Triphenylphosphine catalysed stereoselective synthesis of *O*-vinylcyclopentenones

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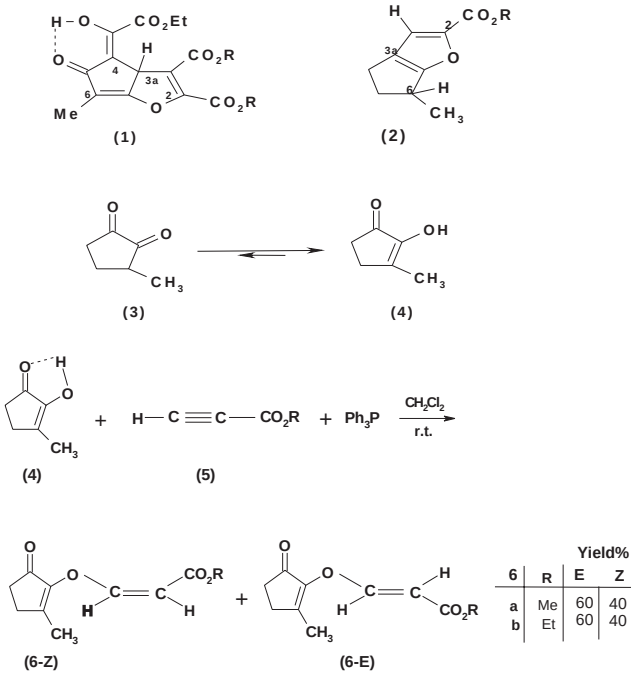
The addition of 2-hydroxy-3-methylcyclopent-2-enone to propiolate esters is catalysed by triphenylphosphine to form *O*-vinylcyclopentenones in moderate yields.

Keywords: alkyl propiolate, triphenylphosphine, *O*-vinylcyclopentenones, organophosphorus compounds

Organophosphorus compounds have been extensively used in organic synthesis as useful reagents as well as the ligands of a number of transition metal catalysts.[1,2] However, there are few reactions in which organophosphorus(III) species work as catalysts.[3,4]

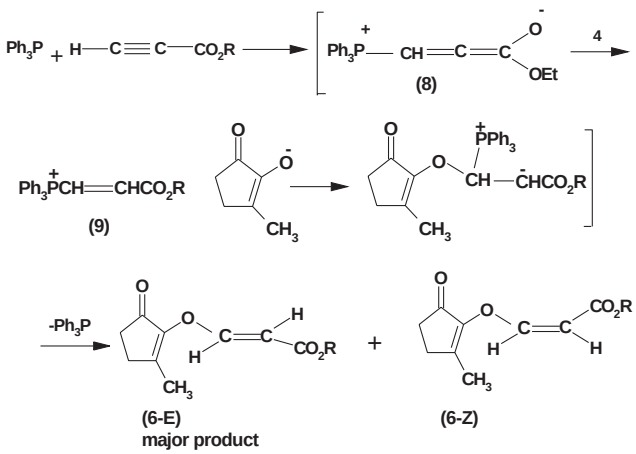
We have already described[5] the synthesis of cyclopenta [b]furans (**1**) from the reaction of triphenylphosphine, 3-ethoxalyl-5-methylcyclopentane-1,2,4-trione and symmetric electrophiles such as dialkyl acetylenedicarboxylates using an intramolecular Wittig reaction.[6,7] With the intention of preparing the novel class of cyclopenta[b]furans having unsubstituted β-positions (C-3), such as (**2**), we performed the reaction of triphenylphosphine with unsymmetrical electrophiles such as alkyl propiolates and α-diketones (**3**). This reaction did not afford the corresponding furan(**2**), but yielded the *O*-vinylcyclopentenones(**6Z,6E**) in good yields (Scheme 1).



Scheme 1

3-Methylcyclopentane-1,2-dione(**3**) is a readily available system from natural sources, which is apparently completely enolised in the liquid phase, as indicated by ^{1}H and ^{13}C NMR spectroscopy.[8] The enol tautomer (**4**) is more stable because of intramolecular hydrogen bonding and dipolar effects.

The *O*-vinylcyclopentenones **6-Z** and **6-E** apparently result from initial attack of triphenylphosphine at the β-carbon atom of the alkyl propiolate to form the intermediate (**8**). Then, concomitant protonation of this 1:1 adduct by the enol (**4**) leads to the corresponding phosphonium salts (**9**). Conjugate addition of the enol anion to the β-triphenylphosphonium acrylate counterpart followed by elimination of the triphenylphosphine to be recycled as a catalyst would lead to the *O*-vinylcyclopentenones (**6-Z,6-E**) as the final products.



Scheme 2

Structures **6-Z** and **6-E** were assigned to the isolated adducts on the basis of their elemental analyses and IR, ^{1}H NMR and ^{13}C NMR spectral data. ^{1}H NMR spectroscopy revealed, in each case, an AX system with $^3J_{HH}$ values of **12.2** and **6.9** Hz for each of the two compounds, in agreement with the disubstituted olefins with *E* and *Z*-configurations,[9] respectively.

The ^{13}C NMR spectrum of **6a(Z, E)** exhibited **10** distinct resonances in agreement with the structures of these compounds. Partial assignments of these resonances are given in the experimental section. The two methine carbon atoms of the vinyl moiety exhibit very different chemical shifts. The signal at about 154–158 ppm is assigned to C-β, and the high field signal at δ = 98–101 ppm is assigned to C-α. The latter shift is very similar to those reported[10,11] for the C-2 atoms of ethylene groups bearing electron releasing substituents in the C-1 positions.

