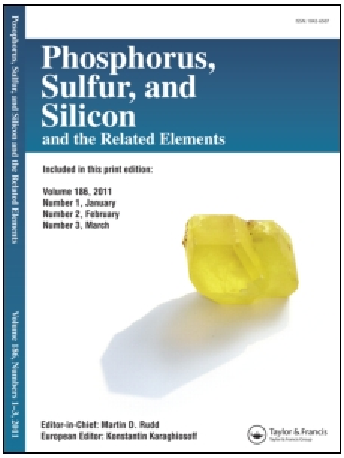

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Tributylphosphine Catalyzed O -Vinylation of 2-Hydroxy-3-methyl-2-cyclopenten-1-one

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TRIBUTYLPHOSPHINE CATALYZED *O*-VINYLATION OF 2-HYDROXY-3-METHYL-2-CYCLOPENTEN-1-ONE

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Protonation of the highly reactive 1:1 intermediates produced in the reaction between tributylphosphine and dialkyl acetylenedicarboxylates by 2-hydroxy-3-methyl-2-cyclopenten-1-one leads to vinyltributylphosphonium salts, which undergo an addition-elimination reaction in CH_2Cl_2 *at room temperature to produce dialkyl 2-[(2-methyl-5-oxo-1-cyclopentenyl)-oxy]-2-butenedioates (1:1 mixtures of* E *and* Z *isomers) in fairly high yields.*

Keywords: 2-Hydroxy-3-methyl-2-cyclopenten-1-one; acetylenic esters; catalyst; tributylphosphine; vinyltributylphosphonium salt

INTRODUCTION

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.[1–9] Organophosphorus compounds have been used extensively in organic synthesis as useful reagents as well as ligands of a number of transition metal catalysts.[10] However, there are few reactions in which organophosphorus (III) species work as catalysts.[5,11] In recent years, we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[2–8] In this article, we report facial one-pot synthesis of dialkyl 2-[(2-methyl-5-oxo-1-cyclopentenyl)-oxy]-2-butenedioates **6** (1:1 mixtures of *E* and *Z* isomers) in fairly high yields (Scheme 1).

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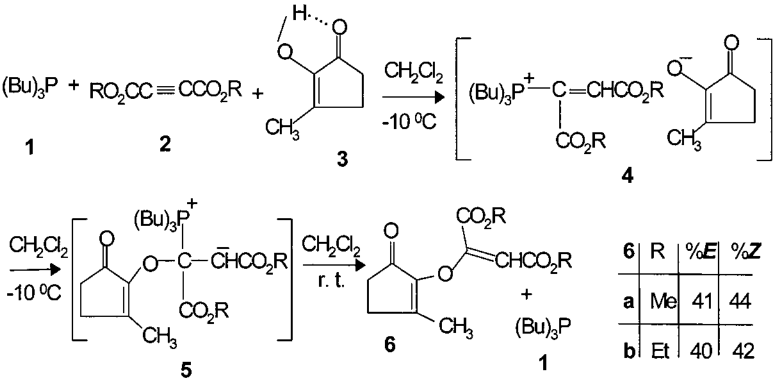

6	R	%E	%Z
a	Me	41	44
b	Et	40	42

SCHEME 1

RESULTS AND DISCUSSION

Reactions are known in which an α,β-unsaturated carbonyl compound is produced from phosphonium salts.[11] Thus, compounds **6** may result from an initial addition of tributylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct by the 2-hydroxy-3-methyl-2-cyclopenten-1-one (**3**) to form the corresponding tributylphosphonium salts **4**. Conjugate addition of the 2-hydroxy-3-methyl-2-cyclopenten-1-one (**3**) anion to the vinyltributylphosphonium cation counterpart followed by elimination of the tributylphosphine to be recycled as a catalyst would lead to the dialkyl 2-[(2-methyl-5-oxo-1-cyclopentenyl)-oxy]-2-butenedioates **6** (1:1 mixtures of *E* and *Z* isomers) as the final product in fairly high yields (Scheme 1).

The structures **6a–b** were deduced from their elemental analyses and their UV, IR, ^{1}H, and ^{13}C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at m/z of 254 and 282 respectively.

In summary, we have developed a convenient, one-pot synthesis of dialkyl 2-[(2-methyl-5-oxo-1-cyclopentenyl)-oxy]-2-butenedioates **6** utilizing in situ generation of the vinyltributylphosphonium salt **4**. 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 spectrophothometer. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^{1}H 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 2-[(2-methyl-5-oxo-1-cyclopentenyl)-oxy]-2-butenedioates (**6a–b**): To a magnetically stirred solution of tributylphosphine (**1**) (2 mmol) and 2-hydroxy-3-methyl-2-cyclopenten-1-one **3** (2 mmol) in CH_2Cl_2 (10 ml) was added drop-wise a mixture of **2** (2 mmol) in CH_2Cl_2 (6 ml) at -10°C over 15 min. The mixture was allowed to warm up to room temperature and stirred for 24 h. The solvent was removed under reduced pressure and the viscous residue was purified by flash column chromatography (silica gel; ethyl acetate-light petroleum ether). The solvent was removed under reduced pressure and the products were obtained as viscous light yellow oils (**6a–b**). The characterization data of dialkyl 2-[(2-methyl-5-oxo-1-cyclopentenyl)-oxy]-2-butenedioates (**6a–b**) are given below:

