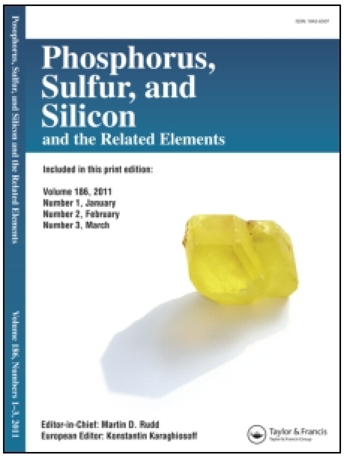

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Vinyltriphenylphosphonium Salt Mediated One-Pot Stereoselective Synthesis of Dialkyl (E)-2-(2-methyl-5-oxo-1-cyclopentenyl)-2-butenedioates

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VINYLTRIPHENYLPHOSPHONIUM SALT MEDIATED ONE-POT STEREOSELECTIVE SYNTHESIS OF DIALKYL (*E*)-2-(2-METHYL-5-OXO-1-CYCLOPENTENYL)-2-BUTENEDIOATES

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Protonation of the highly reactive 1:1 intermediates produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates by 2-hydroxy-3-methyl-2-cyclopenten-1-one leads to vinyltriphenylphosphonium salts, which undergo an intramolecular Wittig reaction to produce the corresponding cyclobutene derivatives. The cyclobutene derivatives are not isolable and undergo electrocyclic ring-opening reactions in CH_2Cl_2 at room temperature to produce dialkyl (E*)-2-(2-methyl-5-oxo-1-cyclopentenyl)-2-butenedioates in moderate yields.*

Keywords: 2-Hydroxy-3-methyl-2-cyclopenten-1-one; acetylenic esters; electrocyclic ring-opening reaction; triphenylphosphine; Wittig reaction

Vinyltriphenylphosphonium salts have found wide applications in organic synthesis.[1] β-Additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes has attracted much attention as a very convenient and synthetically useful method in organic synthesis.[1] In recent years we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the vinyltriphenylphosphonium salts.[2–5] In this article, we report on a one-pot stereoselective synthesis of dialkyl (*E*)-2-(2-methyl-5-oxo-1-cyclopentenyl)-2-butenedioates (**8**) in moderate yields.

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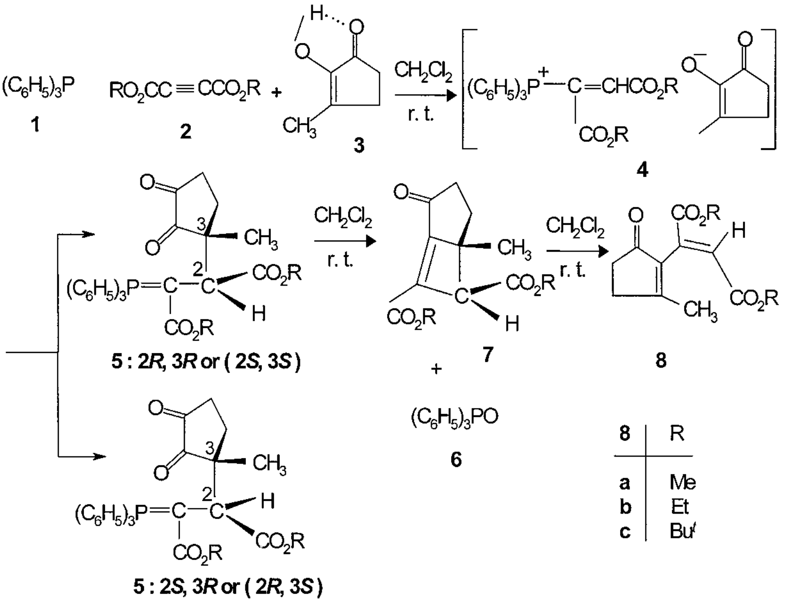
RESULTS AND DISCUSSION

