A Novel Deoxygenation–Isomerization Reaction of 4-Hydroxy-2-ynoic Esters and γ-Hydroxy-α,β-ynones

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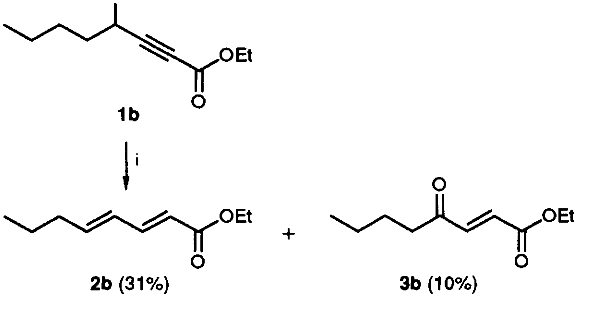
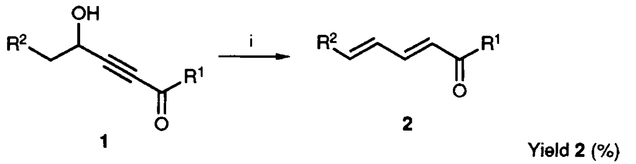
(2*E*, 4*E*)-Dienoic esters and (*E*, *E*)-α,β : γ,δ-dienones have been stereoselectively synthesized from 4-hydroxy-2-ynoic esters and γ-hydroxy-α,β-ynones by their reactions with triphenylphosphine under mild conditions.

In our studies on transition metal catalysed organic synthesis, we wanted to prepare 4-oxo-2-enoic esters from 4-hydroxy-2-ynoic esters since ynols isomerize to enones under the catalysis of transition metal complexes.[1,2] The isomerization of ethyl 4-hydroxyoct-2-ynoate **1b** using $Pd(OAc)_2$ (2.5 mol%)–Ph_3P(35 mol%) as the catalyst, surprisingly gave ethyl octa-2,4-dienoate **2b** as the major product and ethyl 4-oxooct-2-enoate **3b** as the minor one (Scheme 1). The yield of **2b** depended on the quantity of triphenylphosphine added, when 1 equiv. of triphenylphosphine was used **2b** was the sole product and no **3b** was produced.

In blank experiments, dienes **2** were obtained in good yields without the addition of a palladium complex by using only triphenylphosphine at room temp. (Scheme 2). The spectral data of the products **2** were identical with those obtained from transition metal catalysed isomerization of alkynones and alkynoates.[3]

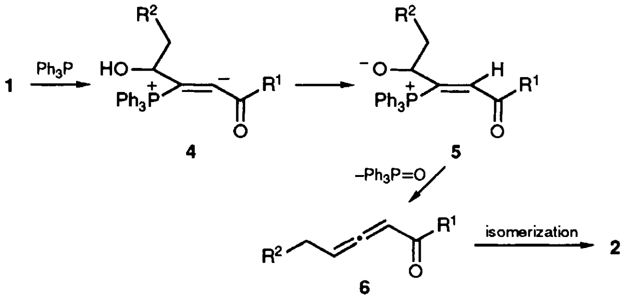


Scheme 1 *Reagents and conditions*: i, $Pd(OAc)_2$–Ph_3P, toluene, reflux 31 h



		Yield 2 (%)
a; R^1 = OEt,	R^2 = Et	85
b; R^1 = OEt,	R^2 = Pr^n	86
c; R^1 = Bu^n,	R^2 = Pr^n	83
d; R^1 = n-C_5H_{11},	R^2 = Et	86

Scheme 2 *Reagents and conditions*: i, Ph_3P (1 equiv.), benzene, room temp., 8 h



Scheme 3

These results made us consider that the mechanism of the reaction does not involve palladium. It has been reported[4,5] that triphenylphosphine can add nucleophilically to the electron-poor triple bond. A possible mechanism for the deoxygenation–isomerization reaction is shown in Scheme 3. Triphenylphosphine first adds to the triple bond to afford intermediate **4**. Proton exchange then occurs between the vinyl carbanion and the hydroxy group to give **5**, which is similar to the intermediate of the Wittig reaction. Triphenylphosphine oxide is then lost to form the allene **6**, which further isomerizes to diene **2** by catalysis with triphenylphosphine.[6] The reaction of **1a** was stopped halfway through and IR spectra of the reaction mixture showed an absorption at 1955 cm^{-1}, showing the existence of the allene intermediate **6**. In addition, triphenylphosphine oxide was obtained almost quantitatively when the reaction was complete.

A typical procedure is as follows: A mixture of **1a** (235 mg, 1.38 mmol) and Ph_3P (362 mg, 1.38 mmol) in benzene (5 ml) was stirred at room temp. The reaction was complete after 8 h as monitored by TLC. The solvent was removed under vacuum and the residue chromatographed on a silica gel column (eluting with 5% ethyl acetate in petroleum ether, b.p. 60–90 °C) to give **2a** (180 mg, 85%).†

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† *Note added in proof*: Recently, Trost also reported that phosphine can catalyse the isomerization of allenone to dienone, see B. M. Trost and U. Kazmaier, *J. Am. Chem. Soc.*, 1992, **114**, 7933.