*Dimethyl (**E**)-2-[(2-methyl-5-oxo-1-cyclopentenyl)-oxy]-2-butenedioate (**6aE**)*:Viscous light yellow oil. Yield: 41%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 295, 3.72. IR (CCl_4) (ν_{max}, Cm^{-1}): 2969, 1727, 1650, 1449. ^1H NMR ($CDCl_3$) δ_H: 2.07 (3H, s, CH_3), 2.48–2.51 (2H, m, CH_2C=); 2.60–2.63 (2H, m, CH_2CO); 3.69 and 3.91 (6H, 2 s, 2 OCH_3); 5.18 (1H, s, CH=). ^{13}C NMR ($CDCl_3$) δ_C: 13.61 (CH_3); 27.74 ($^{13}CH_2C$=); 32.65 ($^{13}CH_2CO$); 51.83 and 53.10 (2 OCH_3); 98.75 (CH=); 147.40, 157.53 and 162.13 (3 C); 162.66 and 165.40 (2C=O of esters); 198.76 (C=O, ketone). MS (m/z, %): 255 ($M^+ + 1$, 43), 254 (M^+, 14); 235 (100); 223 (81); 195 (100); 179 (90); 153 (58); 137 (68); 94 (50). Found: C, 56.97; H, 5.63. $C_{12}H_{14}O_6$ requires C, 56.69; H, 5.55%.

*Dimethyl (**Z**)-2-[(2-methyl-5-oxo-1-cyclopentenyl)-oxy]-2-butenedioate* (**6aZ**): Viscous light yellow oil. Yield: 44%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 301, 4.01. IR (CCl_4) (ν_{max}, Cm^{-1}): 2953, 1727, 1677, 1650. ^1H NMR ($CDCl_3$) δ_H: 2.11 (3H, s, CH_3), 2.36–2.39 (2H, m, CH_2C=); 2.49–2.52 (2H, m, CH_2CO); 3.73 and 3.80 (6H, 2 s, 2 OCH_3); 6.27 (1H, s, CH=). ^{13}C NMR ($CDCl_3$) δ_C: 14.86 (CH_3); 27.29 ($^{13}CH_2C$=); 32.50 ($^{13}CH_2CO$); 51.66 and 52.96 (2 OCH_3); 108.93 (CH=); 149.42, 151.13 and 152.55 (3 C); 162.55 and 164.22 (2C = O of esters); 199.96 (C=O, ketone). MS (m/z, %): 255 ($M^+ + 1$, 57), 254 (M^+, 53); 223 (38); 195 (100); 153 (100); 135 (43); 59 (6). Found: C, 57.51; H, 6.08. $C_{12}H_{14}O_6$ requires C, 56.69; H, 5.55%.

*Diethyl (**E**)-2-[(2-methyl-5-oxo-1-cyclopentenyl)-oxy]-2-butenedioate* (**6bE**):Viscous light yellow oil. Yield: 40%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 293, 2.44. IR (CCl_4) (ν_{max}, Cm^{-1}): 3061, 2989, 1727, 1642, 1337. ^1H NMR ($CDCl_3$) δ_H: 1.25 and 1.37 (6H, 2 t, $^3J_{HH} = 7.1$ Hz, 2 CH_3 of 2 Et); 2.07 (3H, s, CH_3), 2.48–2.51 (2H, m, CH_2C=); 2.60–2.63 (2H, m, CH_2CO); 4.15 and 4.37 (4H, 2 q, $^3J_{HH} = 7.1$ Hz, 2 OCH_2 of 2 Et); 5.16

(1H, s, CH=). ^{13}C NMR ($CDCl_3$) δ_C: 13.88 and 14.11 (2 CH_3 of 2 Et); 15.16 (CH_3); 27.73 ($^{13}CH_2C$=); 32.65 ($^{13}CH_2CO$); 60.72 and 62.42 (2 OCH_2); 98.88 (CH=); 147.50, 157.66 and 162.09 (3 C); 162.25 and 164.93 (2C=O of esters); 198.88 (C=O, ketone). MS (m/z, %): 283 ($M^+ + 1$, 25), 282 (M^+, 9); 254 (40); 226 (30); 208 (100); 193 (44); 108 (22). Found: C, 59.89; H, 6.21. $C_{14}H_{18}O_6$ requires C, 59.57; H, 6.43%.

*Diethyl (**Z**)-2-[(2-methyl-5-oxo-1-cyclopentenyl)-oxy]-2-butenedioate* (**6bZ**): Viscous light yellow oil. Yield: 42%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 294, 2.53. IR (CCl_4) (ν_{max}, Cm^{-1}): 3061, 1734, 1272. ^{1}H NMR ($CDCl_3$) δ_H: 1.28 and 1.31 (6H, 2 t, $^3J_{HH} = 7.1$ Hz, 2 CH_3 of 2 Et); 2.11 (3H, s, CH_3), 2.37–2.39 (2H, m, CH_2C=); 2.50–2.52 (2H, m, CH_2CO); 4.19 and 4.26 (4H, 2 q, $^3J_{HH} = 7.1$ Hz, 2 OCH_2 of 2 Et); 6.27 (1H, s, CH=). ^{13}C NMR ($CDCl_3$) δ_C: 14.01 and 14.17 (2 CH_3 of 2 Et); 14.84 (CH_3); 27.25 ($^{13}CH_2C$=); 32.50 ($^{13}CH_2CO$); 60.50 and 62.20 (2 OCH_2); 109.02 (CH=); 149.43, 151.22 and 152.17 (3 C); 162.08 and 163.86 (2C=O of esters); 199.96 (C=O, ketone). MS (m/z, %): 255 ($M^+ + 1$, 43), 254 (M^+, 14); 235 (100); 223 (81); 195 (100); 179 (90); 153 (58); 137 (68); 94 (50). Found: 283 ($M^+ + 1$, 23), 282(M^+, 11); 254 (31); 226 (37); 208 (100); 193 (34); 108 (14). C, 59.79; H, 6.24. $C_{14}H_{18}O_6$ requires C, 59.57; H, 6.43%.

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