.48 (C=O ketone).

Ethyl-2-[2-oxo-1,2-diphenyl ethyl)acrylate (11b, $C_{19}H_{18}O_3$)

White powder, mp 52–54°C, yield 70%; IR (KBr) (υ_{max}, cm^{-1}): 1712 and 1704 (C=O), 1645 (C=C); MS, *m/z* (%): 294 (M^+) (4), 249 (8), 115 (37), 105 (100), 77 (85); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.23 (3H, t, $^3J_{HH}$ 7.1 Hz CH_3), 4.16–4.24 (2H, m, OCH_2), 5.27 (1H, s, CH), 5.89 (1H, s, CH), 6.49 (1H, s, CH), 7.27–7.98 (8H, m, −Ph), 7.98–8.00 (2H, m, −Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 14.06 (CH_3), 55.37 (CH), 61.16 (OCH_2), 127.70, 128.44, 128.54, 128.88, 129.11, 129.60, 135.67 and 136.39 (aromatic carbons), 132.95 and 140.59 (olefinic carbons), 166.54 (C=O ester), 197.53 (C=O ketone).

REFERENCES

1. A. W. Johnson, *Ylide Chemistry* (Academic Press, New York, 1966).
2. H. R. Hudson, *The Chemistry of Organophosphorus Compounds: Primary, Secondary and Tertiary Phosphines, Polyphosphines and Organophosphorus (III) Compounds* (Wiley, New York, 1990), vol. 1, pp. 386–472.
3. B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, **89,** 863 (1989).
4. (a) I. Yavari and R. Baharfar, *Tetrahedron Lett.*, **39,** 1051 (1998); (b) I. Yavari, S. Asghari, and A. A. Esmaili, *J. Chem. Res. (S)*, 234 (1999); (c) I. Yavari and S. Asghari, *Tetrahedron*, **55,** 11583 (1999); (d) I. Yavari, M. Adib, and L. Hojabri, *Tetrahedron*, **58,** 6895 (2002).
5. (a) S. Asghari and M. Zaty, *Phosphorus, Sulfur, and Silicon*, **178,** 2097 (2003); (b) S. Asghari, R. Baharfar, and S. Safiri, *Phosphorus, Sulfur, and Silicon*, **180,** 2805 (2005).
6. A. Ramazani, A. R. Kazemizadeh, E. Ahmadi, N. Noshiranzadeh, and A. Souldozi, *Curr. Org. Chem.*, **12,** 59 (2008).

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7. (a) S. Asghari, Z. Sobhaninia, and Z. Naderi, *Acta Chem. Solv.*, **55,** 834 (2008); (b) S. Asghari, M. B. Poushani, and S. Ramezani*, Molecules*, **13,** 331 (2008).
8. S. M. Kalbag, M. D. Nair, P. Rajagopalan, and C. N. Talaty, *Tetrahedron*, **23,** 1911 (1967).
9. D. G. C. Cobridge, *Phosphorus: An Outline of Chemistry, Biochemistry and Uses*, 5th ed. (Elsevier, Amesterdam, 1995), pp. 42–47.
10. K. C. Nicolaou, M. W. Harter, J. L. Gunzner, and A. Nadin, *Liebigs Ann.*, 1283 (1997).
11. O. I. Kolodiazhnyi, *Phosphorus Ylides: Chemistry and Application in Organic Synthesis* (Wiley-VCH, New York, 1999).
12. R. A. Cherkasor and M. A. Pudovic, *Russ. Chem. Rev.*, **63,** 1019 (1994).
13. G. I. G. Cadogan, *Organophosphorus Reagents in Organic Synthesis* (Academic Press, New York, 1979).
14. R. Engel, *Synthesis of Carbon–Phosphorus Bonds* (CRC, Boca Raton, FL, 1998).
15. (a) A. Ramazani and A. Souldozi, *Phosphorus, Sulfur, and Silicon*, **180,** 2801 (2005); (b) A. Ramazani, A. Momeni-Movahhed, and F. Gouranlou, *Phosphorus, Sulfur, and Silicon*, **177,** 903 (2002); (c) A. Ramazani and A. Souldozi, *Phosphorus, Sulfur, and Silicon*, **178,** 2189 (2003).
16. S. Asghari and A. Khabbazi Habibi, *Phosphorus, Sulfur, and Silicon*, **180,** 2451 (2005).

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