O-vinylcyclopentenone derivatives **6a–b (Z**,**E)** may be considered as potentially useful synthetic intermediates because they possess carbon atoms with different oxidation states. The procedure described here represents a simple and efficient entry into the stereoselective synthesis of *O*-vinylcyclopentenones

Experimental

Alkyl propiolates, triphenylphosphine and cyclotene were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. ^{1}H, ^{13}C-NMR spectra were measured with a Bruker DRX-500 AVANCE spectrometer at 500 and 125.8 MHz, respectively. IR spectra were recorded on a Shimadzu IR-470 spectrometer.

General procedure for synthesis of alkyl (Z,E)-3-[(2-methyl-5-oxo-1-cyclopentenyl)oxy]-2-propenoate **6a(Z,E)**: To a magnetically stirred solution of alkyl propiolate (0.167ml, 2mmol) and **3** (0.224 g, 2 mmol) in CH_2Cl_2 (1 ml) was added, dropwise, a mixture of triphenylphosphine (0.524 g, 2 mmol) in CH_2Cl_2 (3 ml) at –10°C over

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10 min. The reaction mixture was allowed to stand at room temperature and stirred for 24 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–pentane. The solvent was removed under pressure and the product was obtained.

6a(Z): Yellow oil, yield 40%, IR(ν_{max}, cm^{-1}): 1699 and 1762 (C=O), 1610 (C=C); ^{1}H NMR (500MHz, $CDCl_3$): δ_H 2.13(3 H, s, CH_3), 2.47–2.53(4 H, m, 2 CH_2), 3.73(3 H, s, OCH_3), 5.07(1 H, d, $^3J_{HH}$ = 6.9 Hz, CH), 7.25(1 H, d, $^3J_{HH}$ = 6.9 Hz, OCH); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ_C 15.08(CH_3), 27.37 and 33.04 ($2CH_2$), 51.04(OCH_3), 98.22(C=*C*H), 149.08(=*C*-CH_3), 154.03(O*C*H=CH), 157.51(–O–*C*=C-CH_3), 165.07(C=O, ester), 200.24(C=O, ketone). (Found: C, 61.8; H, 6.25 ; $C_{10}H_{12}O_4$ requires C, 61.22; H, 6.16 %).

6a(E): Yellow oil, 60%, IR(ν_{max}, cm^{-1}): 1699 and 1762 (C=O), 1610 (C=C); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 2.04(3 H, s, CH_3), 2.47–2.56(4 H, m, 2 CH_2), 3.70(3 H, s, OCH_3), 5.40(1 H, d, $^3J_{HH}$ = 12 Hz, CH), 7.79(1 H, d, $^3J_{HH}$ = 12 Hz, OCH); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ_C 14.99 (CH_3), 27.37 and 32.77(2 CH_2), 51.32(OCH_3), 100.72(CH), 148.93(=*C*-CH_3), 158.59(–O–*C*=C-CH_3), 158.96 (O*C*H=CH), 167.28 (C=O, ester), 199.90 (C=O, ketone). (Found: C, 61.8; H, 6.26. $C_{10}H_{12}O_4$ requires C, 61.22; H, 6.16 %).

6b(Z): Yellow oil, yield 40%, IR(ν_{max}, cm^{-1}): 1662 and 1702(C=O), 1620(C=C); ^{1}H NMR(500 MHz, $CDCl_3$): δ_H 1.23(3 H, t, $^3J_{HH}$ = 7.14 Hz, CH_3), 2.06(3 H, s, CH_3), 2.04–2.47(4 H, m, 2 CH_2), 4.12(2 H, q, $^3J_{HH}$ = 7.14 Hz, OCH_2), 4.98(1H, d, $^3J_{HH}$=6.9 Hz, CH), 7.20(1 H, d, $^3J_{HH}$=6.9 Hz, OCH); ^{13}C NMR(125.77 MHz, $CDCl_3$): δ_C 14.35(CH_3), 15.04(–O–CH_2-*C*H_3), 27.30 and 33.07(2 CH_2), 59.73(OCH_2), 98.62(=CH), 149.04(=*C*-CH_3), 153.75(OCH), 157.38 (–O–*C*=C-CH_3), 164.68(C=O, ester), 200.24(C=O, ketone). (Found: C, 63.30; H, 6.8. $C_{11}H_{14}O_4$ requires C, 62.85; H, 6.71 %).

6b(E): Yellow oil, 60 %, IR (ν_{max}, cm^{-1}): 1663 and 1702 (C=O), 1620 (C=C); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.23(3 H, t, $^3J_{HH}$ = 7.13 Hz, CH_3), 2.00(3 H, s, CH_3), 2.44 and 2.52 (4 H, m, 2 CH_2), 4.13 (2 H, q, $^3J_{HH}$ = 7.13 Hz, OCH_2), 5.35 (1H, d, $^3J_{HH}$ = 12.2 Hz, CH), 7.74 (1 H, d, $^3J_{HH}$ = 12.2 Hz, OCH); ^{13}C NMR (125.77 MHz, $CDCl_3$): δ_C 14.35 (CH_3), 15.02 (–O–CH_2–*C*H_3), 27.41 and 32.77 (2 CH_2), 60.10 (OCH_2), 101.06 (=CH), 148.97 (=*C*–CH_3), 158.79 (OCH), 158.43 (–O–*C*=C–CH_3), 166.87 (C=O, ester), 199.95 (C=O, ketone). (Found: C, 63.30; H, 6.8. $C_{11}H_{14}O_4$ requires C, 62.85; H, 6.71 %).

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