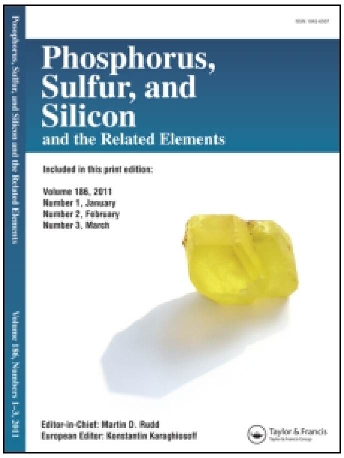

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Tributylphosphine Catalyzed O -Vinylation of 3-Hydroxy-2-methyl-4 H -pyran-4-one

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TRIBUTYLPHOSPHINE CATALYZED *O*-VINYLATION OF 3-HYDROXY-2-METHYL-4*H*-PYRAN-4-ONE

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*Protonation of the highly reactive 1:1 intermediates produced in the reaction between tributylphosphine and dimethyl acetylenedicarboxylate by 3-hydroxy-2-methyl-4*H*-pyran-4-one leads to vinyltributylphosphonium salts, which undergo an addition-elimination reaction in CH_2Cl_2 at room temperature to produce dimethyl 2-[(2-methyl-4-oxo-4*H*-pyran-3-yl)oxy]-2-butenedioate (1:1 mixtures of* E *and* Z *isomers) in fairly good yields.*

Keywords: Acetylenic ester; catalyst; 3-hydroxy-2-methyl-4*H*-pyran-4-one; tributylphosphine; vinyltributylphosphonium salt

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 a facile one-pot synthesis of dimethyl 2-[(2-methyl-4-oxo-4*H*-pyran-3-yl)oxy]-2-butenedioate **6** (1:1 mixtures of *E* and *Z* isomers) in fairly good yields (Scheme 1).

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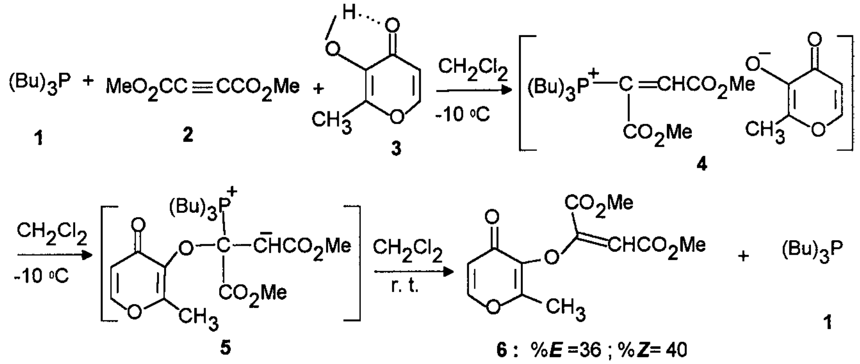

SCHEME 1

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 3-hydroxy-2-methyl-4*H*-pyran-4-one (**3**) to form the corresponding tributylphosphonium salts **4**. Conjugate addition of the 3-hydroxy-2-methyl-4*H*-pyran-4-one (**3**) anion to the vinyltributylphosphonium cation counterpart followed by elimination of the tributylphosphine to be recycled as a catalyst would lead to dimethyl 2-[(2-methyl-4-oxo-4*H*-pyran-3-yl)oxy]-2-butenedioate **6** (1:1 mixtures of *E* and *Z* isomers) as the final product in fairly good yields (Scheme 1).

In summary, we have developed a convenient, one-pot synthesis of dimethyl 2-[(2-methyl-4-oxo-4*H*-pyran-3-yl)oxy]-2-butenedioate **6** utilizing in situ generation of the vinyltributylphosphonium salt **4**. Other aspects of this process are under investigation.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively.

*Procedure for the preparation of dimethyl 2-[(2-methyl-4-oxo-4*H*-pyran-3-yl)oxy]-2-butenedioate (**6**):* To a magnetically stirred solution of tributylphosphine (**1**) (2 mmol) and 3-hydroxy-2-methyl-4*H*-pyran-4-one **3** (2 mmol) in CH_2Cl_2 (12 ml) was added dropwise a mixture of **2** (2 mmol) in CH_2Cl_2 (8 ml) at −10°C over 15 min. The mixture was allowed to warm 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 (**6*E*** and **6*Z***). The characterization data of dimethyl 2-[(2-methyl-4-oxo-4*H*-pyran-3-yl)oxy]-2-butenedioate (**6*E*** and **6*Z***) are given below:

*Dimethyl (***E***)-2-[(2-methyl-4-oxo-4*H*-pyran-3-yl)oxy]-2-butenedioate (**6*E**).* Viscous, light yellow oil. Yield: 36%. ^{1}H NMR ($CDCl_3$) δ_H: 2.34 (3H, s, CH_3), 3.69 and 3.92 (6H, 2 s, 2 OCH_3); 5.23 (1H, s, CH=), 6.40 and 7.70 (2H, 2 d, $^{3}J_{HH} = 5.6$ Hz, 2 CH of pyran ring). ^{13}C NMR ($CDCl_3$) δ_C: 14.87 (CH_3); 51.84 and 53.15 (2 OCH_3); 98.66 (CH=); 117.50 and 154.31 (2 CH, pyran ring), 139.76, 157.51, 160.55, 162.66, 165.34 and 171.13 (6 C).

*Dimethyl (***Z***)-2-[(2-methyl-5-oxo-1-cyclopentenyl)-oxy]-2-butenedioate (**6*Z**).* Viscous, light yellow oil. Yield: 40%. ^{1}H NMR ($CDCl_3$) δ_H: 2.45 (3H, s, CH_3), 3.75 and 3.81 (6H, 2 s, 2 OCH_3); 6.22 (1H, s, CH=), 6.31 and 7.64 (2H, 2 d, $^{3}J_{HH} = 5.6$ Hz, 2 CH of pyran ring). ^{13}C NMR ($CDCl_3$) δ_C: 18.87 (CH_3); 51.60 and 52.92 (2 OCH_3); 106.80 (CH=); 116.17 and 153.64 (2 CH, pyran ring), 139.64, 157.43, 160.58, 162.51, 165.44 and 171.18 (6 C).

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