Reactions are known in which an α,β-unsaturated carbonyl compound is produced from a phosphorane and a carbonyl compound such as an aldehyde or ketone.[1] Thus, compounds **8** may be regarded as the product of an intramolecular Wittig reaction. Such addition-olefination products may result from an initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct, followed by attack of the 2-hydroxy-3-methyl-2-cyclopenten-1-one anion on the vinyltriphenylphosphonium cation to form phosphorane **5**, which undergoes intramolecular Wittig reaction in dichloromethane at room temperature to produce the cyclobutene derivatives **7** and triphenylphosphine oxide **6**.[6,7] Compounds **7a–c** undergo electrocyclic ring-opening reaction to produce the dialkyl (*E*)-2-(2-methyl-5-oxo-1-cyclopentenyl)-2-butendioates (**8**) (Scheme 1). TLC indicated formation of ylides **5** in CH_2Cl_2. It seems that the ylides **5** (**2R, 3R** or **2S, 3S**) are more reactive than the ylides **5** (**2S, 3R** or **2R, 3S**) toward intramolecular Wittig reaction. Presence of steric interactions in the transition state may be plausible factors in the reduction of the activity of the ylides **5** (**2S, 3R** or **2R, 3S**) toward intramolecular Wittig reaction. TLC indicated that the formation of the compounds **8** from ylides **5** (**2R**, **3R** or



8	R
a	Me
b	Et
c	Bu^t

SCHEME 1

2S, 3S) were completed in CH_2Cl_2 at room temperature after 6 h. The cyclobutene derivatives **7** are not isolable and also are not observable on TLC. It seems that the compounds **7** are unstable in the reaction conditions, which are converted to the corresponding but-1,3-diene derivatives **8a–c**. Presence of Angle strains in cyclobutene derivatives **7** may be plausible factors in the reduction of the stability of them. Ylides **5** (**2S, 3R** or **2R, 3S**) are highly stable even at reflux temperature (toluene as solvent) after 24 h. TLC indicated that the solution contained unreacted ylides **5** (**2S, 3R** or **2R, 3S**). We tried to assign the structure of the ylides **5** (**2*S*, 3R** or **2R, 3S**) by their elemental analyses and their UV, IR, ^1H, ^{13}C, and ^{31}P NMR spectra and mass spectrometry, but ^1H, ^{13}C, and ^{31}P NMR spectra of them are highly complex ($CDCl_3$ as solvent) and therefore we were not able to interpret them. Investigation (such as single crystal x-ray diffraction) of the structure of the ylides **5** (**2S, 3R** or **2R, 3S**) are under progress and full results will be report in the future.

The structures **8a–c** were deduced from their elemental analyses and their UV, IR, ^1H, and ^{13}C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at m/z of 238, 266, and 322 respectively.

In summary, we have found that the reaction of dialkyl acetylenedicarboxylates with 2-hydroxy-3-methyl-2-cyclopenten-1-one in the presence of triphenylphosphine leads to a facile stereoselective synthesis of dialkyl (*E*)-2-(2-methyl-5-oxo-1-cyclopentenyl)-2-butenedioates (**8a–c**). Other aspects of this process are under investigation.

EXPERIMENTAL

Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. UV spectra were recorded on a Shimadzu UV-2100 spectrophotometer. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^1H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz respectively. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

General Procedure for the Preparation of Dialkyl (*E*)-2-(2-methyl-5-oxo-1-cyclopentenyl)-2-butenedioates (8a–c)

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1 mmol) and 2-hydroxy-3-methyl-2-cyclopenten-1-one **3** (0.112 g, 1 mmol) in CH_2Cl_2 (5 ml) was added dropwise a mixture of **2** (1 mmol) in CH_2Cl_2 (3 ml) at −10°C over 15 min. The reaction mixture was then allowed to warm up to room temperature and stirred for 6 h. The solvent was removed under reduced pressure and the viscous residue was purified by silica gel (Merck silica gel 60, 230–400 mesh) column chromatography using ethyl acetate-light petroleum ether (1:4) as eluent. The solvent was removed under reduced pressure and the products were obtained as colourless, viscous oils (**8a–c**). The characterization data of the dialkyl (*E*)-2-(2-methyl-5-oxo-1-cyclopentenyl)-2-butenedioates (**8a–c**) are given:

*Dimethyl(*E*)-2-(2-methyl-5-oxo-1-cyclopentenyl)-2-butenedioate (**8a**):* Colorless viscous oil; Yield: 41%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 220, 3.88. IR (CCl_4) (ν_{max}, Cm^{-1}): 3051, 2961, 1720, 1441, 1263. ^1H NMR ($CDCl_3$) δ_H : 1.99 (3H, s, CH_3), 2.50–2.54 (2H, m, $CH_2C{=}$); 2.65–2.69 (2H, m, CH_2CO); 3.70 and 3.78 (6H, 2 s, 2 OCH_3); 7.06 (1H, s, CH=). ^{13}C NMR ($CDCl_3$) δ_C : 18.54 (CH_3); 32.26 ($^{13}CH_2C{=}$); 34.95 ($^{13}CH_2CO$); 52.01 and 52.90 (2 OCH_3); 131.19 (CH=); 135.60 and 136.80 (2 C); 164.86 and 165.41 (2C=O of esters); 174.15 (C2, =CMe); 205.39 (C=O, ketone). MS (m/z, %): 239 (M^++1, 8), 238 (M^+, 80); 207 (50); 206 (100); 179 (92); 178 (30); 147 (72); 59 (7). Found: C, 60.61; H, 6.02. $C_{12}H_{14}O_5$ requires C, 60.50; H, 5.92%.

*Diethyl(*E*)-2-(2-methyl-5-oxo-1-cyclopentenyl)-2-butenedioate (**8b**):* Colorless viscous oil; Yield: 38%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 220, 4.09. IR (CCl_4) (ν_{max}, Cm^{-1}): 3052, 2937, 1719, 1449, 1395, 1256. ^1H NMR ($CDCl_3$) δ_H : 1.26 and 1.30 (6H, 2 t, $^3J_{HH}$ = 7.1 Hz, 2 CH_3 of 2 Et); 2.01 (3H, s, CH_3); 2.50–2.55 (2H, m, $CH_2C{=}$); 2.66–2.70 (2H, m, CH_2CO); 4.15 and 4.25 (4H, 2 q, $^3J_{HH}$ = 7.1 Hz, 2 OCH_2 of 2 Et); 7.06 (1H, s, CH=). ^{13}C NMR ($CDCl_3$) δ_C : 14.07 and 14.08 (2 CH_3 of 2 Et); 18.57 (CH_3); 32.22 ($^{13}CH_2C{=}$); 34.96 ($^{13}CH_2CO$); 60.94 and 61.95 (2 OCH_2); 131.48 (CH=); 135.85 and 136.68 (2 C); 164.56 and 164.92 (2 C=O of esters); 173.80 (C2, =CMe); 205.33 (C=O, ketone). MS (m/z, %): 266 (M^+, 51), 238 (4); 221 (38); 220 (49); 193 (100); 147 (41); 120 (29). Found: C, 63.62; H, 7.02. $C_{14}H_{18}O_5$ requires C, 63.15; H, 6.81%.

*Di-tert-butyl(*E*)-2-(2-methyl-5-oxo-1-cyclopentenyl)-2-butenedioate (**8c**):* Colorless viscous oil; Yield: 36%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 222, 3.84. IR (CCl_4) (ν_{max}, Cm^{-1}): 3050, 2984, 1719, 1371, 1279, 1164. ^1H NMR ($CDCl_3$) δ_H : 1.44 and 1.48 (18H, 2 s, 2 $C(CH_3)_3$); 2.00 (3H, s, CH_3); 2.48–2.53 (2H, m, $CH_2C{=}$); 2.63–2.67 (2H, m, CH_2CO); 6.89 (1H, s, CH=). ^{13}C NMR ($CDCl_3$) δ_C : 18.53 (CH_3); 27.89 and 27.98 (2 $OC(^{13}CH_3)_3$); 32.08 ($^{13}CH_2C{=}$); 34.94 ($^{13}CH_2CO$); 81.39 and 82.26 (2 $O^{13}C(CH_3)_3$); 132.70 (CH=); 136.32 and 136.41 (2 C); 164.20 and 164.24 (2 C=O of esters); 172.97 (C2, =CMe); 205.30 (C=O, ketone). MS (m/z, %): 323 (M^++1, 7), 322 (M^+, 1); 266 (36); 249 (43); 210 (100);

193 (100); 165 (100); 148 (94). Found: C, 67.33; H, 8.40. $C_{18}H_{26}O_5$ requires C, 67.06; H, 8.13%.

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